Spectroscopy and Dynamics of Weakly-bound Anions Using Full- and Reduced-dimensional Theoretical Models

Dissertation

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By

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Abstract

Reduced-dimensional theoretical models are used to study the vibrational structure and dynamics of weakly-bound anionic systems. In the first part of the work presented here, the low frequency vibrational modes ($< 2000 \text{ cm}^{-1}$) of $X^-\cdot\text{H}_2\text{O}$ species ($X = \text{F, Cl, Br, and I}$) are investigated using one- and two-dimensional models. In some cases a one-dimensional treatment works well at capturing the large amplitude, anharmonic motions of these systems, as in the case of the out-of-plane bend. In other cases, mode-mode coupling must be included, either explicitly through a two-dimensional treatment or through inclusion of zero point energies in the other vibrational degrees of freedom. To test the veracity of these methods and proposed mechanisms, comparisons are drawn to relevant experimental studies and through isotopic substitution of the solvent molecule, specifically $\text{H}_2\text{O}$, $\text{HDO}$, and $\text{D}_2\text{O}$. In the $\text{F}^-\cdot\text{H}_2\text{O}$ system, a two-dimensional treatment is employed to study both the $\text{OF}$ and $\text{OH}_b$ stretches. In doing so, quantitative agreement with experiment is achieved and the extent of proton transfer promoted through vibrational excitation is examined. The extent of proton transfer is over 45% for states with one or more quanta of excitation in the $\text{OH}_b$ stretch. For examination of the in- and out-of-plane bend, investigations of the intensity patterns reveal that electrical anharmonicity is a key player in the anomalously large intensity in $2\nu_{\text{oop}}$, but similar intensity patterns in
$2\nu_p$ are not observed. In the second part, the photoinduced dissociation dynamics of anions is examined, both with and without the presence of a solvating molecule. Similar reduced-dimensional methods as those for $X^-\cdot H_2O$ are utilized but high level *ab initio* calculations (MR-SO-CISD) and full quantum dynamics are also employed. For IBr$^-$ the robustness of previous classical analyses of this system are tested by solving the time-dependent Schrödinger equation with the inclusion of temporal pulse information. Results of these calculations show that while there are some effects related to pulse width, especially for short delay times ($\Delta t < 500$ fs), the majority of the structure in the spectra reflects the difference in potential energies between the anion and neutral surfaces at a particular I···Br separation with all of the excited molecules dissociating to form $I^- + Br$. For solvated molecular ions, the role of solvent orientation in promoting or hindering dissociation are investigated in Cu$^-$-(CD$_3$OD) and IBr$^-$-(CO$_2$) systems. In IBr$^-$-(CO$_2$) the presence of a single solvent molecule is enough to induce two additional channels. One of the channels is the electron transfer channel where the charge hops from the $I^-$ to Br fragment when the IBr distance is roughly 7 Å. This observation is investigated and interpreted by analyzing the change in the IBr$^-$ electronic structure due to the presence of CO$_2$. In a companion study on Cu$^-$-(CD$_3$OD), the effects of the couplings between the solvent internal degrees of freedom and the molecular (Cu···CD$_3$OD) dissociation coordinate are investigated using a reduced-dimensional treatment. From these results, comparisons are drawn to earlier studies on Cu$^-$-(H$_2$O), and from which the effects of substituent substitution (CD$_3$ vs. H) on the photoinduced dissociation dynamics are discussed.
In loving memory of Grandpap
To Grandma
To Mom & Dad
To Mike
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**Fields of Study**

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CHAPTER 1

Introduction

From a general point of view, the making and breaking of chemical bonds is at the core of chemistry and governs many macroscopic processes that we use everyday, from the combustion engines that propel our vehicles to the conversion of raw materials into useable products.\(^\text{11}\) These types of processes are governed by “chemical interactions,” but many other important processes, such as biological and aerosol chemistry, are governed by “weaker” interactions. As shown in Table 1.1, hydrogen-bonding (H-bonding) and electrostatic interactions are intermediate in the hierarchy with strengths of a few kcal/mol. These weaker H-bonding and electrostatic interactions are crucial in the chemistry that takes place at the microscopic scale and give rise to interesting macroscopic properties, for example the high boiling point of water.

Of particular interest to the work presented here is \textit{how} the molecular structure and molecular properties of a species change upon the introduction of an excess electron or ion. Specifically, how important are the electrostatic and H-bonding interactions, and how do they manifest themselves in the spectroscopy and dynamics of these species. We begin our discussion by addressing the properties of anion chemistry and the
effects of solvation and conclude with the role of experiment and theory in studying these systems.

Table 1.1: Classification of chemical interactions in order of interaction strength.

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³ Information taken from Ref. 11

1.1 Anion chemistry

Over the past 40 years, there has been significant advancement in the preparation and trapping of negatively charged species, and studies of weakly-bound neutral complexes can begin with formation of their anionic counterparts. Anions, not surprisingly, are distinctly different from these others species. When an anion interacts with a solvent, such as in the hydrogen-bonding arrangement in \(\text{Cu}^-\)(\(\text{H}_2\text{O}\)) for example, the dipole orientation of the solvent molecule has the positive end toward the solute, but this is opposite for cations; moreover, the solvent orientation depends on
the functional group on the solute that is closest to the solvent in interactions with neutral species. Additionally, it is not surprising that anions have large polarizabilities because of their weakly-bound valence electrons and therefore have stronger van der Waals interactions with surrounding molecules than the less polarizable and more compact neutrals or cations.

In general the electron binding energies of anions tend to be smaller than either of their neutral or cation counterparts, and it is also rare for anionic species to have many bound electronic states, unlike for cations and neutrals that have several. These differences lie in the potentials that influence the movement of electrons within these species. Figure 1.1 shows how the electronic structure of the systems changes, more specifically how the Coulomb attractive and repulsive forces impact the electronic structure of the system, depending on how the system is charged.

Interestingly, for singly charged anions, an electron in the valence shell does not experience any Coulomb attraction in the asymptotic region; however, for neutrals and cations, there are Coulomb attractions \((-Z_{\text{eff}}e^2/r, \text{where } Z_{\text{eff}} \text{ is the effective nuclear charge and } Z_{\text{eff}} = 1 \text{ for neutrals and } 2 \text{ for cations, etc.});\) for multiply charged anions, there is actually a Coulomb repulsion because \(Z_{\text{eff}} < -1.\) Because of this, the leading terms that dominate the anion attraction are charge-dipole and charge-quadrupole interactions, so while neutral and cation interactions fall off as \(1/r,\) anion interactions decrease much more quickly as \(1/r^n,\) where \(n = 3 \text{ for charge-dipole and }\) \(n = 5 \text{ for charge-quadrupole interactions.}\) This key difference in the large-\(r\) behavior of the potential leads to extreme differences in the radial extent, the electron binding
Figure 1.1: Qualitative representation of the Coulomb potentials acting on the valence electrons of neutrals and cations as well as on singly and multiply charged anions: total valence energy vs. distance from the molecule, $r$. The horizontal lines represent the bound electronic states within each corresponding potential. Taken from Figure 1.1 from Ref. 1.
energies, and the number and pattern of bound electronic states between anions, cations, and neutrals.¹

This large-\(r\) dependence also partially gives rise to the deeper electron-molecule potential wells of neutrals and cations relative to anions, and in general anions tend to have only one significantly bound electronic state (\(> 100 \text{ cm}^{-1}\)), and this limits the types of experiments that can be performed as many “standard” techniques rely on bound electronic states.¹ Take, for example, \(\text{Cu}^-(\text{H}_2\text{O})\) and \(\text{Cu}^+(\text{H}_2\text{O})\). In \(\text{Cu}^-(\text{H}_2\text{O})\) there is a strong asymmetric, H-bonding configuration with one of the two hydrogens in \(\text{H}_2\text{O}\); however, in \(\text{Cu}^+(\text{H}_2\text{O})\) the strongest interaction is between \(\text{Cu}\) and \(\text{O}\) in a \(C_{2v}\) configuration.¹² The binding energies of \(\text{Cu}^-(\text{H}_2\text{O}),\) \(\text{Cu}(\text{H}_2\text{O}),\) and \(\text{Cu}^+(\text{H}_2\text{O})\) differ quite substantially with the cation being bound by nearly four times as much as the anion: 3750, 1750, and 14 600 \(\text{cm}^{-1}\), respectively.¹²

From the information presented above, it sounds as though all anionic species are difficult to calculate because of the uniqueness of their large-\(r\) behavior. For example, commonly used functionals in DFT methods tend to (1) not have the correct large-\(r\) behavior in general and (2) use the \(1/r\) term that is incorrect for anions.¹ Yet, for singly charged anions that have the excess electron in a valence shell that is tightly bound, many of the same theoretical methods and basis sets that we use for neutrals and cations are well applied to these anions,¹ anions such as \(X^-\) (\(X = \text{F, Cl, B, or I}\)) as presented in Chapters 2 and 3. However for negatively charged species that have small electron binding energies and large radial extent, more accurate methods and parameterized basis sets are required.¹
1.2 The role of solvation

The interactions of ions with each other or with solvent are ubiquitous in nature. Ion transport through biological membranes and ion channels are vital to physiological biochemistry, and these interactions can be relatively simple, such as the transport of salt across members, or as complicated as controlling the firing of neurons in synaptic pathways. Aside from the biochemical aspect, ions play important roles in environmental chemistry, such as at air-water interfaces and in the atmosphere. For example, chloride is extremely prevalent in seawater and is intimately related to radical chlorine, a key player in stratospheric ozone depletion. Moreover, solvents can perturb the electronic states that govern reactions by changing the relative energies of various product channels, raising or lowering barrier heights, and inducing nonadiabatic electronic transitions.\textsuperscript{13} Solvents also provide a source of energy that can be transferred to the reaction coordinate, thus promoting a chemical process.\textsuperscript{13}

Perhaps the most well-known ion-molecule interaction is the interaction of H\textsuperscript{+} with H\textsubscript{2}O. In the gas phase, the most common structures are the “Eigen” or “Zundel” configurations. In the Eigen structure, the dissolution of H\textsuperscript{+} in H\textsubscript{2}O is characterized by asymmetric, unequal sharing of the proton, giving rise to the ion well-known to general chemistry students, H\textsubscript{3}O\textsuperscript{+}.\textsuperscript{14} However in the Zundel structure, there is equal sharing of the proton, leading to the less-commonly known H\textsubscript{5}O\textsubscript{2}\textsuperscript{+}.\textsuperscript{14} In light of what is observed in the gas phase, one would think that a similar observation would occur in the condensed phase, i.e.: H\textsubscript{3}O\textsuperscript{+} or H\textsubscript{5}O\textsubscript{2}\textsuperscript{+} would diffuse dynamically throughout the remaining solvent as a single ionic unit. However, what actually happens is that
no single H\(^+\)-related species diffuses, but rather the defect resulting from the extra proton diffuses via proton transfer.\(^{15}\) These so-called defects propagate themselves throughout the water lattice, changing the H-bonding network instantaneously. A qualitative picture of this Grotthuss shuttling mechanism\(^2\) is illustrated in Figure 1.2. Here we see that even a small charged species can have a large impact on the intermolecular forces.

![Figure 1.2: Cartoon representation of the Grotthuss mechanism\(^2\) for H\(^+\) transport in bulk H\(_2\)O. The successive proton-transfer processes step along the H-bond network, resulting in the translocation of the defect throughout the condensed phase.\(^3\)](image)

Proton transfer can occur in many species, not just in H\(^+(\text{H}_2\text{O})_n\) systems, such as in NO\(^+(\text{H}_2\text{O})_n\)\(^{16}\) and OH\(^-(\text{H}_2\text{O})\).\(^{17-19}\) In some cases proton transfer occurs more or less spontaneously, whereas in other cases, proton transfer can be induced through vibrational excitation. In the work on F\(^-(\text{H}_2\text{O})\), even one quantum of excitation in the shared proton stretch transfers the hydrogen from an F\(^-\cdots\text{H}_2\text{O}\) configuration to a FH\(\cdots\text{OH}^-\) one. Furthermore, the bonding motifs of X\(^-(\text{H}_2\text{O})\) (X = F, Cl, Br,
and I) and M−(H2O) (M = Cu, Ag, Au) complexes adopt a single ionic hydrogen-bonded structure with only one of the two equivalent hydrogens, as mentioned above for the studies on Cu−(H2O).12 The strength of this interaction can be so strong that the bonded OH stretch can be redshifted by several hundred to several thousand cm−1.6,18,20

As evidenced by the work on X−(H2O) systems, it can be seen how the solute (in this case X−) can have a large effect on the solvent, in this case by changing the bonding constructs, and not surprisingly the solvent also has a strong effect on the solute. The interplay between the solvent-solute interactions can be static or dynamic in nature.21 Properties of the solute molecule that are static are ones that, in general, do no change significantly with time, properties such as electronic energy, dipole moment, and molecular configuration that depend only on the electronic state of the solute molecule.21 Dynamic properties result from the non-instantaneous solvent reorientation following the induced changes to the electronic properties of the solute.21 Investigations into these dynamics are of particular interest to the chemical physics community, and as Glasbeek and Zhang indicate, these dynamical phenomena can include electron and proton transfer, intramolecular torsional motions, and intramolecular vibrational energy distribution.21 Aspects of each of these processes will be discussed in the chapters that follow.

In the work on Cu−(CD3OD), it will be shown that the presence of the methyl rotor in CD3OD can have a profound effect on the dissociation dynamics because of its ability to accelerate intramolecular vibrational energy redistribution (IVR).22–24
dissociation of IBr\(^-\) (CO\(_2\)), the presence of the solvent molecule CO\(_2\) promotes electron
transfer between the I and Br dissociating fragments. We know this because work on
IBr\(^-\), as presented in Chapter 4, shows that the dissociating molecule produces only
I\(^-\) + Br fragments. Thus the CO\(_2\) molecule must be playing a role in the electron
transfer process. The effects of solvation on reaction dynamics can lead to important
insights into reactions that take place through solvent bridges.

One challenging aspect of these systems, however, is that they can contain hun-
dreds or even thousands of atoms if the solvent molecules are treated explicitly, and
studying these systems in their entirely is extremely difficult, if not impossible in
some cases. However, we can target smaller systems sizes to include only one or a few
of the key interactions found in their larger counterparts and gain valuable insight
into interactions in these ionic systems without the convoluted and competing effects
found with studying the full system. A good example of a smaller system would be
X\(^-\) (X = F, Cl, Br, and I) or M\(^+\) (M = Li, Na, K) interacting with one to a few
water molecules.\(^6,7,25–28\) Numerous water molecules are known to be present in biolog-
ical ion channels and are believed to be strongly responsible for the actual transport
process; thus, studying these smaller systems can yield important information about
how water interacts with ions at a fundamental level. We can probe these funda-
mental interactions in a number of ways. Key experimental techniques that are used
to study these systems are rare-gas predissociation spectroscopy and photoelectron
spectroscopy. A number of theoretical models are also available.
1.3 Using experiment and theory to probe structure and dynamics of weakly-bound anionic systems

Since the dawn of time, humans have observed the world around them and sought to explain these observations. From that point on to present day, the explanation of observation has been rooted in human culture and invariably led to the advancement and pursuit of science. As we began to perceive the world in a more complicated manner, the search for the explanation had also become more complicated. These were the beginnings of the delicate interplay between theory and experiment. The relevance and importance of theoretical treatments, i.e. quantum (and not classical) mechanics, came to the forefront of science around the turn of the 20th century with the explanation of the blackbody radiation by Planck\textsuperscript{29} and the elucidation of the photoelectric effect by Einstein.\textsuperscript{30}

Since then the treatment of systems by quantum mechanics has become increasingly more important to the world of experiment, so much so that many of today’s experimentalists run their own quantum chemistry calculations. However, experiment and theory have not always seen “eye-to-eye,” partially because what was amenable to calculation were not necessarily the same systems that were amenable to experiment, and theory, for a long time, did not have the accuracy required to be comparable with experiment.\textsuperscript{31} However, today experimentalists and theorists work closely to solve many challenging problems.\textsuperscript{31} The work presented in this dissertation further strengthens this relationship by the presentation of several studies of anionic systems with strong emphasis on the codependence of theory and experiment. Most of the
work presented here is in collaboration with mainly two experimental groups: Prof. Mark Johnson and co-workers at Yale University and Prof. W. Carl Lineberger and co-workers at JILA and the University of Colorado at Boulder.

1.3.1 Previous and current experimental work

1.3.1.1 Photoelectron studies

The spectroscopy of anion systems has a rich history, stretching back for the last 40 years.¹ The spectroscopy of negative molecular ions has sought to uncover electron affinities, chemical reaction dynamics, and molecular structure.¹ When we think about negative ion chemistry, we immediately think of the pioneering work done by Lineberger, whose extensive work in this area has led to many scientific elucidations and advancements.³²–⁴¹ The work on negative ions by Lineberger and his contemporaries is characterized by the study of bound-to-free transitions because, as was mentioned above, anions have relatively few bound states compared to their neutral counterparts.¹,⁴¹ In light of this, a large fraction of negative ion chemistry involves bound-to-free transitions, i.e.: photodetachment.³⁴

Within the study of electron photodetachment, there are two schools of experiments, photoelectron spectroscopy and photodetachment threshold spectroscopy, and both can give information about the molecular structure and the electron affinities of negative ions.³⁴ This leading work on combining the experimental techniques of forming negative clusters and using mass selection as a way to facilitate precise chemistry⁴² paved the way for a number of other work on photoelectron studies of charged
diatomic and triatomic molecules, both in isolation and in the presence of a small number of solvating atoms or molecules.\textsuperscript{8, 43–62}

A prototypical photoelectron experimental set-up is shown in Figure 1.3. In the experiments, a focused beam of high kinetic energy (\(~1\ \text{keV}\)) electrons intersects the gas expansion and forms a wide range of cluster anions by slow secondary electron attachment. The anions are then mass selected using time-of-flight methods. After the photochemistry takes place, a variety of information can be obtained, such as the number of cation or neutral molecules that are formed and/or the velocity and angular distribution of the ejected electrons. The experiments on Cu\textsuperscript{−}(CD\textsubscript{3}OD) obtain data regarding the resulting Cu\textsuperscript{+}(CD\textsubscript{3}OD) and Cu\textsuperscript{+} ions that form after double electron detachment. In the work on IBr\textsuperscript{−} and IBr\textsuperscript{−}(CO\textsubscript{2}), the electron kinetic energy distribution is obtained after photoexcitation and photodetachment. One unfortunate downside of these experiments is that the cluster temperatures are not easily determined, and one often obtains “hot” distributions, with temperatures ranging anywhere from 50 K to 200 K.\textsuperscript{4, 62–64} Such hot distributions tend to produce broad photoelectron spectra.

1.3.1.2 Rare-gas predissociation studies

One way to obtain colder molecules while still exploiting the mass-to-charge ratio of anions is through use of rare-gas (tagged) predissociation spectroscopy. Rare-gas predissociation spectroscopy can present a complementary picture to the photoelectron spectra of ionic clusters because it utilizes infrared light to examine the
vibrational spectra of these systems rather than the ionizing the complex, thus providing a more subtle probe of the system. In tagging experiments, rare gas atoms that double as the carrier gas are electrostatically bound to charged molecules, and these $X^-(\text{H}_2\text{O})\cdot\text{Ar}_n$ clusters, for example, then thermalize upon adiabatic expansion. Thermalization occurs because several of the rare gas atoms are “boiled off” due to the extreme change in pressure, taking with them a significant amount of internal energy from the cluster, a energy equivalent to the binding energy of the rare gas atom. This process is extremely efficient way of producing “cold” clusters, which in turn produces narrow, well-resolved vibrational spectra. The process holds for “water tagged” species as well; however, due to the much larger binding energy of water, the clusters come out warmer and the spectra much broader. A cartoon of these processes is shown in Figure 1.4. Rare-gas tagging has been used to isolate a number of weakly-bound anion and cation clusters.

Figure 1.3: Schematic diagram of the photodetachment photoionization apparatus. Reproduced from Ref. 4.
Figure 1.4: Cartoon of the cooling mechanism present in rare gas- and water-tagged vibrational predissociation experiments. Reproduced from Ref. 5 with permission.
With the cool clusters now well isolated, tagging experiments further exploit the weakly bound interaction of the rare gas atom by performing excitation of different vibrational modes. The vibrational excitation energy redistributes among the other degrees of freedom in the complex and eventually couples to the $X^-(\text{H}_2\text{O})\cdots\text{Ar}$ dissociation coordinate, and the rare gas atom loss channel can be captured by mass-selection techniques, resulting in the well-resolved vibrational spectra of these species. Such techniques are employed in the work on $X^-(\text{H}_2\text{O})$ systems as presented in Chapters 2 and 3. A similar idea holds for the water-tagged species; however, because of the larger binding energy of water, the water loss channel is not as efficient but is well utilized for $(\text{H}_2\text{O})_n$ systems because $\text{H}_2\text{O}$ molecules in the higher solvent shells are more weakly bound than those in the first or second solvation shells.

One of the simplest negative ion clusters studied by tagging experiments is $\text{F}^-\,(\text{H}_2\text{O})$. $\text{F}^-\,(\text{H}_2\text{O})$ has been of wide interest to both the experimental and theoretical community because it represents an interesting intermediate case of ionic hydrogen bonding because different charge delocalization regimes are accessed by the first few vibrational levels of the shared proton stretch. The work on $\text{F}^-\,(\text{H}_2\text{O})$ and the related $X^-(\text{H}_2\text{O})$ species ($X = \text{Cl, Br, I, O, and OH}$) has provided information about caged network surrounding the ion, and these studies have paved the way for a greater understanding of other ions solvated by water and by other solvents, such as coinage metal- and alkali metal-water complexes. Of specific interest in the systems are the implications of hydrogen bonding in anion-water complexes and the anion’s effect on the molecular motions and molecular structure. Studies often focus
on mainly higher energy regions of the spectrum, the well-characterized OH stretching region (near 3000 cm$^{-1}$); however, the lower energy modes, at or below 1600 cm$^{-1}$, can vary greatly with the characteristics of the anion as discussed in Chapters 2 and 3.

1.3.2 Previous and current theoretical work

Work on the predictive aspect of spectroscopy and dynamics comes from solving the time-independent and time-dependent Schrödinger equations. In general to obtain vibration spectra, we first need the potential energy surface, most often the ground electronic state. However in studying reaction dynamics, the electronic wave function often samples several electronic states, and to obtain these, one often needs high level \textit{ab initio} methods. In general, calculating potential energy surfaces for large molecules is especially challenging and obtaining said surfaces calculated at a level comparable to experimental accuracy is even more challenging. Valiant strides have been made in this area, such as the work by Bowman$^{87-90}$ and Jordan$^{91-96}$ however, we are still limited to about ten or so atoms and even less if molecular symmetry cannot be exploited. As such there has been a lot of work on reduced-dimensional and model Hamiltonian methods. Here the vibrational coordinate of interest is mapped out, along with other modes that could be strongly coupled to the mode of interest, and then this reduced-dimensional potential surface is calculated and used in the associated set of reduced-dimensional differential equations. The use of model potentials, such as the common pair-wise additive or Lennard-Jones functional forms, can also
reduce the dimensionality of the problem. Many groups have taken these approaches and have had much success and have good agreement with experiment.\textsuperscript{97–105}

1.3.2.1 Time-independent methods

Since about 1990,\textsuperscript{106} one theoretical approach that has become widely used is discrete variable representation (DVR) and is utilized in the work presented here. Discrete variable representation as been discussed by several individuals,\textsuperscript{106–108} and in general, DVR can be used in the evaluation of both time-independent and time-dependent properties,\textsuperscript{106} but for use in the chapters that follow, it will be applied to the time-independent Schödinger equation. Specifically, DVR is a representation in which the associated basis functions are localized about discrete values of the variable of interest (or variables of interest if more than one dimension).\textsuperscript{106}

There are two distinct advantages to DVR. (1) The kinetic energy matrix elements are straightforward to evaluate, and the potential energy matrix elements are the value of the potential energy at the DVR points; therefore, no integral evaluations of the potential energy are necessary.\textsuperscript{106} (2) DVR can be extended to multiple dimensions, and the resulting Hamiltonian for these direct product DVRs is sparse and operation of the Hamiltonian on the wave function is computationally efficient.\textsuperscript{106} Beyond these general characteristics of DVR, a brief derivation is presented below of how a finite basis representation (FBR) is related to this discrete variable representation.

To begin, we will assume a finite basis representation and that the full Hamiltonian for the system is the sum of a model Hamiltonian ($\hat{H}^0$) and a correction term ($\hat{H}'$). The model Hamiltonian can take a variety of forms, such as that for the Harmonic
Oscillator as presented in the next chapter or the Particle-in-a-Box as discussed in Chapters 4 and 6. Table 1.2 shows the functional forms of $\hat{H}^0$ and $\hat{H}'$ for several one-dimensional model systems along with the associated eigenfunctions of $\hat{H}^0$. As mentioned above, $\hat{H}$ can be $N$-dimensional, but for simplicity, we will take $\hat{H}$ to be one-dimensional in the general coordinate space, $q$.

Table 1.2: Model Hamiltonians in the finite basis representation (FBR) with corresponding eigenfunctions of $\hat{H}^0$ projected onto coordinate space $q$, $\langle q|\phi_j\rangle$.

| model system (1-d) | $\hat{H}^0$ | $\hat{H}'$ | $\langle q|\phi_j\rangle$ |
|---------------------|-------------|-------------|-----------------------------|
| Particle-in-a-Box   | $\hat{p}_q^2/(2m)$ | $\hat{V}(q)$ | $\sqrt{(2/L)}\sin(j\pi q/L)$ |
| Harmonic Oscillator | $\hat{p}_q^2/(2m) + \frac{1}{2}k\hat{q}^2$ | $\hat{V}(q) - \frac{1}{2}k\hat{q}^2$ | $N_jH_j(\alpha^{1/2}q)e^{-\alpha q^2/2}$ |
| Rigid Rotor         | $\hat{J}^2/(2\mu R^2)$ | $\hat{V}(q)$ | $\frac{1}{\sqrt{2\pi}}e^{\pm jq}$ |

Within the FBR, the basis functions are the eigenfunctions of $\hat{H}^0$ as shown in Table 1.2, and the solutions to $\hat{H}^0$ are given by

$$\hat{H}^0|\phi_j\rangle = E^0_j|\phi_j\rangle. \quad (1.1)$$

The DVR grid points, $|\chi_n\rangle$, are related to the FBR basis functions by a similarity transformation:

$$|\chi_n\rangle = \sum_j c_{jn}|\phi_j\rangle \quad (1.2)$$
where $c_{jn}$ are the eigenvectors that come from diagonalizing the matrix representation of the position operator in the $|\phi_j\rangle$ basis. As a result of this transformation, $|\chi_n\rangle$ are eigenfunctions of $\hat{q}$ and of any well-behaved functions of $q$, such as $\hat{V}(q)$, but not so for operators that depend on the momentum operator. However, there are well-defined functional forms for the kinetic energy matrix elements for several coordinate definitions. The general solution to an $N$-dimensional system is the product of $N$, one-dimensional functions, as mentioned above, and given by

$$\Psi_{n_1,n_2,\ldots,N}(q_1, q_2, \ldots, q_N) = \sum_{n_1} \sum_{n_2} \cdots \sum_{n_N} d_{n_1,n_2,\ldots,N} \times \chi_{n_1}(q_1)\chi_{n_2}(q_2)\cdots\chi_N(q_N).$$

(1.3)

A schematic representation of the transformation between finite basis and discrete variable representations is shown in Figure 1.5.

![Figure 1.5: Representation of the similarity transformation between finite basis and discrete variable representation, FBR and DVR, respectively.](image-url)
An important point about $|\chi_n\rangle$ is that these functions are nonzero at the DVR points about which they are “localized” and zero at all of the rest of the grid points; this does not mean, however, that they are zero everywhere.\textsuperscript{107,108} Finally while the energies evaluated in a DVR are not variationally bound, the assumption is that convergence of energies to the level of accuracy desired here can be achieved by increasing the number of DVR grid points. It is also important to note that when when $\hat{H}^0$ is the Particle-in-a-Box Hamiltonian, the range of $L$ is also an important factor when considering convergence. For the data discussed in this dissertation, the energies are accurate to within a few hundredths of a cm$^{-1}$ whereas the uncertainties for the experimental observables discussed herein are much larger.

1.3.2.2 Time-dependent methods

While time-independent methods give valuable information about transition frequencies and molecular structure, solutions to the time-dependent Schrödinger equation allows one to follow the reaction dynamics of the system, such as quantum scattering effects\textsuperscript{109,110} or vibrationally-induced proton transfer.\textsuperscript{111,112} There are several types of propagation schemes used to solve quantum mechanical problems depending on the system and quantity of interest. A brief summary of some common methods is shown in Table 1.3.\textsuperscript{113}

Unfortunately, the need to fully represent the wave function on a grid or using a basis becomes prohibitively expensive for even a few molecular degrees of freedom.\textsuperscript{114} As such a variety of methods have been developed to address the quantum mechanical nature of the problem at hand while treating the “less important” degrees of freedom
Table 1.3: Overview of propagation methods.

<table>
<thead>
<tr>
<th>method</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>second-order differencing</td>
<td>simple; accounts for interaction between potentials</td>
</tr>
<tr>
<td>split operator</td>
<td>simple and stable, but no position-momentum cross terms in $\hat{H}$</td>
</tr>
<tr>
<td>Chebychev</td>
<td>a global, long-time method; exact to computer accuracy</td>
</tr>
<tr>
<td>Lanczos</td>
<td>faster, but subspace depends on initial state</td>
</tr>
</tbody>
</table>

*a Information taken from Ref. 113

classically, such as quantum-mechanics/molecular-mechanics, semi-classical, and path integral methods.\textsuperscript{114} While it is clear that time-dependent approaches can be quite costly, they are critical when it comes to the time-resolved experiments that are at the forefront of spectroscopy. Such experiments that utilize time-resolved photoelectron or two-dimensional infrared spectroscopies necessitate the use of such theoretical techniques as linear response theory and full quantum dynamics to account for numerous aspects of the experiment, an important parameter being the temporal pulse width. In light of this, we examine the time-resolved photoelectron spectra of IBr$^-$ in Chapter 4.

1.4 Conclusions

In summary, the work presented in this dissertation will focus on two aspects of anionic species, vibrational spectroscopic characterizations and photoinduced dissociation dynamics. In the work regarding vibrational spectroscopy, we investigate the spectral signatures of hydrogen bonding in halide-water complexes, focusing mainly
on the spectral region below 1600 cm\(^{-1}\) that encompasses many of the low frequency bending modes but also one of the OH stretches, which become significantly redshifted due to strong interactions with the anion. In the second half of the dissertation, we investigate dissociation of molecular ions and solvated molecular ions upon multi-photon ionization. In particular we examine how aspects of the dissociation change upon addition of a solvent molecule and/or variation of the nature of the solvent. In all cases, we work closely with colleagues to provide rich structural, energetic, electronic, and dynamical information about these complexes.
CHAPTER 2

Vibrationally induced proton transfer in $\text{F}^-(\text{H}_2\text{O})$ and $\text{F}^-(\text{D}_2\text{O})$

2.1 Introduction

Ion–water complexes have become the topic of numerous spectroscopic studies covering both the intermolecular OH stretching region and, more recently, the lower frequency region that involves fundamental and overtone bands of the ion-molecule vibrational modes. Even within the simple class of the halide monohydrates, which all adopt asymmetric minimum energy structures involving ion attachment with a single hydrogen bond, a wide range of behavior is displayed according to the proton affinity (PA) of the anions. Large ions with relatively low PA, like iodide for example, can be treated in a perturbative limit. For these systems, a cut through the potential along the hydrogen bonded OH bond length ($\text{OH}_b$) appears very Morse-like, and the $\text{OH}_b$ stretching fundamental is redshifted from that of isolated $\text{H}_2\text{O}$ by several hundred cm$^{-1}$.$^{18,75}$ In such cases, one expects that a one-dimensional model in which the $\text{OH}_b$ vibration is uncoupled from the other degrees of freedom will be adequate. However as the PA of the anion approaches that of $\text{OH}^-$, the complexes become
prototypical examples of short, strong hydrogen bonding and exhibit a number of interesting features.\textsuperscript{12, 14, 18, 19, 115–120}

In general, the potential energy curve associated with the motion of the light hydrogen atom parallel to the heavy atom axis becomes flattened relative to the typical quadratic shape. This allows for large amplitude motion of the shared proton even at the vibrational zero point level\textsuperscript{18, 116} and is manifested in very low $\text{OH}_b$ vibrational frequencies (typically $< 2000 \text{ cm}^{-1}$). In the limit of $\text{OH}^-(\text{H}_2\text{O})$, for example, even though the potential that describes the displacement of the shared proton displays a small barrier at the midpoint, the zero point averaged ground state structures have the most probable position of the shared hydrogen equidistant between the heavy atoms.\textsuperscript{121} In this case, shared proton motion away from the center of mass of the complex is strongly coupled to other low frequency vibrations, in particular the OO stretch as well as the wags and rocks of the flanking OH groups. A similar coupling between the shared proton and heavy-atom stretching motions has been reported by Del Bene and Jordan, based on their studies of $\text{XH}^-\text{NH}_3$ ($\text{X} = \text{F, Cl, and Br}$) complexes.\textsuperscript{122} For these reasons a one-dimensional picture cannot correctly capture the essential spectroscopic patterns displayed by these species.\textsuperscript{120, 123}

In this chapter, we explore the coupled nature of the heavy atom with that of the shared proton within a two-dimensional model of $\text{F}^-\text{(H}_2\text{O})$ in which displacements of the heavy atom bond ($R_{\text{OF}}$) and the $\text{OH}_b$ bond ($r_{\text{OH}_b}$) are treated explicitly. The study addresses the extended level structure that is revealed by new measurements
of the fundamental and overtone bands of the shared proton-based vibrations in $\text{F}^-(\text{H}_2\text{O})$ and $\text{F}^-(\text{D}_2\text{O})$ and the first overtone band of $\text{F}^-(\text{HOD})$.

2.2 Overview of previous work on the $\text{F}^-(\text{H}_2\text{O})$ complex

We focus on the $\text{F}^-(\text{H}_2\text{O})$ complex because it represents an interesting intermediate case of ionic hydrogen bonding, where different charge delocalization regimes are accessed by the first few vibrational levels of the shared proton stretch. The inset in Figure 2.1 shows its minimum energy structure, calculated at the MP2/aug-cc-pVTZ level of theory and basis. Here, the bonded hydrogen forms a nearly linear $\text{O-}^\text{H}_b\cdots\text{F}^-$ hydrogen bond, such that the $\text{OH}_b$ bond length is extended by 0.106 Å relative to that in bare $\text{H}_2\text{O}$ (0.961 Å). The length of the other OH bond is only 0.001 Å shorter than that in the bare species, and this second, free OH bond will be designated as $\text{OH}_f$ in the discussion that follows.

Figure 2.1 also includes the one-dimensional cut through the potential surface, plotted as a function of the shared proton displacement from the center of the $\text{OF}$ bond, with the $\text{OH}_f$ distance and $\text{H}_2\text{O}$ angle allowed to vary so as to minimize the energy of the system. The remaining three vibrational degrees of freedom are constrained to their equilibrium values. Similar potentials have been calculated by several other groups,\textsuperscript{119,124} and the overall qualitative picture is independent of the level of theory/basis. An important feature of this potential is the characteristic “shelf” structure near $r_{	ext{sp}} \approx +0.1$ Å that results from the relatively low-lying energy of the $\text{HO}^-\cdots\text{HF}$ intracluster proton transfer configuration.
Figure 2.1: The one-dimensional potential, calculated at the MP2/aug-cc-pVTZ level of theory/basis, is plotted as a function of $r_{sp} \approx r_{OH} - \frac{1}{2} R_{OF}$, which is approximately the displacement of the shared proton from the center of the OF bond. The minimum energy structure of the F$^-$(H$_2$O) complex is also shown.
Schaefer and co-workers\textsuperscript{124} were the first to treat the level structure expected for the shared proton in $\text{F}^-(\text{H}_2\text{O})$. They employed a one-dimensional approximation using the calculated potential curve at the CISD/TZ2P+diff level of theory/basis, with the OF distance frozen at the equilibrium geometry and the shared proton confined to the heavy atom axis. Interestingly, subsequent measurement of the first overtone transition at 2905(20) cm$^{-1}$ is in very good agreement with their predicted value of 2968 cm$^{-1}$\textsuperscript{125}. Extension of the experimental coverage to the fundamental region was not accomplished until several years later,\textsuperscript{18} and the observed 1523 cm$^{-1}$ value was significantly below the 1667 cm$^{-1}$ energy predicted for the fundamental transition on the same potential surface. Kim and co-workers\textsuperscript{119} refined the one-dimensional approach (again at fixed OF distance) with a calculation at the CCSD(T)/TZ(2df,2pd)++ level of theory/basis and obtained fundamental (1481 cm$^{-1}$) and overtone energies (2951 cm$^{-1}$) in better agreement with experiment. More recently, Gerber and co-workers\textsuperscript{118} used their CC-VSCF method to obtain fully coupled vibrational frequencies of the fundamental and first overtone of the shared proton stretch at the CCSD(T)/aug-cc-pVTZ level of theory/basis. They obtained frequencies of 1488 and 2888 cm$^{-1}$,\textsuperscript{118} respectively, which are close to those obtained from the one-dimensional study of Kim and co-workers\textsuperscript{119} and still underestimate the fundamental transition.

In considering the qualitative features of the level structure, it is interesting to note that, after accounting for zero point energy, the energy of the first excited state is anticipated to be on the order of 2400 cm$^{-1}$. This energy is sufficient to sample the shelf region of the potential plotted in Figure 2.1. In spite of the fact that this level
accesses very anharmonic regions of the potential, all three calculations described above recover a frequency for the first overtone that is roughly twice that of the fundamental.

In this chapter, we further explore the nature of the shared proton motion in a combined theoretical and experimental study of the $\text{F}^-(\text{H}_2\text{O})$ system. Presented herein is the work of Roscioli and Johnson where they have extended earlier work on the $\text{F}^-(\text{H}_2\text{O})$ vibrational structure to include states with up to three quanta in the $\text{OH}_b$ ($\text{OD}_b$) stretch in both the $\text{F}^-(\text{H}_2\text{O})$ and $\text{F}^-(\text{D}_2\text{O})$ isotopologues as well as the state with two quanta in the $\text{OH}_b$ stretch in $\text{F}^-(\text{HOD})$. Inclusion of these additional transitions and mass combinations allows us to more quantitatively determine how accurately the level structure can be accommodated within a one-dimensional picture.

From a theoretical standpoint, systems as small as these can be treated effectively with multidimensional anharmonic methods, but it is often non-trivial to extract simple physical pictures from the final results. Here we take a more intuitive approach where we revisit the one-dimensional treatment described above, and then expand this analytical treatment to include a two-dimensional picture, where we elucidate how the shared proton vibration is coupled to the heavy atom stretch. In our two-dimensional calculations, we develop both potential energy and dipole moment surfaces, which extend over the range of the $\text{OH}_b$ and $\text{OF}$ distance coordinates that are explored by the lowest three or four vibrational levels involving excitation in the $\text{OH}_b$ stretch. The resulting eigenstates are then combined with the calculated dipole moment surface to yield predicted band intensities, which
can then be compared to the observed spectra. This analysis indicates that the one-dimensional model qualitatively fails to recover the observed isotope-dependence of the level structure, and agreement is substantially improved with the two-dimensional treatment.

2.3 Experimental details

The experimental spectra were obtained by Roscioli and Johnson at Yale University, and these experiments were described in detail previously.\textsuperscript{6,38,129} Briefly, infrared spectra were recorded via argon predissociation spectroscopy.\textsuperscript{6,130,131}

\begin{equation}
X^- (H_2O) \cdot Ar_n + h\nu \rightarrow X^- (H_2O) \cdot Ar_m + (n - m)Ar
\end{equation}

(2.1)

where the argon-solvated anionic clusters were photoexcited with infrared pulses with frequencies between 600-3800 cm\textsuperscript{-1}, with a resolution of \(\sim 3\) cm\textsuperscript{-1}, and with an accuracy of \(\pm 4\) cm\textsuperscript{-1}.\textsuperscript{6}

2.4 Theoretical details

The approach used to characterize the F\textsuperscript{−}(H\textsubscript{2}O) complexes is based on both \textit{ab initio} electronic structure and vibrational energy determinations. \textit{Ab initio} calculations, performed using the Gaussian 03 software package,\textsuperscript{132} were used to obtain one- and two-dimensional potential energy surfaces (PESs) and dipole moment surfaces (DMSs) as functions of \(r_{OH_b}\) (1-d) or \(r_{OH_b}\) and \(R_{OF}\) (2-d). These surfaces were
calculated using second-order Møller-Plesset perturbation theory (MP2) with aug-cc-pVTZ Dunning basis sets, a combination of theory and basis set that has been reliable for halide-water systems.\textsuperscript{11,133}

Three sets of potential energy and dipole moment surfaces are explicitly considered, which will be described as 1-d unrelaxed, 1-d relaxed, or 2-d in the presentation below. The calculated DMSs were shifted to have their origins at the center of mass and were rotated into an Eckart frame.\textsuperscript{134,135} After rotation, the $a$-axis lies along the heavy atom axis, the $b$-axis is perpendicular to $a$, and these two axes define the plane of the molecule. The PESs and resulting DMSs were then used to calculate vibrational energies, wave functions, and transition moments in a potential optimized discrete variable representation (PO-DVR).\textsuperscript{107,136,137}

To construct the one-dimensional unrelaxed PES, the electronic energy was calculated as a function of $r_{\text{OH}_b}$ over a range of 0.3 to 1.8 Å in increments of 0.1 Å with $R_{\text{OF}} = R_{\text{OF},e} = 2.43112$ Å. For this potential energy slice, the remaining OH bond length ($r_{\text{OH}_i}$) and the water angle ($\theta_{\text{HOH}}$) were allowed to relax, while all other internal coordinates were fixed at their equilibrium values. The one-dimensional DMS for the unrelaxed study was calculated over the same range of $r_{\text{OH}_b}$.

For the one-dimensional relaxed surface, the electronic energy was also calculated as a function of the $r_{\text{OH}_b}$ distance, which ranged from 0.5 to 5.9 Å in increments of 0.05 Å. The internal coordinates related to the water molecule, $r_{\text{OH}_i}$ and $\theta_{\text{HOH}}$, were relaxed as for the above one-dimensional surface. However, the important difference between these two, one-dimensional PESs is that the heavy atom distance, $R_{\text{OF}}$, is
allowed to relax at every value of $r_{OHb}$. The remaining two geometric parameters were held constant at their respective equilibrium values. The one-dimensional relaxed DMS was calculated on a smaller grid than its corresponding PES, 0.60 to 2.50 Å in increments of 0.05 Å. For the calculations of the PESs and DMSs presented above, the planarity of the complex was retained.

Finally for the two-dimensional surface, the electronic energy was calculated over a range from 1.83112 to 3.43112 Å in $R_{OF}$ and 0.56680 to 3.15680 Å in $r_{OHb}$, both in increments of 0.01 Å. For these calculations, the four atoms were constrained to remain planar, and the H$_f$OF angle was fixed at its equilibrium value of 100.61816°. All other internal coordinates were allowed to relax. The two-dimensional DMS was calculated over a range from 2.03112 to 3.03112 Å in $R_{OF}$ and 0.66680 to 1.76680 Å in $r_{OHb}$ in increments of 0.1 Å. The ranges for all one- and two-dimensional PESs and DMSs were chosen such that they spanned the region of the potential that is sampled by the vibrational wave functions of the states with up to three quanta of excitation in the $r_{OHb}$ stretch.

For the two, one-dimensional calculations, the Hamiltonian is given by

$$\hat{H} = -\frac{1}{2\mu_r} \frac{d^2}{dr^2} + V(r)$$  \hspace{1cm} (2.2)$$

where $\hbar = 1$ throughout this discussion. In equation (2.2) $V(r)$ is obtained by using a cubic spline interpolation of the ab initio data points. For the relaxed one-dimensional surface, $r = r_{OHb}$, and the reduced mass is that associated with an OH stretch. For the calculations using the unrelaxed potential, $r = r_{OHb} - \frac{1}{2}R_{OF,e}$, or $r \approx \frac{1}{2}(r_{OHb} - r_{HF})$. Here $\mu_r$ is the reduced mass associated with this motion when the angle between
$r_{\text{OH}_b}$ and $r_{\text{HF}}$ is fixed at its equilibrium value of 177.53916°. For the 1-d relaxed and 1-d unrelaxed studies of the OH$_b$ (OD$_b$) stretch, the reduced masses are 0.948087 (1.788848) amu and 0.979847 (1.904547) amu, respectively. For the relaxed PES, $r$ varied from 0.45 to 6.5 Å with 550 grid points, while the unrelaxed PES ranged from −1.0 to 1.0 Å with 400 grid points.

The general two-dimensional stretch Hamiltonian, which incorporates both $r_{\text{OH}_b}$ and $R_{\text{OF}}$, is given by

$$
\hat{H} = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r_{\text{OH}_b}^2} - \frac{1}{2\mu_R} \frac{\partial^2}{\partial R_{\text{OF}}^2} - \frac{1}{2} \frac{\partial}{\partial r_{\text{OH}_b}} \frac{\cos \theta(r_{\text{OH}_b}, R_{\text{OF}})}{m_O} \frac{\partial}{\partial R_{\text{OF}}} \\
- \frac{1}{2} \frac{\partial}{\partial R_{\text{OF}}} \frac{\cos \theta(r_{\text{OH}_b}, R_{\text{OF}})}{m_O} \frac{\partial}{\partial r_{\text{OH}_b}} + V(r_{\text{OH}_b}, R_{\text{OF}})
$$

(2.3)

where $\mu_i$ ($i = r$ or $R$) is the reduced mass associated with each stretch coordinate, 0.948087 (1.788848) amu and 8.683882 amu for the OH$_b$ (OD$_b$) and OF bonds, respectively, and $m_O$ is the mass of oxygen. In the mixed partial derivatives $\theta(r_{\text{OH}_b}, R_{\text{OF}})$ is the H$_b$OF angle and has an equilibrium value of 1.38125°. A bicubic spline interpolation of the ab initio points was used to calculate $\theta(r_{\text{OH}_b}, R_{\text{OF}})$ at every value of $r_{\text{OH}_b}$ and $R_{\text{OF}}$ on the two-dimensional grid. The two-dimensional potential energy surface for the two stretch coordinates, $V(r_{\text{OH}_b}, R_{\text{OF}})$, was similarly acquired. To solve equation (2.3), we used a PO-DVR in each of the two stretch coordinates. These potentials were obtained by fitting a slice through the two-dimensional PES at the equilibrium value of the other coordinate ($R_{\text{OF}} = 2.43112$ Å or $r_{\text{OH}_b} = 1.06680$ Å) to a 5th order Taylor series expansion in the OF bond displacement coordinate and an 8th order expansion in the displacement of $r_{\text{OH}_b}$. The one-dimensional Schrödinger equations were each solved in a harmonic oscillator basis using 400 functions.
eigenfunctions were then transformed to generate a DVR with 50 points, and the matrix representations of the momenta conjugate to \( r_{\text{OH}} \) and \( R_{\text{OF}} \) were evaluated in this representation. The two-dimensional stretch Hamiltonian was solved in the product basis, using the 50 DVR points in both \( r_{\text{OH}} \) and \( R_{\text{OF}} \).

The wave functions were then used to evaluate the vibrationally averaged rotational constants, which were used to obtain the rotational energies for each vibrational state and line strengths of the transitions. As such the rotational and vibrational stick spectra were convoluted together with a Gaussian with a half width half maximum (HWHM) of 1 cm\(^{-1}\). These spectra were calculated over a range of vibrational temperatures (50 – 100 K). As the temperature dependence of the spectra is small, only the results for 50 K will be reported.

### 2.5 Results and discussion

#### 2.5.1 Appearance and isotope dependence of the Ar-tagged F\(^-\)(H\(_2\)O) spectra

Figure 2.2 presents the Ar-predissociation spectra of the F\(^-\)(H\(_2\)O) and F\(^-\)(D\(_2\)O) complexes in traces 2.2(a) and 2.2(b), respectively, obtained by Roscioli and Johnson.\(^6\) The OH and OD stretching fundamentals are very intense features because of the low-lying HO\(^-\)···HF configuration, which allows for significant charge transfer upon vibrational excitation.\(^18\) This anharmonicity lends itself to the observation of overtones in the OH\(_b\) stretch, and these (albeit weaker) transitions are labeled in Figure 2.2 by \( \nu^{n=0}_{\text{IHB}} \), where \( n \) represents the number of quanta in the intramolecular hydrogen bond (IHB) after vibrational excitation. Note that the IHB stretch bands
all exhibit significant multiplet structure, the origin of which is not yet understood. Roscioli and Johnson have found these band profiles to be dependent upon the number of Ar atoms attached to the cluster, and future studies are therefore aimed at obtaining the infrared spectrum of the Ne-tagged or bare ion complexes to determine the role of Ar in the band profiles.

We also point out several other experimentally observed transitions. First, the HOH bend, ($\nu_{\text{HOH}}^{1-0}$ in Figure 2.2(a)) appears just above the strong IHB fundamental at 1638 cm$^{-1}$, near the bend frequency of a free water molecule (1595 cm$^{-1}$). This implies that the fluoride-bound water molecule is largely intact at the zero point level. However upon excitation to the state with one quantum in the OH$_b$ stretch, we would expect its frequency to dramatically change due to the charge transfer nature of the IHB transition. The DOD bend should be redshifted from that of the HOH by roughly the ratio of the bend frequencies of isolated DOD and HOH (0.739), but this estimated value of 1210 cm$^{-1}$ falls in the center of the OD$_b$ fundamental. Interestingly, despite the fact that the OD$_b$ stretch and the bend are nearly degenerate, they do not appear to mix significantly; in fact, the shared OD $\nu_{\text{IHB}}^{1-0}$ band is actually less structured than its OH counterpart. This experimental observation is supported by the normal mode picture, in which little coupling is observed between the OD stretch and the DOD bend at the harmonic level.

In what follows we will focus on the coupling between the shared proton and OF stretching vibrations as the key to understanding the level structure, and one way to empirically investigate the role of the dangling OH$_f$ is to determine how the
Figure 2.2: Ar-predissociation spectra of (a) F$^-$(H$_2$O) and (b) F$^-$(D$_2$O) observed by Roscioli and Johnson. Reproduced from Ref. 6.
energies of the OH\textsubscript{b} stretch levels respond to H/D substitution at this site. Roscioli and Johnson have therefore also studied the F\textsuperscript{−}(HOD) complex.\textsuperscript{6} Because the lighter H fractionates very efficiently to the shared position,\textsuperscript{75} Roscioli and Johnson were only able to compare the shared proton vibrations for the F\textsuperscript{−}(H\textsubscript{2}O) and F\textsuperscript{−}(HOD) variations,\textsuperscript{6} with the results presented as a footnote in Table 2.1. The IHB bands are quite similar in these two molecules, indicating that the motions of the dangling hydrogen atoms are not intimately coupled to the shared proton band positions.

Table 2.1: Comparison of various calculated anharmonic frequencies with experiment. All frequencies are given in cm\textsuperscript{−1}, and the relative values of $M_{\text{H/D}}^t$ (defined in eq. (2.5)) are listed in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>1-d unrelaxed</th>
<th>1-d relaxed</th>
<th>2-d</th>
<th>experiment\textsuperscript{a,b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsuperscript{−}(H\textsubscript{2}O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{1←0}</td>
<td>1497 (1.1888)</td>
<td>1405 (1.3757)</td>
<td>1533 (1.0000)</td>
<td>1430–1570</td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{2←0}</td>
<td>3159 (0.0204)</td>
<td>2649 (0.1366)</td>
<td>2934 (0.0216)</td>
<td>2815–2930</td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{3←0}</td>
<td>5009 (0.0009)</td>
<td>3810 (0.0171)</td>
<td>4469 (0.0007)</td>
<td>4110–4450</td>
</tr>
<tr>
<td>F\textsuperscript{−}(D\textsubscript{2}O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{1←0}</td>
<td>1089 (0.8326)</td>
<td>1084 (1.0690)</td>
<td>1166 (0.5479)</td>
<td>1160–1270</td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{2←0}</td>
<td>2177 (0.0223)</td>
<td>2035 (0.0848)</td>
<td>2142 (0.0238)</td>
<td>2120–2263</td>
</tr>
<tr>
<td>$\nu_{\text{IHB}}$\textsubscript{3←0}</td>
<td>3421 (0.0010)</td>
<td>2929 (0.0080)</td>
<td>3230 (0.0013)</td>
<td>3125–3265</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Observed by Roscioli and Johnson. Reproduced from Ref. 6.
\textsuperscript{b} F\textsuperscript{−}(HOD): $\nu_{\text{IHB}}$\textsubscript{2←0} range 2800–2930 cm\textsuperscript{−1}.

### 2.5.2 Investigation of OH\textsubscript{b} frequency progressions

To characterize the shared proton potential, it is useful to first consider what the experimental frequencies tell us about the potential surface. It has long been
recognized that the progression of vibrational levels of an XH oscillator can be well described by a Morse potential for which

$$\tilde{\nu}_n = \tilde{\nu}_e n - \tilde{\nu}_e \chi_e (n^2 + n).$$  \hspace{1cm} (2.4)

To obtain fundamental and anharmonicity constants, we fit the center of intensity for each observed band to eq. (2.4). Based on this analysis, we find that the ratio of the anharmonicity to the frequency is roughly 0.02 for the OH$_b$ stretch and approximately 0.04 for the OD$_b$ stretch. While it is surprising to find an OD stretch that is more anharmonic than an OH stretch, the ratios are not significantly larger than what one would obtain for bare H$_2$O or D$_2$O for which the ratios are both approximately 0.01.$^{139}$

This relatively small anharmonicity was not foreseeable given the large (> 2000 cm$^{-1}$) redshift in the OH$_b$ fundamental transition relative to the free OH stretch at $\sim$ 3690 cm$^{-1}$.\textsuperscript{18} Clearly a single one-dimensional Morse oscillator will not reproduce the observed isotope-dependent level structure. To explore the connection of the spectral features to the underlying potential surface, we start with the same approach that has been used in a number of earlier studies\textsuperscript{119,124} on this system and examine the one-dimensional PESs and their resulting frequencies.

### 2.5.3 Examination of transition energies from the 1-d PESs

The one-dimensional unrelaxed potential energy surface is shown as the thick, black curve in Figure 2.3. An important feature of this surface is the presence of the shelf structure, which arises from an avoided crossing between the two diabatic
potentials that correspond to the $\text{F}^- \cdots \text{H}_2\text{O}$ and $\text{HO}^- \cdots \text{HF}$ complexes. These two configurations are illustrated by the natural bond orbitals (NBOs) for the excess electron$^{140-142}$ shown at the top of Figure 2.3. The NBO in Figure 2.3(I) is localized on the fluoride; however, the other NBO, in Figure 2.3(II), is localized on the oxygen. Thus for $r_{\text{OH}_b} < 1.286 \text{ Å}$, the excess electron can be considered to be localized on the F atom, while for longer $\text{OH}_b$ distances, the excess electron has migrated from F to O. This value of $r_{\text{OH}_b}$ coincides with the shelf region of the potential plotted in Figure 2.3.

As described above, the vibrational levels for the shared proton motion, based on this potential, were obtained by numerically solving the Schrödinger equation based on the Hamiltonian given in eq. (2.2). These results are reported in Table 2.1 and are represented by red and black horizontal lines in Figure 2.3. As was mentioned earlier, the state with one quantum of excitation in the OH$_b$ stretch lies above the shelf region. As such we expect it to exhibit some HO$^- \cdots \text{HF}$ character.

To aid in the comparison between the experimental and calculated frequencies, the experimental transition energies are depicted by the black and red vertical arrows for the OH and OD stretches, respectively, with their origins placed at the calculated zero point levels. Like the previous one-dimensional treatments,$^{124}$ this PES reproduces the fundamental and first overtone frequencies for the OH stretch in $\text{F}^-($H$_2\text{O})$, and in addition yields a reasonable value for fundamental and first overtone transitions of the OD stretch in $\text{F}^-($D$_2\text{O})$ as well. There is, however, poor agreement for the
Figure 2.3: The 1-d unrelaxed PES with black and red horizontal lines indicating the calculated energies of the OH$_b$ and OD$_b$ stretches, respectively. The black and red arrows provide the center of the experimental ranges reported in Table 2.1. Natural bond orbitals for the excess electron are shown above.
second overtone frequency in both the OH and OD stretches as shown in Table 2.1. No single, multiplicative scaling of the potential can correct for this discrepancy.

To further investigate these systems, we now turn our attention to the one-dimensional, relaxed PES shown in Figure 2.4. Note that this treatment is analogous to an adiabatic adjustment of the OF distance along the shared proton stretch coordinate, providing a contrasting scenario to the situation presented in Figure 2.3, where there was no coupling between these motions. By allowing $R_{OF}$ to change, the shelf structure is lost entirely, making the effects of proton transfer less visible. Here the fundamental frequencies for the both OH stretch in $F^-(H_2O)$ and the OD stretch in $F^-(D_2O)$ agree well with experiment. However, the energy of the first and second overtones in the OH and OD stretches are now too low, and again no single, multiplicative scaling of the PES will correct this.

Based on these two limiting models, we find that the one-dimensional PESs each reproduce a portion of the experimental progression for $F^-(H_2O)$ and $F^-(D_2O)$ but all six transitions cannot simultaneously be reproduced with either one-dimensional picture. In considering how to fully describe the $H^+$ transfer dynamics in $F^-(H_2O)$, we note that there is strong coupling between $R_{OF}$ and $r_{OH_b}$ as shown in Figure 2.4(a), with large changes in $R_{OF}$ over relatively a small range in $r_{OH_b}$, even near the equilibrium, $r_{OH_b} = 1.067 \, \text{Å}$. 
Figure 2.4: The lower panel (b) is the same as that shown in Figure 2.3, but with the 1-d relaxed PES, as described in the text. In panel (a), we plot the OF internuclear distance as a function of the OH_b bond length, plotted on the same scale as panel (b).
2.5.4 Results from the 2-d treatment

2.5.4.1 Comparison between calculated and experimental transition frequencies

The two-dimensional PES is plotted as a function of $r_{\text{OH}_b}$ and $R_{\text{OF}}$ in Figure 2.5. This potential can be divided into three regions, denoted by their corresponding structures. The minimum energy configuration, $\text{F}^- \cdots \text{H}_2\text{O}$, is indicated as structure I; at large values of $R_{\text{OF}}$, the complex dissociates into $\text{F}^- + \text{H}_2\text{O}$, (structure II), while at large values of both $r_{\text{OH}_b}$ and $R_{\text{OF}}$, the complex dissociates into $\text{HO}^- + \text{HF}$, (structure III). We include the associated anharmonic transition frequencies in Table 2.1. Comparing the three sets of calculated values, we find that this model provides the best agreement with the experimental values for both isotopologues. To obtain this agreement, we multiplied all of the electronic energies used to construct the two-dimensional surface by 0.99, which is consistent with the scaling factors used for this level of theory and a comparable basis set.\textsuperscript{143–145} This scaling led to a decrease in the transition frequencies of roughly 0.6% or between 9 and 33 cm\textsuperscript{$-1$}, and even without scaling, the calculated frequencies are in very good agreement with experiment.

2.5.4.2 Comparison of calculated spectra with experiment

Having demonstrated that the experimental frequency progressions are reproduced by a two-dimensional \textit{ab initio} potential surface, we turn our attention to the calculated spectra, which we compare with experiment in Figure 2.6. The red curve is a convolution of the stick spectra calculated at a rotational temperature of 50 K and convoluted with a Gaussian with a HWHM of 1 cm\textsuperscript{$-1$}. The experimental spectra are
Figure 2.5: The two-dimensional potential for F$^-$(H$_2$O). Complex I is the minimum energy structure, F$^-$···H$_2$O. Complex II shows the dissociation of the minimum energy structure into H$_2$O + F$^-$ upon excitation in R$_{OF}$. Complex III shows the dissociation of the minimum energy structure into HO$^-$ + HF upon excitation in both R$_{OF}$ and r$_{OH_b}$. 
shown as the black traces in Figure 2.6 and are identical to those shown in Figure 2.2.

In Table 2.1 we report the square of the transition moments for the OH\textsubscript{b} or OD\textsubscript{b} stretch,

\[ M^\text{H/D}_n = \frac{|\langle n | \vec{\mu} | 0 \rangle |_{\text{H/D}}^2}{|\langle 1 | \vec{\mu} | 0 \rangle |_{\text{H}}^2} \]  

for the fundamental and first two overtone transitions. All of the reported transition moments have been normalized with respect to the fundamental transition of the OH\textsubscript{b} stretch in F\textsuperscript{−}(H\textsubscript{2}O), |\langle 1 | \vec{\mu} | 0 \rangle |_{\text{H}}^2, from the 2-d calculation. We have reported \( M^\text{H/D}_n \) values rather than the usual intensities because the reported experimental signal reflects the measured signal divided by the laser power. This ratio is equivalent to dividing the calculated intensity by the transition frequency.

To begin, we will consider the F\textsuperscript{−}(D\textsubscript{2}O) spectrum shown in Figure 2.6(b). The three OD\textsubscript{b} stretch frequencies agree very well with experiment, and the relative peak heights are in qualitative agreement. Upon closer examination of the deuterated spectrum, there is additional structure near two of the three transitions. There is a strong feature that lies underneath the \( \nu^{1\leftarrow 0}_{\text{H/HB}} \) experimental peak. This band occurs at 1232 cm\(^{-1}\) and is attributed to the \( \nu^{3\leftarrow 0}_{\text{OF}} \) band. This feature might be leading to some of the extra structure seen in the \( \nu^{1\leftarrow 0}_{\text{H/HB}} \) peak in the experimental spectrum. A second peak of interest lies to the blue of \( \nu^{2\leftarrow 0}_{\text{H/HB}} \). This peak appears at 2263 cm\(^{-1}\) and is attributed to the \( \nu^{1\leftarrow 0}_{\text{H/HB}} + \nu^{2\leftarrow 0}_{\text{OF}} \) combination band.

As with the F\textsuperscript{−}(D\textsubscript{2}O) spectrum, the calculated positions of the three main transitions in the F\textsuperscript{−}(H\textsubscript{2}O) spectrum agree well with experiment, but the relative peak
Figure 2.6: Comparison of the convoluted stick spectra with experiment for (a) $\text{F}^-(\text{H}_2\text{O})$ and (b) $\text{F}^-(\text{D}_2\text{O})$. Each pair of spectra has been scaled so that they have the same value for the maximum peak height. Experimental spectra are obtained by Roscioli and Johnson and are reproduced from Ref. 6.
heights are in less good agreement. In addition, bands in the experimental \( \text{F}^- (\text{H}_2\text{O}) \) spectrum are even more structured than those in \( \text{F}^- (\text{D}_2\text{O}) \). For example the \( \nu_{\text{IHB}}^{2\leftarrow0} \) band is clearly a doublet. Upon closer examination of the region near \( \nu_{\text{IHB}}^{1\leftarrow0} \), there is a second, much smaller peak that is close to our calculated \( \nu_{\text{OF}}^{3\leftarrow0} \) band at 1308 cm\(^{-1}\). This transition is much weaker than the corresponding transition in \( \text{F}^- (\text{D}_2\text{O}) \) because the \( \nu_{\text{OF}}^{3\leftarrow0} \) peak is separated from \( \nu_{\text{IHB}}^{1\leftarrow0} \) by \( \sim 225 \) cm\(^{-1}\), whereas this difference is only \( \sim 65 \) cm\(^{-1}\) for the deuterated species. In the calculated spectrum, a second peak to the red of \( \nu_{\text{IHB}}^{2\leftarrow0} \) occurs at 2668 cm\(^{-1}\) and corresponds to the \( \nu_{\text{IHB}}^{1\leftarrow0} + \nu_{\text{OF}}^{2\leftarrow0} \) combination band. This peak has comparable transition strength to that of \( \nu_{\text{IHB}}^{3\leftarrow0} \). Moreover there is a similarly spaced peak present in the experimental spectrum. As is evident by the experimental spectrum of \( \text{F}^- (\text{H}_2\text{O}) \), \( \nu_{\text{IHB}}^{3\leftarrow0} \), like the other two transitions, has intriguing peak structure. There are two calculated features in this region at 3950 and 4439 cm\(^{-1}\) that are combination bands of \( \nu_{\text{IHB}}^{2\leftarrow0} + \nu_{\text{OF}}^{2\leftarrow0} \) and \( \nu_{\text{IHB}}^{2\leftarrow0} + \nu_{\text{OF}}^{3\leftarrow0} \), respectively. These two transitions have calculated integrated intensities that are nearly equal to that of the nearby \( \nu_{\text{IHB}}^{3\leftarrow0} \) transition.

Both the experimental and calculated \( \text{F}^- (\text{H}_2\text{O}) \) spectra show additional structure in the region between 2000 and 2400 cm\(^{-1}\). In the calculated spectrum, the feature at 2112 cm\(^{-1}\) results from a combination band of \( \nu_{\text{IHB}}^{1\leftarrow0} + \nu_{\text{OF}}^{1\leftarrow0} \) and might correspond to the experimental feature near 2250 cm\(^{-1}\). Based on our calculations, we find that this transition has similar transition strength as the first overtone in the \( \text{OH}_b \) stretch. As a final note, we suspect that the experimental feature near 2000 cm\(^{-1}\) is the overtone in the out-of-plane bend\(^7\) and will be discussed in the following chapter.
Up to this point, we have focused on transitions with energies equal to or greater than 600 cm\(^{-1}\), i.e.: spectral regions where transitions can be measure experimentally. In addition to these transitions, we determine the \(\nu_{OF}^{1-0}\) feature for both \(F^- (H_2O)\) and \(F^- (D_2O)\) to have frequencies and transition moments of 465 (0.2234) and 427 (0.3051) cm\(^{-1}\), respectively. The first overtones are predicted to occur at 898 and 833 cm\(^{-1}\), respectively, and are anticipated to have comparable transition moments to that of \(\nu_{\text{IHB}}^{3-0}\).

2.5.4.3 Quantifying the vibrational level dependence of the extent of proton transfer

We conclude our discussion of the fluoride-water complexes by focusing on other properties that can be derived by analysis of the wave functions. Paramount among these is understanding and quantifying the degree to which proton transfer is driven by vibrational excitation of the OH\(_b\) stretch. To do so we focus on the two-dimensional wave functions of \(F^- (H_2O)\) and \(F^- (D_2O)\), which are displayed in Figure 2.7 and plotted on top of the PES, where the white or pink striations denote the phase of the wave function. The state labels correspond to the number of quanta in \(r_{OH_b}\) and \(R_{OF}\), respectively. Thus the plots labeled by in Figure 2.7 are of the ground vibrational states of \(F^- (H_2O)\) and \(F^- (D_2O)\), respectively. The remaining six plots in Figure 2.7 have one, two, and three quanta of excitation in the OH\(_b\) stretch.

Examination of the excited state wave functions indicates that, when the OH\(_b\) bond is vibrationally excited, the wave function exhibits significant amplitude in the
Figure 2.7: Two-dimensional wave functions for F−(H2O) and F−(D2O) are overlaid on the two-dimensional potential. The state labels provide the numbers of quanta in the OHb and OF stretches, respectively.
proton transfer region \( (r_{\text{OH}} \gtrsim 1.286 \text{ Å}) \). To quantify the extent to which \( \text{H}^+ \) transfer is driven by vibrational excitation of the OH or OD stretch, we define\textsuperscript{18,146,147}

\[
\rho_{\text{PT}} = (r_{\text{OH}} - r_{\text{OH}}^0) - (r_{\text{HF}} - r_{\text{HF}}^0),
\]

which is an index that allows us to quantify the degree of proton transfer in proton-bound complexes. In equation (2.6) \( r_{\text{XH}}^0 \) denotes the equilibrium OH or HF distance in a bare water or HF molecule, respectively. For the case of bare water, \( r_{\text{OH}}^0 = 0.96148 \text{ Å} \), and for HF, \( r_{\text{HF}}^0 = 0.92183 \text{ Å} \), as calculated at the MP2/aug-cc-pVTZ level of theory/basis. With this definition, we can then determine what fraction of the probability amplitude can be characterized as \( \text{HO}^- \cdots \text{HF} (\rho_{\text{PT}} > 0) \), which provides a measure of the percentage of proton transfer in each vibrational state.

These percentages, along with \( \langle \rho_{\text{PT}} \rangle \), are listed in Table 2.2. The percent of proton transfer in the ground state is 15% for \( \text{F}^- (\text{H}_2\text{O}) \) and 9% for \( \text{F}^- (\text{D}_2\text{O}) \). However, even one quantum in \( r_{\text{OH}} \) yields proton transfer of \( \sim 60\% \) for \( \text{F}^- (\text{H}_2\text{O}) \) and \( \sim 50\% \) \( \text{F}^- (\text{D}_2\text{O}) \). Note that while there is a substantial increase in the percentages of proton transfer from the ground to first excited state, they remain nearly constant for the three excited states. While this observation may seem surprising, it reflects a buildup of probability amplitude above the shelf region of the potential in these excited states.

### 2.6 Conclusion

Through H/D isotopic substitution and spectroscopic observation of the fundamental and first two overtone transitions associated with the shared proton, we obtain an extensive database from which to explore both the nature of the shared proton
Table 2.2: The average values of $\rho_{PT}$ (as defined by eq. (2.6)) and the percent of proton transfer. For $\rho_{PT} > 0$, the proton is associated with F rather than O.

<table>
<thead>
<tr>
<th>state</th>
<th>$\langle \rho_{PT} \rangle / \text{Å}$</th>
<th>% proton transfer</th>
</tr>
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<tr>
<td>$\text{F}^- (\text{H}_2\text{O})$</td>
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<td></td>
</tr>
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</tr>
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</tr>
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</tr>
<tr>
<td>$n = 3$</td>
<td>0.0037</td>
<td>53.32</td>
</tr>
</tbody>
</table>

potential surface and the extent to which its motion is coupled to the motions of other atoms in the complex. Although one-dimensional treatments are common in the literature, we find that such a simple analysis cannot accurately recover either the higher overtones or the isotope dependence of the observed bands. We identify the OF stretch as the critical motion necessary to include for an accurate description of the observed levels. Explicit two-dimensional analysis of the vibrational levels and transition moments on an extended potential surface yield transitions quite close to the observed bands. This is a reflection of the effective OF distance being elongated at the higher levels of shared proton excitation. Analysis of the resulting wave functions indicates that while the zero point level is largely charge localized on the
fluoride ion, all the excited states associated with the shared proton stretch conform
to situations where the bridging proton is largely equally shared. The large intensity
of the infrared transitions can thus be traced to optically driven, intracluster proton
transfer, as inferred in earlier reports of the spectrum.\textsuperscript{125}
CHAPTER 3

Anharmonicities and isotopic effects in the vibrational spectra of $X^- \cdot H_2O$, $\cdot HDO$, and $\cdot D_2O$ [$X = Cl, Br, \text{and} I$] binary complexes

3.1 Introduction

Although the identification of hydrated halides as independent species is a central concept in aqueous electrolyte chemistry,\textsuperscript{148} the molecular-level nature of the interactions has only recently been unveiled as experimental and theoretical tools have finally become equal to the challenge of accurately treating them. Examples where such knowledge is critical include the theoretical treatment of the heterogeneous chemistry of aerosol particles,\textsuperscript{149–152} and the transport of ions across channels in biological membranes.\textsuperscript{153,154} The modeling of such complex systems at finite temperatures often relies on the use of interaction potentials,\textsuperscript{155–157} and these potentials are, in turn, derived from a detailed analysis of the elementary binary interaction between the water molecule and the ion.\textsuperscript{158}

In recent years, several reports have described the analysis of the vibrational structure arising from halide-water complexes using the “messenger” atom technique,\textsuperscript{6,18,28,75,131,159–163} which can now be carried out with sufficient spectral coverage to identify vibrational transitions associated with five of the six expected normal
modes. A significant aspect of this effort is the observation of a variety of strong anharmonic effects that give rise to many more bands than are predicted based on the calculated vibrational spectrum within the usual harmonic oscillator and linear dipole approximations.

From a molecular physics perspective, these extra transitions are quite useful. Their presence reveals the strength and nature of the coupling between the modes and the coordinate dependence of the electric dipole moment surface. The variety of anharmonicities observed include Fermi resonances, combination bands, and overtone transitions arising from both distorted potential curves as well as intra-complex charge transfer.6,18,74,161

In a recent paper, work that is not included in this dissertation,18 Roscioli et al. discussed the spectral signatures associated with the vibrations arising from a proton that is hydrogen-bonded to a variety of anions; here we focus on the implications of the spectra on the lower energy motions arising from frustrated rotation of the water molecule against the ion. We accomplish this by analyzing a comprehensive data set involving the Cl\(^-\), Br\(^-\), and I\(^-\) ions combined with three isotopic variations of the water molecule (H\(_2\)O, HDO, and D\(_2\)O). We are particularly interested in exploring the behavior of the in-plane (ip) and out-of-plane (oop) bending modes.

The equilibrium geometry of the halide water complexes can be described as an asymmetric (single ionic hydrogen-bonded) structure with the general arrangement depicted in Figure 3.1(a). One important finding of the extensive earlier studies\(^{18,19}\) was the unexpected large intensity in the overtone transition in the out-of-plane bend
(2ν_{oop}). In Cl^{-}\cdot{H_2}O and Br^{-}\cdot{H_2}O the intensity of the overtone in the out-of-plane bend was found to be almost equal to that of the fundamental in the water bend (ν_{HOH}). In our analysis of this band, we were surprised to find that a one-dimensional model of this vibration described not only the frequencies of these transitions, but also their unexpectedly large intensities, which were attributed to electrical anharmonicities (i.e., the shape of the electric dipole moment surface). Here we follow the evolution of these effects upon all possible deuterations of the water molecule to effectively change the range of the surface explored by the overtone and thus better quantify the dominant cause of the anomalous overtone intensities.

The minimum energy structure displayed in Figure 3.1(a) is, of course, one of two equivalent structures that are separated by a low-lying saddle point with C_{2v} symmetry, shown in Figure 3.1(b). The in-plane bend, which can be thought of as the frustrated rotation of the water molecule about its c inertial axis, is the coordinate that connects these minima and leads to exchange of the hydrogen atoms in the double minimum potential. Experimentally, this is the least accessible motion of the six normal modes, and its activity has only been tentatively identified through a combination band involving one quantum in the in-plane bend and one quantum in the water bend in the Cl^{-}\cdot{H_2}O system in Ref. 18.

In this chapter, we extend the spectroscopic studies to follow the dependence of this putative combination band on partial and full deuteration and on the strength

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*The notation in this chapter is slightly different than that presented in the previous chapter. There are only small differences in the referencing of the molecular species, for example, Cl^{-}\cdot{H_2}O versus Cl^{-}(H_2O). The notation of the vibrational bands is also slightly different: ν_{HHB}^{n-0} versus ν_{OH}. Despite this, all the notion within a given chapter is consistent.
Figure 3.1: \( \text{X}^-\cdot\text{H}_2\text{O} \) structures. In (a) and (b), the two low-energy stationary points are shown, with (a) providing the minimum-energy structure with \( C_s \) symmetry and (b) the \( C_{2v} \) transition-state structure. Panels (c) and (d) show the definitions of the in-plane (\( \theta_{ip} \)) and out-of-plane bend coordinates (\( \theta_{oop} \)). \( a, b, \) and \( c \) represent the three inertial axes.
of the $X^-\cdot\text{H}_2\text{O}$ interaction in the $X = \text{Cl}, \text{Br}, \text{and I}$ systems. Particularly interesting aspects regarding the behavior of the in-plane bend is the role of tunneling splitting and the question of whether transitions involving overtones in the in-plane bend display similar intensity anomalies as those observed in transitions based on the out-of-plane vibration. Given that these transitions are likely to only be observed as combination bands, this raises the issue of how well the spectra of these complexes are described by a series of one-dimensional cuts through the potential surface and to what extent does inter-mode coupling need to be explicitly taken into account. This last issue is of particular interest as it provides insight into when one can unravel spectra through a series of fully anharmonic, reduced-dimensional slices through the global potential surface. This will become particularly powerful as we consider larger ion-water complexes, involving multiple water molecules and possibilities for proton translocation.\textsuperscript{16,164}

### 3.2 Experimental details

The experimental spectra were obtained by Elliott, Weddle, Roscioli, and Johnson at Yale University who will heretofore be referred to as Elliott et al. Experiments similar to these were described in the previous chapter and in previous work.\textsuperscript{7,38,129} Relevant to the work presented in this chapter, the argon-solvated anionic clusters were photoexcited with infrared pulses with energy ~800 to 3800 cm$^{-1}$, and the resolution of the laser is ~3 cm$^{-1}$.\textsuperscript{7}
3.3 Theoretical details

The approach used to characterize the X\textsuperscript{−}·H\textsubscript{2}O complexes is based on both \textit{ab initio} electronic structure calculations and harmonic analyses. \textit{Ab initio} calculations are also used to obtain one-dimensional slices of both the potential energy (PES) and dipole moment surfaces for the two vibrational modes of interest. These surfaces are then used to calculate vibrational energies, wave functions, and oscillator strengths in a basis of sine and cosine functions.

3.3.1 Electronic structure calculations

All electronic structure calculations are performed using the Gaussian 03\textsuperscript{132,165} program package. One-dimensional potential energy and dipole moment surfaces are calculated using second-order Möller-Plesset perturbation theory (MP2) and large, diffuse Dunning basis sets (aug-cc-pVTZ). For the I\textsuperscript{−}·H\textsubscript{2}O systems a 28 electron core pseudopotential (PP) and corresponding basis set are used for iodine (aug-cc-pVTZ-PP).\textsuperscript{166,167} This core potential and basis set are chosen because the pseudopotential is parameterized for halogen-oxygen interactions as well as for anionic properties, and the basis set is of similar size and quality as that used for the lighter atoms. This combination of theory/basis has proven to be reliable for these hydrogen-bonded systems while at the same time remaining computationally feasible.\textsuperscript{11}

Using this level of theory, we perform two sets of calculations. First we evaluate the harmonic spectra at the minimum energy geometries of the four isotopologues of each X\textsuperscript{−}·H\textsubscript{2}O complex. We also evaluate the potential and dipole surfaces along two
different one-dimensional slices through the global six-dimensional potentials: one along the in-plane (ip) bend coordinate and a second as a function of the out-of-plane (oop) bend coordinate.

The in-plane bend angle ($\theta_{ip}$) is depicted in Figure 3.1(c) and is defined as the angle between one of the OH bonds and the OX$^{-}$ axis. The in-plane bend angle is calculated in increments of 5.0° starting from the $C_{2v}$ transition state, where the HOX$^{-}$ angle is represented by $\theta_{C_{2v}HOX}$. More specifically,

$$
\theta_{ip} = \begin{cases} 
\theta_{C_{2v}HOX} - \theta_{H_{2}OX} & \text{for } \theta_{ip} < 0 \\
\theta_{H_{2}OX} - \theta_{C_{2v}HOX} & \text{for } \theta_{ip} > 0 
\end{cases},
$$

(3.1)

where the $C_{2v}$ structure is shown in Figure 3.1(b). The values of $\theta_{ip}$ at the $C_{s}$ minima depend on the equilibrium HOH angle in the complex and differ slightly among the halides. The equilibrium values for the three halides are reported in Table 3.1. For the calculations of the electronic energy as a function of this coordinate, the complex is constrained to remain planar. The OH$_{b}$, OH$_{f}$, and OX$^{-}$ distances and the water angle are relaxed to their optimized values. It should be noted that since halide-water complexes have $C_{s}$ symmetry in their equilibrium configurations, the one-dimensional PESs along the in-plane coordinate, $V(\theta_{ip})$, are symmetric about their $C_{2v}$ geometries, and $\theta_{ip} = 0°$ at this stationary point.

The other coordinate of interest is the out-of-plane bend angle ($\theta_{oop}$), shown in Figure 3.1(d). To obtain the potential as a function of the out-of-plane bend coordinate, we perform a scan in $\chi_{oop}$, which is the angle between the plane that contains the water molecule and the plane defined by the heavy atom axis and the OH$_{f}$ bond. It is varied over a range of 0.01° to 75.01° in increments of 5.0° in the calculated
Table 3.1: Equilibrium geometries of $X^-\cdot H_2O$ complexes. All distances, $r$, have units of angstroms (Å), and all angles, $\phi$, $\psi$, and $\theta$, have units of degrees ($^\circ$).

<table>
<thead>
<tr>
<th>parameter</th>
<th>Cl$^-\cdot H_2O$</th>
<th>Br$^-\cdot H_2O$</th>
<th>I$^-\cdot H_2O$</th>
</tr>
</thead>
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<tr>
<td>$r_{OH_f}$</td>
<td>0.961</td>
<td>0.961</td>
<td>0.961</td>
</tr>
<tr>
<td>$r_{OH_b}$</td>
<td>0.991</td>
<td>0.986</td>
<td>0.981</td>
</tr>
<tr>
<td>$r_{XH_b}$</td>
<td>2.115</td>
<td>2.292</td>
<td>2.548</td>
</tr>
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<td>$\phi_{H_fOH_b}$</td>
<td>100.7</td>
<td>100.6</td>
<td>100.7</td>
</tr>
<tr>
<td>$\phi_{OH_bX}$</td>
<td>168.9</td>
<td>167.5</td>
<td>165.4</td>
</tr>
<tr>
<td>$\psi_{H_fOH_bX}$</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
<tr>
<td>$</td>
<td>\theta_{ip}^{Cs}</td>
<td>$</td>
<td>47.62</td>
</tr>
</tbody>
</table>

cuts through the potential along this coordinate. In these calculations of the electronic energy as a function of an out-of-plane angle ($\chi_{oop}$), only the $OH_b$ distance and the water angle are relaxed, while the $OX^-$ distance, the $OH_f$ bond length, and the $H_fOX^-$ angle are constrained to their equilibrium values. Because the equilibrium structure is planar, the one-dimensional potentials evaluated as a function of $\chi_{oop}$, $V(\chi_{oop})$, are symmetric about $\chi_{oop} = 0^\circ$.

The above treatment defines the out-of-plane angle as the angle between two planes, rather than the angle between the $OH_b$ bond and the molecular plane (which we will make the $ab$ plane). In order to obtain the latter description of the out-of-plane bend ($\theta_{oop}$), we take advantage of the fact that the scans employed a dummy atom (Y) that is coplanar with the halide ion and the $OH_f$ bond. The dummy atom has a $YOX^-$ angle that is constrained in the scans. To determine $\theta_{oop}$, we first define the $a$-axis to contain the two heavy atoms (O and $X^-$) and the dummy atom to lie in
the $ab$ plane. We then equate $\theta_{oop}$ with the angle between the OH$_b$ bond and the $ab$ plane. Although $\chi_{oop}$ and $\theta_{oop}$ are not identical, their values differ by no more than 1° over the range of these coordinates for which the wave functions have amplitude.

The dipole surfaces, which are plotted in Figures 3.3(a)-(c) and 3.2(a)-(b), are evaluated as functions of each of these coordinates and are obtained for the same values of $\theta_{ip}$ and $\theta_{oop}$ that are used to evaluate the corresponding potentials. In order to separate the three components of the dipole moment, we need to obtain a consistent definition of the three Cartesian axes. We start by shifting the origin of the molecule to the center of mass of the complex. For the in-plane bend, we use the Eckart conditions,$^{134}$ as described by Louck and Galbraith.$^{135}$ For this treatment, we need to choose a reference geometry, and we use the $C_{2v}$ saddle point structure, shown in Figure 3.1(b). Since the definition of $\theta_{oop}$ relies on the definitions of the $a$, $b$, and $c$ axes, we rotate the dipole moment vectors to this axis system.

The ranges for the one-dimensional potential and dipole moment surfaces are chosen such that they span the ranges sampled by the vibrational wave functions of the states of interest.

3.3.2 Vibrational coordinates and Hamiltonians

3.3.2.1 In-plane (ip) bend

The in-plane bend motion is strongly coupled to several other vibrational modes, particularly, the HOH bend. This coupling is illustrated by the plots of the value of the water angle as a function of $\theta_{ip}$, shown in Figure 3.4(a). Here the water angle varies by $\sim 15^\circ$ for $0^\circ \leq \theta_{ip} \leq 90^\circ$. While the two OH bond lengths also change along
Figure 3.2: Dipole moment surfaces for the in-plane bend in X⁻·H₂O complexes. Coordinate-dependent dipole surfaces are shown in (a) and (b), and those obtained via the fixed charge model are in (c) and (d). In all cases, Cl⁻·H₂O is shown as the dashed trace in green, Br⁻·H₂O as the solid trace in red, and I⁻·H₂O as the dot-dashed trace in purple.
Figure 3.3: Dipole moment surfaces for the out-of-plane bend in X⁻·H₂O complexes. Coordinate-dependent dipole surfaces are shown in (a)-(c), and those obtained via the fixed charge model are in (d)-(f). In all cases, Cl⁻·H₂O is shown as the dashed trace in green, Br⁻·H₂O as the solid trace in red, and I⁻·H₂O as the dot-dashed trace in purple.
this cut, the differences between their values at the $C_s$ minima and the $C_{2v}$ saddle point are only 1–2%. Plots that show these effects are provided in Figure 3.5.

In order to include the effects of the couplings of the in-plane bend to the other coordinates, we employ a reaction path formalism.\textsuperscript{168,169} This approach allows us to incorporate the energies in the remaining degrees of freedom at the harmonic level and provides effective (i.e., vibrationally adiabatic) potential energy surfaces as a function of $\theta_{ip}$. In this representation the potential energy as a function of $\theta_{ip}$ can be expressed as,

$$V(\theta_{ip}) = V_{\text{MEP}}(\theta_{ip}) + \sum_i \left( n_i + \frac{1}{2} \right) \omega_i(\theta_{ip}),$$

(3.2)

where $V_{\text{MEP}}(\theta_{ip})$ is the potential energy along the minimum energy path, or the energies calculated by the electronic structure methods listed above, and $\omega_i$ are the harmonic frequencies of the $3N - 7$ degrees of freedom.\textsuperscript{168,169} The $n_i$ provide the number of quanta in the remaining $3N - 7$ degrees of freedom in evaluating the potential.

The Hamiltonian for these one-dimensional calculations (in atomic units) is given by

$$\hat{H}_{ip} = -\frac{d}{d\theta_{ip}} b_{eff}(\theta_{ip}) \frac{d}{d\theta_{ip}} + V(\theta_{ip}) + V'(\theta_{ip}).$$

(3.3)

Transforming the kinetic energy operator from Cartesian to internal coordinates introduces a coordinate dependence to this operator and produces an additional term in the Hamiltonian: $V'(\theta_{ip})$. The effective mass term in eq. (3.3), $b_{eff}(\theta_{ip})$, is derived from the $G$-matrix elements. The functional forms of the $G$-matrix elements and the additional $V''(\theta_{ip})$ terms used in the in-plane bend study are derived from the
Figure 3.4: Plot of the water angle as a function of both (a) the in-plane bend angle ($\theta_{ip}$) and (b) the out-of-plane bend angle ($\theta_{oop}$). The water bend frequency is also plotted as a function of the in-plane bend angle in (c). Cl$^-$·H$_2$O is shown as the green circles, Br$^-$·H$_2$O as the red triangles, and I$^-$·H$_2$O as the purple circles.
Figure 3.5: Plots of the (a) OX, (b) OH$_1$, and (c) OH$_2$ distances (see Figure 3.1(b)) as a function of the in-plane bend angle ($\theta_{ip}$). Cl$^-$·H$_2$O is shown as the green points, Br$^-$·H$_2$O as the red points, and I$^-$·H$_2$O as the purple points.
expressions given by Frederick and Woywod. Because X⁻·H₂O complexes have Cₙ symmetry, there are five modes with A' symmetry and one mode with A'' symmetry. Thus, the G-matrix is block diagonal with a 5 × 5 and a 1 × 1 block, where the 1 × 1 block constitutes the out-of-plane bend. The effective mass for the in-plane bend, bₑff(θᵢp), contains contributions from the remaining terms in the 5 × 5 block due to changes of the other symmetric coordinates along the reaction path.

It should be noted that partial deuteration will lower the symmetry of bₑff(θᵢp), V(θᵢp), and V'(θᵢp) in eqs. (3.2) and (3.3), as these terms depend on the mass of the two hydrogen atoms. The mass dependence of V'(θᵢp) is reflected in its functional form. The mass dependence of V(θᵢp) is more subtle and is introduced through the mass dependence of the harmonic frequencies in eq. (3.2). To reflect the asymmetry of the singly deuterated complexes, we define θᵢp > 0 when X⁻ is closer to the deuterium atom (X⁻·DOH) and θᵢp < 0 when X⁻ is closer to the hydrogen atom (X⁻·HOD).

3.3.2.2 Out-of-plane (oop) bend

Based on symmetry, the out-of-plane bend is much less strongly coupled to the other vibrational degrees of freedom. This is supported by the dependence of θ_HOH on θ_oop, plotted in Figure 3.4(b). In contrast to its variations with θᵢp, the θ_HOH value changes by < 4° when θ_oop is increased from 0° to 70°. Based on this, we find that the reaction path approach described above is not necessary to characterize the dependence of the potential surface on the out-of-plane angle, and we employ a simplified version of eq. (3.3) for the out-of-plane bend:

\[
\hat{H}_{oop} = -\frac{d}{d\theta_{oop}} b_{eff}(\theta_{oop}) \frac{d}{d\theta_{oop}} + V_{MEP}(\theta_{oop}).
\]
As in the calculation involving $\theta_{ip}$, $V_{\text{MEP}}(\theta_{oop})$ is the one-dimensional PES for $\theta_{oop}$ and is obtained from the electronic structure calculations described above.

In the case of the out-of-plane bend, $V'(\theta_{oop}) = 0$ because of symmetry and therefore is not included in eq. (3.4). The $b_{\text{eff}}(\theta_{oop})$ terms are the elements of the aforementioned $1 \times 1$ block of the $G$-matrix. These $1 \times 1$ elements are derived from the Wilson $B$-matrix\textsuperscript{171} and are calculated using finite differencing.

### 3.3.3 Numerical details

In order to make a direct comparison with the experimental results, in addition to obtaining the transition frequencies, we calculate the relative line strengths,

$$M_{i,n_i} = \frac{|\langle n_i | \tilde{\mu} | 0 \rangle|^2}{|\langle n_{\text{HOH}} = 1 | \tilde{\mu} | 0 \rangle|^2}. \quad (3.5)$$

Here $n_i$ represents the number of quanta in the $i$th mode, and the calculated line strength for the water bend (in the denominator) is evaluated at the harmonic level. The line strengths for the four isotopologues of each $X^- \cdot \text{H}_2\text{O}$ complex are normalized independently.

The effective mass terms in eqs. (3.3) and (3.4) are calculated at the same values of the angles as those used to determine the respective \textit{ab initio} potential and dipole surfaces. All integrals are evaluated numerically, and the terms in eqs. (3.3)–(3.5) that depend on the bend coordinates are interpolated using cubic splines. This study is performed in a basis of cosine, $\cos(m\theta)$, and sine, $\sin(m'\theta)$, functions, where $m$ and $m' \leq 100$. 

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3.4 Appearance of the Spectra

Figures 3.6 through 3.10 present the argon predissociation spectra for the various halide ion-water complexes as reported by Elliott et al. at Yale University.7 The observed transition frequencies are collected in Table 3.2. For comparison, the harmonic frequencies and associated relative line strengths are reported in Table 3.3. We have chosen to present these spectra first by halogen for the pure water and pure deuterium isotopologues (Figures 3.6–3.8) and then give a comparison of the mixed isotope data for three halogens in Figures 3.9 and 3.10. While the spectra reported in Figures 3.9 and 3.10 are identical, features assignable to the X−·DOH isotopomers are highlighted in Figure 3.9, while those traced to X−·HOD are highlighted in Figure 3.10.

The spectra for Cl−·H2O and Cl−·D2O are displayed in Figure 3.6. The fundamentals in the three intramolecular water modes (νHOH, νOHb, νOHf) are color coded to follow the expected redshifts upon deuteration. Similar trends are found for the Br− and I− complexes, shown in Figures 3.7 and 3.8, respectively. In the case of the Cl−·H2O complex, a fourth fundamental is reported, the out-of-plane bend (νoop), but this transition shifts out of the spectral detection range for the deuterated analogs. As is indicated in Table 3.3, the fundamentals in the remaining two modes are below 400 cm−1, putting them outside the experimental detection range.

As we compare and contrast the spectra of the twelve species studied here, we will divide the spectra into three regions. We will start the discussion with the high frequency region that includes the OH and OD stretch fundamentals. Next
Figure 3.6: The vibrational predissociation spectra of (a) Cl$^-$·H$_2$O·Ar and (b) Cl$^-$·D$_2$O·Ar. The shifts in absorption frequencies upon isotopic substitution of the hydrogen atoms are indicated. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
Figure 3.7: Same as Figure 3.6 but for (a) $\text{Br}^- \cdot \text{H}_2\text{O} \cdot \text{Ar}$ and (b) $\text{Br}^- \cdot \text{D}_2\text{O} \cdot \text{Ar}$. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
Figure 3.8: Same as Figure 3.6 but for (a) $\Gamma^{-} \cdot \text{H}_2\text{O} \cdot \text{Ar}$ and (b) $\Gamma^{-} \cdot \text{D}_2\text{O} \cdot \text{Ar}$. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
Figure 3.9: The vibrational predissociation spectra of (a) $\text{Cl}^{-}\cdot\text{DOH}\cdot\text{Ar}$, (b) $\text{Br}^{-}\cdot\text{DOH}\cdot\text{Ar}$, and (c) $\text{I}^{-}\cdot\text{DOH}\cdot\text{Ar}$. The frequency shifts upon $X^{-}$ substitution are revealed as well as the differences in frequencies due to H versus D in the bound position. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
Figure 3.10: Same as Figure 3.9 but for (a) Cl$^-$·HOD·Ar, (b) Br$^-$·HOD·Ar, and (c) I$^-$·HOD·Ar. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
Table 3.2: A summary of the experimentally observed transition frequencies of the X⁻·H₂O complexes. Frequencies are obtained by Elliott et al. and are reproduced from Ref. 7.

<table>
<thead>
<tr>
<th>species</th>
<th>$\nu_{oop}$</th>
<th>$2\nu_{oop}$</th>
<th>$\nu_{\text{HOH}}$</th>
<th>$\nu_{\text{HOH}} + \nu_{\text{ip}}$</th>
<th>$\nu_{\text{OH}_b}$</th>
<th>$2\nu_{\text{HOH}}$</th>
<th>$\nu_{\text{OH}<em>b} + \nu</em>{\text{OX}}$</th>
<th>$2\nu_{\text{HOH}} + \nu_{\text{OX}}$</th>
<th>$\nu_{\text{OH}_f}$</th>
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</thead>
<tbody>
<tr>
<td>Cl⁻·H₂O</td>
<td>738</td>
<td>1404</td>
<td>1653</td>
<td>1962</td>
<td>3146</td>
<td>3289</td>
<td>3356</td>
<td>3521</td>
<td>3697</td>
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<td>Cl⁻·DOH</td>
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<td>1404</td>
<td>1687</td>
<td>2357</td>
<td>2880</td>
<td>2547</td>
<td>3697(^b)</td>
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<td>Cl⁻·HOD</td>
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<td>1750</td>
<td>3156</td>
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<td>3360</td>
<td>2716(_{\text{f}})</td>
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<td>Cl⁻·D₂O</td>
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<td>1870/1922(^d)</td>
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<td>I⁻·DOH</td>
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</tr>
<tr>
<td>I⁻·D₂O</td>
<td>1208</td>
<td>2511/2527(_a)</td>
<td>2401</td>
<td>2728</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Transition appears as a doublet in the experimental spectrum.
\(^b\) Value assigned based on suppression of the fine structure with multiple Ar attachment (Ref. 159).
\(^c\) Frequency from Ref. 18.
\(^d\) Value is the higher-energy component of a tunneling doublet.
\(^e\) Value assigned by taking the centroid of the rotational substructure.
\(^f\) Frequency from Ref. 162.
Table 3.3: Harmonic fundamental frequencies for $X^-\cdot \text{H}_2\text{O}$ complexes with $M_{i,ni}$ values (eq. (3.5)) given in parentheses.

<table>
<thead>
<tr>
<th>species</th>
<th>$\nu_{\text{OH}_f}$</th>
<th>$\nu_{\text{OH}_b}$</th>
<th>$\nu_{\text{HOH}}$</th>
<th>$\nu_{\text{ip}}$</th>
<th>$\nu_{\text{OX}}$</th>
<th>$\nu_{\text{oop}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}^-\cdot \text{H}_2\text{O}$</td>
<td>3894 (0.1380)</td>
<td>3335 (5.7054)</td>
<td>1669 (1.0000)</td>
<td>366 (2.1619)</td>
<td>203 (2.2109)</td>
<td>754 (1.1876)</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot \text{DOH}$</td>
<td>3891 (0.0785)</td>
<td>2428 (3.8788)</td>
<td>1413 (1.0000)</td>
<td>311 (1.8074)</td>
<td>199 (2.0886)</td>
<td>549 (1.2322)</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot \text{HOD}$</td>
<td>2825 (0.0833)</td>
<td>3341 (8.4162)</td>
<td>1516 (1.0000)</td>
<td>298 (2.0268)</td>
<td>198 (3.7648)</td>
<td>751 (1.4779)</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot \text{D}_2\text{O}$</td>
<td>2834 (0.2528)</td>
<td>2422 (6.4806)</td>
<td>1219 (1.0000)</td>
<td>265 (2.0174)</td>
<td>195 (4.1773)</td>
<td>545 (1.6452)</td>
</tr>
<tr>
<td>$\text{Br}^-\cdot \text{H}_2\text{O}$</td>
<td>3889 (0.1570)</td>
<td>3426 (4.4919)</td>
<td>1664 (1.0000)</td>
<td>339 (2.1525)</td>
<td>170 (0.8422)</td>
<td>704 (1.0631)</td>
</tr>
<tr>
<td>$\text{Br}^-\cdot \text{DOH}$</td>
<td>3885 (0.0828)</td>
<td>2494 (3.0323)</td>
<td>1417 (1.0000)</td>
<td>286 (1.7134)</td>
<td>166 (0.7754)</td>
<td>515 (1.1137)</td>
</tr>
<tr>
<td>$\text{Br}^-\cdot \text{HOD}$</td>
<td>2821 (0.0748)</td>
<td>3432 (6.7951)</td>
<td>1503 (1.0000)</td>
<td>277 (2.2353)</td>
<td>165 (1.5393)</td>
<td>700 (1.2989)</td>
</tr>
<tr>
<td>$\text{Br}^-\cdot \text{D}_2\text{O}$</td>
<td>2830 (0.2770)</td>
<td>2487 (4.9930)</td>
<td>1216 (1.0000)</td>
<td>245 (2.1082)</td>
<td>161 (1.6264)</td>
<td>509 (1.4067)</td>
</tr>
<tr>
<td>$\text{I}^-\cdot \text{H}_2\text{O}$</td>
<td>3896 (0.1593)</td>
<td>3608 (2.6117)</td>
<td>1635 (1.0000)</td>
<td>346 (1.8600)</td>
<td>137 (0.4506)</td>
<td>632 (0.8899)</td>
</tr>
<tr>
<td>$\text{I}^-\cdot \text{DOH}$</td>
<td>3895 (0.1076)</td>
<td>2620 (1.7201)</td>
<td>1408 (1.0000)</td>
<td>289 (1.3683)</td>
<td>134 (0.4129)</td>
<td>466 (0.9448)</td>
</tr>
<tr>
<td>$\text{I}^-\cdot \text{HOD}$</td>
<td>2831 (0.1035)</td>
<td>3609 (4.0699)</td>
<td>1462 (1.0000)</td>
<td>288 (2.1012)</td>
<td>131 (0.8270)</td>
<td>627 (1.0602)</td>
</tr>
<tr>
<td>$\text{I}^-\cdot \text{D}_2\text{O}$</td>
<td>2836 (0.2888)</td>
<td>2614 (2.7475)</td>
<td>1195 (1.0000)</td>
<td>253 (1.7740)</td>
<td>128 (0.8271)</td>
<td>458 (1.1185)</td>
</tr>
</tbody>
</table>
we consider the low frequency region that contains the fundamental in the out-of-plane bend. Finally we consider the intermediate region that contains the water bend fundamental.

3.4.1 OH and OD stretch fundamental region [2250–3750 cm$^{-1}$]

As noted in earlier studies,$^{6,18,19,75}$ the interaction of water with a halide ion redshifts the bonded OH stretch frequency ($\nu_{\text{OH}_b}$), while the frequency of the free OH stretch ($\nu_{\text{OH}_f}$) is relatively unaffected by the presence of the halide ion. The interaction with the halide ion also increases the intensity of the $\nu_{\text{OH}_b}$ band relative to the intensity of the fundamental in the free OH stretch. In going from chloride to iodide, the halide-water interaction strength decreases, and the position of $\nu_{\text{OH}_b}$ shifts to higher frequency, moving closer to the frequency of the $\nu_{\text{OH}_f}$ band. These trends are reproduced in the harmonic calculations in which the free OH/OD stretch frequencies change by less than 10 cm$^{-1}$ for these complexes, while the $\nu_{\text{OH}_b}$ frequencies increase by 250 cm$^{-1}$ from the chloride to the iodide complex. Similar trends are seen for the fully deuterated complexes.

In the case of the partially deuterated complexes (shown in Figures 3.9 and 3.10), the bonded OH or OD fundamental dominates in all of the X$^-$-HDO mixed isotopomers. The frequency of the $\nu_{\text{OH}_b}$ band is found to be within 20 cm$^{-1}$ of the band in the corresponding H$_2$O or D$_2$O complexes. In the complexes for which the free OH or OD stretch is assigned, the frequencies of the free hydrogen stretches are also within 20 cm$^{-1}$ of the corresponding OH$_f$ bands in the H$_2$O or D$_2$O complexes.
Several other bands have been previously assigned that are close in energy to the OH\textsubscript{b} and OD\textsubscript{b} stretch fundamentals. In particular, the first overtone in the HOH bend is close in frequency to the fundamental band of the bonded OH stretch. There is a well-known Fermi resonance between the overtone in the water bend and the fundamental in the OH stretch of the same symmetry that typically occurs with an interaction matrix element on the order of 30 cm\(^{-1}\).\(^{74}\) The magnitude of the redshift of the \(\nu_{\text{OH}_b}\) fundamental depends on which halide is present. In the case of the bromide complexes with H\(_2\)O and D\(_2\)O, the redshift of the \(\nu_{\text{OH}_b}\) band puts it within 60 cm\(^{-1}\) of the overtone in the water bend. In the iodide complexes the bend overtone is to the red of the \(\nu_{\text{OH}_b}\) fundamental, while it is found to the blue of the \(\nu_{\text{OH}_b}\) fundamental in the chloride complexes. The smaller energy gap between the \(\nu_{\text{OH}_b}\) and \(2\nu_{\text{HOH}}\) bands in the bromide complexes leads to larger mixing of these two states as is evidenced by the relative intensity of the two bands, plotted in turquoise and red. In the spectra for Br\(^-\)-H\(_2\)O and Br\(^-\)-D\(_2\)O, the \(\nu_{\text{OH}_b}\) and \(2\nu_{\text{HOH}}\) bands have intensities that differ by less than a factor of two (as seen in Figure 3.7), while the intensity of the bend overtone is much lower than the OH stretch fundamental in the Cl\(^-\) and I\(^-\) spectra reported in Figures 3.6 and 3.8, respectively.

The bend frequency in HOD is intermediate between that of H\(_2\)O and D\(_2\)O. As is seen in Figure 3.10, the overtone in the HOD bend is now to the red of the fundamental in the bonded OH stretch in the Cl\(^-\)-HOD complex. With the shift of the \(\nu_{\text{OH}_b}\) fundamental to higher frequency in the bromide and iodide complexes, the intensity of the \(2\nu_{\text{HOD}}\) band is much smaller in the Br\(^-\)-HOD complex, and the corresponding band is not evident in the spectrum for the I\(^-\)-HOD complex.
There is another, lower intensity band that is found to the blue of the OH\textsubscript{b} transition in the Cl\textsuperscript{−}\cdot H\textsubscript{2}O, Cl\textsuperscript{−}\cdot D\textsubscript{2}O, Br\textsuperscript{−}\cdot H\textsubscript{2}O, and I\textsuperscript{−}\cdot H\textsubscript{2}O spectra. This feature has been assigned to the \(\nu_{\text{OH}_b} + \nu_{\text{OX}}\) combination band.\textsuperscript{18} This assignment is based on the evolution of its shift relative to \(\nu_{\text{OH}_b}\) over the series, and the fact that higher-dimensional studies of other similar species (specifically Cl\textsuperscript{−}\cdot H\textsubscript{2}O, F\textsuperscript{−}\cdot H\textsubscript{2}O, H\textsubscript{4}O\textsuperscript{2+}, and H\textsubscript{5}O\textsuperscript{+})\textsuperscript{6,128,172–174} have shown evidence for strong coupling between \(\nu_{\text{OH}_b}\) and the heavy atom stretch, which involves the two atoms between which the shared hydrogen atom is vibrating. In Br\textsuperscript{−}\cdot H\textsubscript{2}O there is an additional peak between \(\nu_{\text{OH}_b}\) and \(\nu_{\text{OH}_b} + \nu_{\text{OX}}\). Based on the strong Fermi resonance in this complex, this band is assigned to the \(2\nu_{\text{HOH}} + \nu_{\text{OX}}\) combination band. These combination bands also appear in the Cl\textsuperscript{−}\cdot H\textsubscript{2}O and Cl\textsuperscript{−}\cdot D\textsubscript{2}O spectra (Figure 3.6). However they are displaced to the blue of the \(\nu_{\text{OH}_b} + \nu_{\text{OX}}\) feature as the ion-bound OH stretch falls to the red of the bend overtone. Fine structure is also observed on the \(\nu_{\text{OH}_b}\) fundamentals of the I\textsuperscript{−}\cdot H\textsubscript{2}O and Cl\textsuperscript{−}\cdot HOD complexes (Figures 3.8(a) and 3.10(a)). Johnson and co-workers have reported the evolution of these features in both the I\textsuperscript{−}\cdot H\textsubscript{2}O and Cl\textsuperscript{−}\cdot H\textsubscript{2}O complexes with increasing numbers of Ar atoms in two previous studies,\textsuperscript{131,159} and find that, in both cases, the structure is highly dependent on the extent of Ar solvation. In the chloride case, this effect was traced to the different isomers available until a sharp band evolved as the icosahedral solvation shell was filled with 11 Ar atoms.\textsuperscript{159} The analogous doublet structure in the I\textsuperscript{−}\cdot H\textsubscript{2}O complex was also explored here and found to persist upon attachment of at least 7 Ar atoms; as such, it appears to arise from an intrinsic coupling in the hydrate rather than an effect due to Ar solvation.
3.4.2 Out-of-plane bend fundamental region [below 1000 cm$^{-1}$]

In the low frequency region of the Cl$^-\cdot$H$_2$O spectrum, the band at 738 cm$^{-1}$ is observed and has been identified as the fundamental in the out-of-plane bend.\textsuperscript{18} This frequency is well-reproduced by our one-dimensional calculations, reported in Table 3.4, as well as by six-dimensional calculations previously reported by Rheinecker and Bowman.\textsuperscript{174,175} Analogous features are not seen in any of the other spectra reported in Figures 3.6–3.10. This is consistent with the harmonic frequencies where we notice that this band redshifts for the heavier halides. Furthermore, its harmonic frequencies in the X$^-\cdot$H$_2$O and X$^-\cdot$HOD complexes differ by less than 5 cm$^{-1}$. Likewise the harmonic frequencies of the out-of-plane bend in X$^-\cdot$D$_2$O and X$^-\cdot$DOH are nearly identical. Since the fundamental transitions are at the edge or slightly below the experimental detection range, experimental verification of this will require identification of overtone or combination bands involving this mode.

3.4.3 Water bend fundamental region [1000–2250 cm$^{-1}$]

3.4.3.1 Water bend fundamental

Next we turn to the intermediate region (\~1000–2000 cm$^{-1}$) of the spectra. A prominent feature that is seen in all of the spectra reported in Figures 3.6–3.10 is the fundamental in the water bend, highlighted in dark blue. This feature occurs near 1650 cm$^{-1}$ for the X$^-\cdot$H$_2$O complexes and around 1200 cm$^{-1}$ for the X$^-\cdot$D$_2$O complexes and remains relatively unchanged with only a small redshift from chloride to iodide. The energies of the bend peaks are also in good agreement with the bare water bend frequencies: 1595 and 1178 cm$^{-1}$ for the H$_2$O and D$_2$O species,
Table 3.4: Calculated fundamental and overtone transition frequencies for the in-plane, water, and out-of-plane bends for $\text{Cl}^-\cdot\text{H}_2\text{O}$ (given in cm$^{-1}$).

<table>
<thead>
<tr>
<th>species</th>
<th>in-plane bend</th>
<th>HOH bend</th>
<th>out-of-plane bend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_{\text{HOH}} = 0^a$</td>
<td>6-d$^b$</td>
<td>$n_{\text{HOH}} = 0^c$</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{H}_2\text{O}$</td>
<td>333/334</td>
<td>343/344</td>
<td>362</td>
</tr>
<tr>
<td></td>
<td>577/577</td>
<td>666/666</td>
<td>1412 (0.3747)</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{DOH}$</td>
<td>291</td>
<td>319.3</td>
<td>1698</td>
</tr>
<tr>
<td></td>
<td>539</td>
<td>1046 (0.1969)</td>
<td>1064</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{HOD}$</td>
<td>280</td>
<td>305.1</td>
<td>1772</td>
</tr>
<tr>
<td></td>
<td>523</td>
<td>1412 (0.5392)</td>
<td>1423</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{D}_2\text{O}$</td>
<td>249/249</td>
<td>249/249</td>
<td>264.4</td>
</tr>
<tr>
<td></td>
<td>467/467</td>
<td>478/478</td>
<td>1046 (0.3281)</td>
</tr>
</tbody>
</table>

$^a$ For each isotopic species, two sets of frequencies are given, the frequency of the fundamental transition (first row) and the frequency of the overtone transition (second row). As is discussed in the text for $\text{X}^-\cdot\text{H}_2\text{O}$ and $\text{X}^-\cdot\text{D}_2\text{O}$, the two columns represent transitions for the two members of the tunneling doublets. For more details, see Table 3.8.

$^b$ Full six-dimensional calculations from Ref. 174.

$^c$ Frequencies for the combination band of $\nu_{\text{HOH}} + \nu_{\text{ip}}$. As is discussed in the text for $\text{X}^-\cdot\text{H}_2\text{O}$ and $\text{X}^-\cdot\text{D}_2\text{O}$, the two columns represent transitions for the two members of the tunneling doublets.

$^d$ Water bend frequencies are the differences in the zero point levels obtained from eq. (3.3) for $n_{\text{HOH}} = 0$ and 1.

$^e$ Numbers in parentheses represent the line strengths of the out-of-plane bend transition obtained from eq. (3.5).
respectively.\textsuperscript{139} The water bend overtone, discussed above, is also hardly perturbed in the six $\text{X}^-$-$\text{H}_2\text{O}$ and $\text{X}^-$-$\text{D}_2\text{O}$ complexes. This serves to highlight the robustness of the water bend fundamental to halide substitution.

These trends are also seen in the harmonic frequencies, reported in Table 3.3, and in the frequencies obtained by taking the differences between the solutions to the Hamiltonian described by eqs. (3.2) and (3.3) when $n_{\text{HOH}} = 1$ and 0, reported in Tables 3.4–3.6. The frequency differences between the experimental and calculated values reported in Tables 3.2 and 3.4–3.6 are all smaller than 15 cm\textsuperscript{-1} and much of this difference should be attributed to the failure of harmonic frequencies to capture anharmonic vibrations.

In Table 3.4 we also compare the present calculated frequencies for the chloride-water complexes to the frequencies reported by Rheinecker and Bowman,\textsuperscript{174} which are based on six-dimensional calculations. As the water bend is rather harmonic, the frequencies calculated by the reduced dimensional approach used in the present calculations are in good agreement with those obtained from the six-dimensional calculations for all four isotopologues.

Before we move to other bands, it is interesting to note that in the singly deuterated species, the HOD bend frequencies differ by as much as 100 cm\textsuperscript{-1} for the $\text{X}^-$-$\text{HOD}$ and $\text{X}^-$-$\text{DOH}$ complexes. In all cases, the average of these frequencies is close to the bare HOD bend frequency (1402 cm\textsuperscript{-1}).\textsuperscript{138} The splitting of the frequency of the HOD bend in $\text{X}^-$-$\text{HOD}$ and $\text{X}^-$-$\text{DOH}$ and the observation that the bend frequency in the $\text{X}^-$-$\text{HOD}$ complex is the larger of the two reflect the fact that the bending motions of
Table 3.5: Calculated fundamental and overtone transition frequencies for the in-plane, water, and out-of-plane bends for Br$^{-}$-$\text{H}_2\text{O}$ (given in cm$^{-1}$).

<table>
<thead>
<tr>
<th>species</th>
<th>in-plane bend</th>
<th>HOH bend</th>
<th>out-of-plane bend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_{\text{HOH}} = 0^a$</td>
<td>6-d$^b$</td>
<td>$n_{\text{HOH}} = 0^c$</td>
</tr>
<tr>
<td>Br$^{-}$-$\text{H}_2\text{O}$</td>
<td>286/287</td>
<td>310/311</td>
<td>1936/1937</td>
</tr>
<tr>
<td></td>
<td>495/496</td>
<td>613/614</td>
<td></td>
</tr>
<tr>
<td>Br$^{-}$-$\text{DOH}$</td>
<td>259</td>
<td>1672</td>
<td>1411</td>
</tr>
<tr>
<td></td>
<td>463</td>
<td>493</td>
<td></td>
</tr>
<tr>
<td>Br$^{-}$-$\text{HOD}$</td>
<td>247</td>
<td>1728</td>
<td>1495</td>
</tr>
<tr>
<td></td>
<td>461</td>
<td>507</td>
<td></td>
</tr>
<tr>
<td>Br$^{-}$-$\text{D}_2\text{O}$</td>
<td>221/221</td>
<td>223/223</td>
<td>1429/1429</td>
</tr>
<tr>
<td></td>
<td>396/396</td>
<td>426/426</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ For each isotopic species, two sets of frequencies are given, the frequency of the fundamental transition (first row) and the frequency of the overtone transition (second row). As is discussed in the text for $X^{-}$-$\text{H}_2\text{O}$ and $X^{-}$-$\text{D}_2\text{O}$, the two columns represent transitions for the two members of the tunneling doublets. For more details, see Table 3.8.

$^b$ Full six-dimensional calculations from Ref. 174.

$^c$ Frequencies for the combination band of $\nu_{\text{HOH}} + \nu_{\text{ip}}$. As is discussed in the text for $X^{-}$-$\text{H}_2\text{O}$ and $X^{-}$-$\text{D}_2\text{O}$, the two columns represent transitions for the two members of the tunneling doublets.

$^d$ Water bend frequencies are the differences in the zero point levels obtained from eq. (3.3) for $n_{\text{HOH}} = 0$ and 1.

$^e$ Numbers in parentheses represent the line strengths of the out-of-plane bend transition obtained from eq. (3.5).
Table 3.6: Calculated fundamental and overtone transition frequencies for the in-plane, water, and out-of-plane bends in I⁻·H₂O (given in cm⁻¹).

<table>
<thead>
<tr>
<th>species</th>
<th>in-plane bend</th>
<th>HOH bend</th>
<th>out-of-plane bend</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n_{HOH} = 0</td>
<td>6-d</td>
<td>n_{HOH} = 0</td>
</tr>
<tr>
<td>I⁻·H₂O</td>
<td>185/189</td>
<td>258/263</td>
<td>1817/1822</td>
</tr>
<tr>
<td></td>
<td>399/404</td>
<td>543/548</td>
<td></td>
</tr>
<tr>
<td>I⁻·DOH</td>
<td>195</td>
<td></td>
<td>1609</td>
</tr>
<tr>
<td></td>
<td>357</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I⁻·HOD</td>
<td>181</td>
<td></td>
<td>1624</td>
</tr>
<tr>
<td></td>
<td>384</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I⁻·D₂O</td>
<td>160/161</td>
<td>178/179</td>
<td>1355/1355</td>
</tr>
<tr>
<td></td>
<td>277/278</td>
<td>353/354</td>
<td></td>
</tr>
</tbody>
</table>

a For each isotopic species, two sets of frequencies are given, the frequency of the fundamental transition (first row) and the frequency of the overtone transition (second row). As is discussed in the text for X⁻·H₂O and X⁻·D₂O, the two columns represent transitions for the two members of the tunneling doublets. For more details, see Table 3.8.
b Full six-dimensional calculations from Ref. 174.
c Frequencies for the combination band of ν_{HOH} + ν_{ip}. As is discussed in the text for X⁻·H₂O and X⁻·D₂O, the two columns represent transitions for the two members of the tunneling doublets.
d Water bend frequencies are the differences in the zero point levels obtained from eq. (3.3) for n_{HOH} = 0 and 1.
e Numbers in parentheses represent the line strengths of the out-of-plane bend transition obtained from eq. (3.5).
these species involve larger displacements of the OH\textsubscript{b} bond than of the OH\textsubscript{f} one. As a result, the so-called water bend has a contribution from rotation of the water molecule about an axis perpendicular to the molecular plane (e.g. in-plane bend character). This result hints to the fact that there is strong mixing of the two modes that are nominally pure water bend and pure in-plane bend motions.

3.4.3.2 Overtone in the out-of-plane bend

Of greater interest to the present work are the overtone and combination band structure that aid in the assignment of the low energy modes. As indicated above, only in Cl\textsuperscript{−}\cdot\text{H}_2\text{O} is the fundamental of \(\nu\_\text{oop}\) visible in the spectra reported in Figures 3.6–3.10. We must therefore rely on the overtone to assign these bands in the remaining species of the series. The first overtone for the out-of-plane bend of Cl\textsuperscript{−}\cdot\text{D}_2\text{O} falls at 1028 cm\textsuperscript{−1} leading to an assignment of \(\sim\)514 cm\textsuperscript{−1} for this fundamental. Similar treatments give values of \(\sim\)631 cm\textsuperscript{−1} and \(\sim\)549 cm\textsuperscript{−1} for Br\textsuperscript{−}\cdot\text{H}_2\text{O} and I\textsuperscript{−}\cdot\text{H}_2\text{O}, respectively. These values for the \(\nu\_\text{oop}\) fundamentals must necessarily be approximate as anharmonicities would cause some shift in the true values. This can be seen in the locations of the Cl\textsuperscript{−}\cdot\text{H}_2\text{O} and Br\textsuperscript{−}\cdot\text{H}_2\text{O} transitions (Table 3.2) where the fundamental has been assigned (Br\textsuperscript{−} from Ref. 18). In the case of I\textsuperscript{−}\cdot\text{D}_2\text{O}, the first overtone of the out-of-plane bend disappears into the noise at the low energy end of experimental frequency range, making assignment impossible.

The calculated anharmonic frequencies for these \(\nu\_\text{oop}\)-based transitions are reported in Tables 3.4–3.6. In Figure 3.11 we overlay the calculated frequencies of the out-of-plane transitions (labeled as 1) onto the corresponding experimental spectra.
This figure contains the same experimental spectra that are reported in Figures 3.6–3.10 and are scaled so the height of the $\nu_{\text{HOH}}$, $\nu_{\text{DOH}}$, or $\nu_{\text{DOD}}$ band is the same in all of the plots. The calculated frequencies are shown with dashed lines for systems in which there is a bonded hydrogen atom, and the transitions in systems with a bonded deuterium atom are shown with solid lines. Agreement between calculated and experimental transition frequencies for the overtone in the out-of-plane bend for the H$_2$O and D$_2$O complexes is good, with many of the differences being smaller than 20 cm$^{-1}$. Others are as large as 95 cm$^{-1}$; however, and in all cases, the largest differences between experiment and calculation are found for the X$^-\cdot$HOD complexes. These differences likely reflect both limitations of reduced dimensional treatments and the fact that, in the experiment, the species that is probed has been complexed with an argon atom. Moreover, if we compare the frequencies for Cl$^-\cdot$H$_2$O and Cl$^-\cdot$D$_2$O to those obtained from six-dimensional calculations,$^{174}$ the differences are less than 6 cm$^{-1}$ and under 20 cm$^{-1}$ for Cl$^-\cdot$HOD and Cl$^-\cdot$DOH.

We find that the frequency of the overtone in the out-of-plane bend decreases as the strength of the intermolecular interaction decreases. Given the robustness of the water bend frequencies, the redshift of the out-of-plane bend frequencies for the different halides may at first be surprising. To understand the origins of this shift, we turn to plots of the one-dimensional potentials as functions of $\theta_{\text{oop}}$, shown in Figure 3.12(a). Here the width of these potentials increases from chloride to iodide. This change reflects the decrease in the strength and directionality of the X$^-\cdot\cdot\cdot$H$_b$O
Figure 3.11: Comparison of calculated and experimental transition frequencies in the Ar predissociation spectra for $X^-\cdot H_2O$ (same as those shown in Figures 3.6–3.10). The calculated frequencies are shown as the sticks and are labeled as 1 for $2\nu_{oop}$, as 2 for $\nu_{HOH}$, and as 3 for $\nu_{HOH} + \nu_{ip}$ (see Tables 3.4–3.6 for $\nu_{HOH} + \nu_{ip}$ splittings). The solid lines refer to the $X^-\cdot DOH$ isomer and the dashed lines to the $X^-\cdot HOD$ isomer. Spectra are obtained by Elliott et al. and are reproduced from Ref. 7.
interaction and illustrates an additional manifestation of the weakening of the halide-water bond seen in the redshift of $\nu_{OH_b}$ compared to the OH stretch in bare water, described above.

![Figure 3.12](image.png)

Figure 3.12: (a) One-dimensional cuts through the full-dimensional potentials as a function of the out-of-plane bend coordinate for Cl$^-$·H$_2$O (green dashed), Br$^-$·H$_2$O (red solid), and I$^-$·H$_2$O (purple dot-dashed). The out-of-plane bend wave functions (gray solid), energy levels (gray dashed), and potential surfaces (black) are also shown for (b) Cl$^-$·H$_2$O, (c) Br$^-$·H$_2$O, and (d) I$^-$·H$_2$O.
An interesting feature of the $2\nu_{\text{oop}}$ bands is that its intensity is comparable to, and in some cases even larger than, the fundamental in the water bend. This feature of the spectra should be surprising for two reasons. First, at the harmonic level the out-of-plane fundamental has an intensity that is no more than 1.65 times that of the water bend fundamental, and one generally expects the intensity of the overtone to be at least an order of magnitude smaller than that of the fundamental. Further complicating the situation, the components of the dipole moment that are responsible for intensity of the fundamental and overtone in the out-of-plane bend are different, with the fundamental being a perpendicular transition, whereas the overtone results from changes of the dipole moment components that lie in the molecular plane. The calculated intensities of the overtone, reported in Tables 3.4–3.6, also show larger intensities for the overtone than one might initially anticipate, although not as large as those observed in the experiment.\textsuperscript{18}

Another unexpected aspect of the $2\nu_{\text{oop}}$ bands is the observation that the relative intensities of these overtones are similar for all of the halides, while the frequency spacing between the $\nu_{\text{HOH}}$ and $2\nu_{\text{oop}}$ bands increases as the atomic number of the halide ion increases. This is seen most clearly in Figures 3.9 and 3.10 where the spectra for X$^{-}\cdot$DOH and X$^{-}\cdot$HOD for all three halides are plotted, although it also holds for the X$^{-}\cdot$H$_2$O and X$^{-}\cdot$D$_2$O spectra reported in Figures 3.6–3.8. The robustness of this feature for all twelve spectra, thus, is not consistent with the large intensity of $2\nu_{\text{oop}}$ coming solely from intensity borrowing from the fundamental in the water bend. Rather, it was suggested that the large intensity reflects a “charge sloshing”
(vibrationally mediated intra-complex charge-transfer) mechanism, which has been discussed by Roscioli et al.\textsuperscript{18}

To further explore the possible role of this effect on the spectra of the in-plane vibrational manifold, we review how this mechanism was handled theoretically in our analysis of the out-of-plane vibrational spectra. Two obvious sources of overtone intensity are mechanical anharmonicity and electrical anharmonicity. To evaluate their relative contributions, we model the dipole moment surface using a fixed charge approximation. Changes between the intensity that is predicted by this model, compared to the one obtained using the full dipole surface, provide insights into the magnitude of the contribution of electrical anharmonicity to the intensities of these transitions.

In the fixed charge approximation, we evaluate the intensities using static point charges on each of the four atoms in the complex. Here the equilibrium atomic charges are obtained from an NBO\textsuperscript{141,142} analysis. The dipole surfaces resulting from the fixed charge model are plotted Figures 3.2(c)-(d) and 3.3(d)-(f). When the Cl\textsuperscript{−}·H\textsubscript{2}O coordinate-dependent dipole surface is used, we obtain an intensity ratio of the $\nu_{oop}$ overtone to the fundamental transition of 0.43 when a hydrogen is in the H\textsubscript{b} position, and a ratio of 0.29 for a deuterium in the H\textsubscript{b} position. These ratios drop to 0.02 and 0.01, respectively, when the fixed charge model is used. Similar results are obtained for Br\textsuperscript{−}·H\textsubscript{2}O and I\textsuperscript{−}·H\textsubscript{2}O and are reported Table 3.7. We have performed this analysis using Mulliken charges as well as setting the charges on the hydrogen atoms equal to +1, the halide to −1, and the oxygen to −2. In all three cases, the fixed charge
model gave roughly the same ratio for the intensity of the overtone to the fundamental transition and does not reproduce the experimental intensity of the overtone.

This result is not surprising when one considers that the out-of-plane bending motion results in a charge redistribution among the four atoms. As discussed by Roscioli et al.,\textsuperscript{18} when Mulliken charges were examined on the four atoms in Cl\textsuperscript{−}-H\textsubscript{2}O as a function of the out-of-plane angle, we found that as the angle is increased from 0° to 90°, there is substantial charge rearrangement. Physically this occurs because the out-of-plane displacement effectively “breaks” the highly directional hydrogen bond. Specifically, the charge on the halide tends toward −1 while the charges on the oxygen and hydrogen atoms approach their values in an isolated water molecule, calculated at the same level of theory.

3.4.3.3 In-plane (ip) bend

Next, we turn to signatures of in-plane bend excitation in the recorded spectra. Because of the double well character of the X\textsuperscript{−}-H\textsubscript{2}O in-plane bend potentials, its fundamental band is anticipated to be more structured than the other fundamentals. In the ground vibrational state, the pairs of levels in X\textsuperscript{−}-H\textsubscript{2}O and X\textsuperscript{−}-D\textsubscript{2}O are nearly degenerate with tunneling splittings ranging from 0.007 cm\textsuperscript{−1} in Cl\textsuperscript{−}-D\textsubscript{2}O to 4.766 cm\textsuperscript{−1} in I\textsuperscript{−}-H\textsubscript{2}O. This range reflects the fact that the barrier to isomerization along the in-plane bend coordinate decreases as the polarizability of the anion increases. Likewise, the zero point energy will decrease upon deuteration. The splitting is larger when there is one quantum in the in-plane bend, as is seen in panels (e), (g), and (h) of Figure 3.13. In the case of I\textsuperscript{−}-H\textsubscript{2}O, this pair of levels is above the isomerization
Table 3.7: Comparison of the $M_{\text{oop},n_{\text{oop}}}$ values (eq. (3.5)) of the out-of-plane bend fundamental and overtone transitions of the isotopologues of $X^-\cdot H_2O$, using the coordinate-dependent dipole surface or the dipole surface obtained using the fixed charge model. All frequencies are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>coord. dep.</th>
<th>$f_{\text{oo}}/f_{\text{oo}}$</th>
<th>$M_{\text{oop},n_{\text{oop}}}$</th>
<th>$f_{\text{oo}}/f_{\text{oo}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-\cdot H_2O$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>721</td>
<td>0.86970</td>
<td>0:1</td>
<td>6.72015</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1412</td>
<td>0.37472</td>
<td>1:0</td>
<td>0.12062</td>
<td>1:0</td>
</tr>
<tr>
<td>Cl$^-\cdot DOH$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>531</td>
<td>0.68925</td>
<td>0:1</td>
<td>4.85622</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1046</td>
<td>0.19691</td>
<td>1:0</td>
<td>0.06235</td>
<td>1:0</td>
</tr>
<tr>
<td>Cl$^-\cdot HOD$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>721</td>
<td>1.24771</td>
<td>0:1</td>
<td>9.66356</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1412</td>
<td>0.53916</td>
<td>1:0</td>
<td>0.17346</td>
<td>1:0</td>
</tr>
<tr>
<td>Cl$^-\cdot D_2O$</td>
<td>1 $\leftrightarrow$ 0</td>
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<td>1.14270</td>
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<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1046</td>
<td>0.32806</td>
<td>1:0</td>
<td>0.10374</td>
<td>1:0</td>
</tr>
<tr>
<td>Br$^-\cdot H_2O$</td>
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<td>0.35121</td>
<td>1:0</td>
<td>0.11943</td>
<td>1:0</td>
</tr>
<tr>
<td>Br$^-\cdot DOH$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>493</td>
<td>0.50116</td>
<td>0:1</td>
<td>4.37769</td>
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</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>970</td>
<td>0.17789</td>
<td>1:0</td>
<td>0.05904</td>
<td>1:0</td>
</tr>
<tr>
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<td>1 $\leftrightarrow$ 0</td>
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<td>9.27958</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1309</td>
<td>0.51349</td>
<td>1:0</td>
<td>0.17454</td>
<td>1:0</td>
</tr>
<tr>
<td>Br$^-\cdot D_2O$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>493</td>
<td>0.82897</td>
<td>0:1</td>
<td>7.25220</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
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<td>0.29461</td>
<td>1:0</td>
<td>0.09767</td>
<td>1:0</td>
</tr>
<tr>
<td>I$^-\cdot H_2O$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>596</td>
<td>0.53356</td>
<td>0:1</td>
<td>5.81522</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1163</td>
<td>0.32463</td>
<td>1:0</td>
<td>0.11850</td>
<td>1:0</td>
</tr>
<tr>
<td>I$^-\cdot DOH$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>440</td>
<td>0.36131</td>
<td>0:1</td>
<td>3.83990</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>864</td>
<td>0.15795</td>
<td>1:0</td>
<td>0.05624</td>
<td>1:0</td>
</tr>
<tr>
<td>I$^-\cdot HOD$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>596</td>
<td>0.79720</td>
<td>0:1</td>
<td>8.69235</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>1163</td>
<td>0.48525</td>
<td>1:0</td>
<td>0.17711</td>
<td>1:0</td>
</tr>
<tr>
<td>I$^-\cdot D_2O$</td>
<td>1 $\leftrightarrow$ 0</td>
<td>440</td>
<td>0.58857</td>
<td>0:1</td>
<td>6.26031</td>
<td>0:1</td>
</tr>
<tr>
<td></td>
<td>2 $\leftrightarrow$ 0</td>
<td>864</td>
<td>0.25751</td>
<td>1:0</td>
<td>0.09166</td>
<td>1:0</td>
</tr>
</tbody>
</table>

\(^a\) In all cases, the $b$-type contribution to the overtone intensity is less than 20% of the $a$-type contribution and is not listed in the table.
barrier and differ in energy by 74 cm$^{-1}$, while the splittings for Br$^−$·H$_2$O and Cl$^−$·H$_2$O are 24 and 10 cm$^{-1}$, respectively. This double well character of the potential leads to the fundamental transitions appearing as two sets of doublets. As the splittings of the ground state levels are smaller than 5 cm$^{-1}$, at the resolution of the experiment, only doublets are expected to be resolvable.

The frequencies and relative intensities of the resolvable bands (normalized to the fundamental in the water bend) are reported in Table 3.8 for the chloride complexes and in Tables 3.9 and 3.10 for the other species. In the case of the chloride complexes, we can compare the fundamental frequencies to those reported by Rheinecker and Bowman. In general the agreement is quite good; differences range from 15 to 30 cm$^{-1}$.

Interestingly, the higher dimensional calculations do not capture the tunneling splitting of the first excited states in the in-plane bend in either Cl$^−$·H$_2$O or in Cl$^−$·D$_2$O. We suspect this is a reflection of the facts that in their calculation, Rheinecker and Bowman used normal mode coordinates evaluated at one of the two equivalent potential minima and employed a four-mode representation of the coupling. These choices must have artificially removed the equivalence of the two minima in their calculations, which would lead to the loss of the tunneling doublet structure in their calculated spectra.

As indicated above, the in-plane bend fundamental band in the X$^−$·H$_2$O and X$^−$·D$_2$O spectra is made up of four vibrational transitions. Two are $a$-type transitions that go from the lower or upper member of the tunneling doublet with $n_{ip} = 0$ to
Figure 3.13: The in-plane bend potentials (thick black curves) and energy levels (horizontal lines) when zero and one quanta of excitation in the water bend are included. In (a), (c), (d), (e), (g), and (h), the energy levels are depicted with solid lines for symmetric states and dashed lines for states that have a node at $\theta_{ip} = 0^\circ$. For the HOD/DOH complex, solid lines are used to depict states that are localized in the Cl$^-$·DOH well, while dashed lines are used for states that are localized in the Cl$^-$·HOD well. In all cases, the ground states are depicted with black lines, and the states with one and two quanta in the in-plane bend are shown with blue and red lines, respectively.
Table 3.8: In-plane bend fundamental and overtone frequencies (in cm\(^{-1}\)) and line strengths (in Debye\(^2\)) for the isotopologues of Cl\(^−\)·H\(_2\)O.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>(a)-type(^a)</th>
<th>(b)-type(^a)</th>
<th>(M_{ip,nip})(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^−)·H(_2)O</td>
<td>1 ← 0</td>
<td>333</td>
<td>0.02790</td>
<td>0.03038</td>
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</tr>
<tr>
<td></td>
<td>1 ← 0</td>
<td>343</td>
<td>0.02980</td>
<td>0.02753</td>
<td>2.39880</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>577</td>
<td>0.00600</td>
<td>0.00004</td>
<td>0.25272</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>666</td>
<td>0.00494</td>
<td>0.00036</td>
<td>0.22148</td>
</tr>
<tr>
<td>Cl(^−)·DOH</td>
<td>1 ← 0</td>
<td>291</td>
<td>0.02454</td>
<td>0.02460</td>
<td>1.91412</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>539</td>
<td>0.00329</td>
<td>0.00013</td>
<td>0.13341</td>
</tr>
<tr>
<td>Cl(^−)·HOD</td>
<td>1 ← 0</td>
<td>280</td>
<td>0.02935</td>
<td>0.02368</td>
<td>3.19501</td>
</tr>
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<td></td>
<td>2 ← 0</td>
<td>523</td>
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<td>0.00016</td>
<td>0.21445</td>
</tr>
<tr>
<td>Cl(^−)·D(_2)O</td>
<td>1 ← 0</td>
<td>249</td>
<td>0.02542</td>
<td>0.02158</td>
<td>3.05589</td>
</tr>
<tr>
<td></td>
<td>1 ← 0</td>
<td>249</td>
<td>0.02553</td>
<td>0.02145</td>
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<tr>
<td></td>
<td>2 ← 0</td>
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<td></td>
<td>2 ← 0</td>
<td>478</td>
<td>0.00281</td>
<td>0.00019</td>
<td>0.19158</td>
</tr>
</tbody>
</table>

\(^a\) Transitions of \(a\)- and \(b\)-type differ in energy by the tunneling splitting of the ground state for Cl\(^−\)·H\(_2\)O and Cl\(^−\)·D\(_2\)O, which is 0.2339 and 0.0068 cm\(^{-1}\), respectively. The zero point energies for Cl\(^−\)·H\(_2\)O, Cl\(^−\)·DOH, Cl\(^−\)·HOD, and Cl\(^−\)·D\(_2\)O are 180, 152, 232, and 129 cm\(^{-1}\), respectively.

\(^b\) The \(M_{ip,nip}\) values are obtained by summing the \(a\)- and \(b\)-type line strengths and normalizing with respect to the water bend transition for each isotopologue as shown in eq. (3.5).
Table 3.9: In-plane bend fundamental and overtone frequencies (in cm$^{-1}$) and line strengths (in Debye$^2$) for the isotopologues of Br$^-$-H$_2$O.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>$a$-type$^a$</th>
<th>$b$-type$^a$</th>
<th>$M_{ip,nip}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^-$-H$_2$O</td>
<td>1 ← 0</td>
<td>286</td>
<td>0.02813</td>
<td>0.03834</td>
<td>2.57527</td>
</tr>
<tr>
<td></td>
<td>1 ← 0</td>
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<td>0.02942</td>
<td>2.39826</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
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<td>0.00884</td>
<td>0.00001</td>
<td>0.34288</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>613</td>
<td>0.00531</td>
<td>0.00035</td>
<td>0.21918</td>
</tr>
<tr>
<td>Br$^-$-DOH</td>
<td>1 ← 0</td>
<td>259</td>
<td>0.02634</td>
<td>0.02709</td>
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</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>463</td>
<td>0.00346</td>
<td>0.00004</td>
<td>0.12389</td>
</tr>
<tr>
<td>Br$^-$-HOD</td>
<td>1 ← 0</td>
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<td>0.02663</td>
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</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>461</td>
<td>0.00331</td>
<td>0.00009</td>
<td>0.19277</td>
</tr>
<tr>
<td>Br$^-$-D$_2$O</td>
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<tr>
<td></td>
<td>1 ← 0</td>
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</tr>
<tr>
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<td>0.00006</td>
<td>0.19472</td>
</tr>
<tr>
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<td>2 ← 0</td>
<td>426</td>
<td>0.00319</td>
<td>0.00016</td>
<td>0.19688</td>
</tr>
</tbody>
</table>

$^a$ Transitions of $a$- and $b$-type differ in energy by the tunneling splitting of the ground state for Br$^-$-H$_2$O and Br$^-$-D$_2$O, which is 0.7535 and 0.0340 cm$^{-1}$, respectively. The zero point energies for Br$^-$-H$_2$O, Br$^-$-DOH, Br$^-$-HOD, and Br$^-$-D$_2$O are 159, 135, 213, and 113 cm$^{-1}$, respectively.

$^b$ The $M_{ip,nip}$ values are obtained by summing the $a$- and $b$-type line strengths and normalizing with respect to the water bend transition for each isotopologue as shown in eq. (3.5).
Table 3.10: In-plane bend fundamental and overtone frequencies (in cm$^{-1}$) and line strengths (in Debye$^2$) for the isotopologues of \( {\text{I}}^-\cdot\text{H}_2\text{O} \).

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>( a )-type$^a$</th>
<th>( b )-type$^a$</th>
<th>( M_{ip,a_{ip}} )$^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>( {\text{I}}^-\cdot\text{H}_2\text{O} )</td>
<td>1 ← 0</td>
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</tr>
<tr>
<td></td>
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<td>0.03521</td>
<td>0.02757</td>
<td>2.07497</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>399</td>
<td>0.01395</td>
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<tr>
<td>( {\text{I}}^-\cdot\text{DOH} )</td>
<td>1 ← 0</td>
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<td>0.03805</td>
<td>1.80452</td>
</tr>
<tr>
<td></td>
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<td>357</td>
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<td>0.00006</td>
<td>0.14649</td>
</tr>
<tr>
<td>( {\text{I}}^-\cdot\text{HOD} )</td>
<td>1 ← 0</td>
<td>181</td>
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<td>0.03344</td>
<td>2.82343</td>
</tr>
<tr>
<td></td>
<td>2 ← 0</td>
<td>384</td>
<td>0.00381</td>
<td>0.00000</td>
<td>0.18821</td>
</tr>
<tr>
<td>( {\text{I}}^-\cdot\text{D}_2\text{O} )</td>
<td>1 ← 0</td>
<td>160</td>
<td>0.02285</td>
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</tr>
<tr>
<td></td>
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<td>353</td>
<td>0.00440</td>
<td>0.00003</td>
<td>0.21198</td>
</tr>
</tbody>
</table>

$^a$ Transitions of \( a \)- and \( b \)-type differ in energy by the tunneling splitting of the ground state for \( {\text{I}}^-\cdot\text{H}_2\text{O} \) and \( {\text{I}}^-\cdot\text{D}_2\text{O} \), which is 4.7662 and 0.4807 cm$^{-1}$, respectively. The zero point energies for \( {\text{I}}^-\cdot\text{H}_2\text{O} \), \( {\text{I}}^-\cdot\text{DOH} \), \( {\text{I}}^-\cdot\text{HOD} \), and \( {\text{I}}^-\cdot\text{D}_2\text{O} \) are 130, 113, 193, and 96 cm$^{-1}$, respectively.

$^b$ The \( M_{ip,a_{ip}} \) values are obtained by summing the \( a \)- and \( b \)-type line strengths and normalizing with respect to the water bend transition for each isotopologue as shown in eq. (3.5).
the corresponding member of the tunneling doublet with $n_{ip} = 1$. There are also two $b$-type transitions that connect the other two pairs of states. As indicated by the results reported in Table 3.8, the two types of transitions have roughly equal intensity in the chloride complexes. As the splitting between the two states with $n_{ip} = 0$ is less than 0.25 cm$^{-1}$, the two bands will be overlapping. On the other hand, the 10 cm$^{-1}$ splitting when $n_{ip} = 1$ in Cl$^-\cdot$H$_2$O would lead to a pair of transitions spaced by 10 cm$^{-1}$ that collapses to 0.5 cm$^{-1}$ in Cl$^-\cdot$D$_2$O. Similar behavior is predicted for the bromide and iodide complexes. The decomposition of these bands is given Tables 3.11–3.13.

In light of the large intensity in the overtone in the out-of-plane bend in these systems, we also calculated the frequencies and intensities for the in-plane bend transitions to the first overtone for each of these species using the MP2/aug-cc-pVTZ dipole surfaces. As is shown in Figure 3.13, in all cases the fifth and sixth lowest energy states (which correspond to two quanta in a localized in-plane bend vibration and are represented by the red lines) lie above the isomerization barrier in the X$^-\cdot$H$_2$O complexes. For the X$^-\cdot$D$_2$O species these two states are above the barrier for the iodide complex and below the barrier for Br$^-\cdot$D$_2$O and Cl$^-\cdot$D$_2$O. When we calculate the overtone intensities, we find that they are roughly an order of magnitude smaller than those for the fundamental. In addition, unlike the fundamental, where the $a$- and $b$-type transitions have roughly equal intensity, the intensities of the $a$-type transitions are between a factor of 10 and 100 larger than the intensity of the $b$-type transitions that comprise the $2\nu_{ip}$ bands.
Table 3.11: Comparison of the $M_{ip,nip}$ values (eq. (3.5)) of the in-plane bend fundamental and overtone transitions of the isotopologues of $\text{Cl}^-\cdot\text{H}_2\text{O}$, using the coordinate-dependent dipole surface or the dipole surface obtained using the fixed charge model. All frequencies are given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>coord. dep. $M_{ip,nip}$ $a:b$</th>
<th>fixed charge $M_{ip,nip}$ $a:b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}^-\cdot\text{H}_2\text{O}$</td>
<td>$1^+ \leftarrow 0^+$</td>
<td>334</td>
<td>1.16731 1:0</td>
<td>5.15335 1:0</td>
</tr>
<tr>
<td></td>
<td>$1^+ \leftarrow 0^-$</td>
<td>333</td>
<td>1.27123 0:1</td>
<td>3.99487 0:1</td>
</tr>
<tr>
<td></td>
<td>$1^- \leftarrow 0^+$</td>
<td>344</td>
<td>1.15189 0:1</td>
<td>3.67406 0:1</td>
</tr>
<tr>
<td></td>
<td>$1^- \leftarrow 0^-$</td>
<td>343</td>
<td>1.24690 1:0</td>
<td>5.33320 1:0</td>
</tr>
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<td>$2^+ \leftarrow 0^+$</td>
<td>577</td>
<td>0.25099 1:0</td>
<td>0.45483 1:0</td>
</tr>
<tr>
<td></td>
<td>$2^+ \leftarrow 0^-$</td>
<td>577</td>
<td>0.00173 0:1</td>
<td>0.00000 0:1</td>
</tr>
<tr>
<td></td>
<td>$2^- \leftarrow 0^+$</td>
<td>666</td>
<td>0.01403 0:1</td>
<td>0.02242 0:1</td>
</tr>
<tr>
<td></td>
<td>$2^- \leftarrow 0^-$</td>
<td>666</td>
<td>0.20655 1:0</td>
<td>0.25647 1:0</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{DOH}$</td>
<td>$1^- \leftarrow 0$</td>
<td>291</td>
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<td>7.00557 1:1</td>
</tr>
<tr>
<td></td>
<td>$2^- \leftarrow 0$</td>
<td>539</td>
<td>0.13341 25.3:1</td>
<td>0.18644 27.2:1</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{HOD}$</td>
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<td>11.52825 1.6:1</td>
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<tr>
<td></td>
<td>$2^- \leftarrow 0$</td>
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<td>0.21445 21.3:1</td>
<td>0.29826 28.1:1</td>
</tr>
<tr>
<td>$\text{Cl}^-\cdot\text{D}_2\text{O}$</td>
<td>$1^+ \leftarrow 0^+$</td>
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<td>1.65265 1:0</td>
<td>6.51318 1:0</td>
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<tr>
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<td>$1^+ \leftarrow 0^-$</td>
<td>249</td>
<td>1.40324 0:1</td>
<td>4.27659 0:1</td>
</tr>
<tr>
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<td>$1^- \leftarrow 0^+$</td>
<td>249</td>
<td>1.39443 0:1</td>
<td>4.25382 0:1</td>
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<td>$1^- \leftarrow 0^-$</td>
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<td>1.65975 1:0</td>
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<tr>
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<td>$2^+ \leftarrow 0^+$</td>
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<td>0.24099 1:0</td>
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<tr>
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<td>$2^+ \leftarrow 0^-$</td>
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<td>0.00971 0:1</td>
<td>0.01281 0:1</td>
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<tr>
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<td>$2^- \leftarrow 0^+$</td>
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<td>0.01243 0:1</td>
<td>0.01832 0:1</td>
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<tr>
<td></td>
<td>$2^- \leftarrow 0^-$</td>
<td>478</td>
<td>0.18275 1:0</td>
<td>0.22786 1:0</td>
</tr>
</tbody>
</table>
Table 3.12: Comparison of the $M_{i,p,n,p}$ values (eq. (3.5)) of the in-plane bend fundamental and overtone transitions of the isotopologues of Br$^{-}$-H$_2$O, using the coordinate-dependent dipole surface or the dipole surface obtained using the fixed charge model. All frequencies are given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>coord. dep. $M_{i,p,n,p}$</th>
<th>fixed charge $M_{i,p,n,p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^{-}$-H$_2$O</td>
<td>$1^+ \leftarrow 0^+$</td>
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<tr>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>$1^- \leftarrow 0^-$</td>
<td>310</td>
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</tr>
<tr>
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<td>$2^+ \leftarrow 0^+$</td>
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<tr>
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<td>$2^+ \leftarrow 0^-$</td>
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<td>0.00043 0:1</td>
<td>0.02463 0:1</td>
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<tr>
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<td>0.01179 0:1</td>
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<tr>
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<td>0.20576 1:0</td>
<td>0.26912 1:0</td>
</tr>
<tr>
<td>Br$^{-}$-DOH</td>
<td>1 $\leftarrow$ 0</td>
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</tr>
<tr>
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<td>2 $\leftarrow$ 0</td>
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<tr>
<td>Br$^{-}$-HOD</td>
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<td>11.25055 1:2:1</td>
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<td>2 $\leftarrow$ 0</td>
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<td>0.19277 36.8:1</td>
<td>0.30157 531:1</td>
</tr>
<tr>
<td>Br$^{-}$-D$_2$O</td>
<td>$1^+ \leftarrow 0^+$</td>
<td>221</td>
<td>1.50305 1:0</td>
<td>5.65404 1:0</td>
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<tr>
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<td>$1^+ \leftarrow 0^-$</td>
<td>221</td>
<td>1.37867 0:1</td>
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<tr>
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<td>$1^- \leftarrow 0^+$</td>
<td>223</td>
<td>1.34067 0:1</td>
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<td>$1^- \leftarrow 0^-$</td>
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<tr>
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<td>$2^+ \leftarrow 0^+$</td>
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<td>$2^+ \leftarrow 0^-$</td>
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<tr>
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<td>$2^- \leftarrow 0^+$</td>
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<tr>
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<td>$2^- \leftarrow 0^-$</td>
<td>426</td>
<td>0.18721 1:0</td>
<td>0.26306 1:0</td>
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</table>
Table 3.13: Comparison of the $M_{ip, n_{ip}}$ values (eq. (3.5)) of the in-plane bend fundamental and overtone transitions of the isotopologues of $\Gamma^- \cdot \text{H}_2\text{O}$, using the coordinate-dependent dipole surface or the dipole surface obtained using the fixed charge model. All frequencies are given in cm$^{-1}$.

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>frequency</th>
<th>coord. dep.</th>
<th>fixed charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^- \cdot \text{H}_2\text{O}$</td>
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<tr>
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<tr>
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<td>$1^- \leftarrow 0^+$</td>
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<td>$1^- \leftarrow 0^-$</td>
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<td>4.11731 1:0</td>
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<tr>
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<td>$2^+ \leftarrow 0^+$</td>
<td>404</td>
<td>0.46102 1:0</td>
<td>1.04801 1:0</td>
</tr>
<tr>
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<td>$2^+ \leftarrow 0^-$</td>
<td>399</td>
<td>0.02019 0:1</td>
<td>0.19368 0:1</td>
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<tr>
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<td>$2^- \leftarrow 0^+$</td>
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<td>0.00028 0:1</td>
</tr>
<tr>
<td></td>
<td>$2^- \leftarrow 0^-$</td>
<td>543</td>
<td>0.19207 1:0</td>
<td>0.26200 1:0</td>
</tr>
<tr>
<td>$\Gamma^- \cdot \text{DOH}$</td>
<td>$1 \leftarrow 0$</td>
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<td>1.80452 0.6:1</td>
<td>6.14396 0.7:1</td>
</tr>
<tr>
<td></td>
<td>$2 \leftarrow 0$</td>
<td>357</td>
<td>0.14649 82.5:1</td>
<td>0.33190 10.9:1</td>
</tr>
<tr>
<td>$\Gamma^- \cdot \text{HOD}$</td>
<td>$1 \leftarrow 0$</td>
<td>181</td>
<td>2.82343 0.7:1</td>
<td>9.76750 0.8:1</td>
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<td>$2 \leftarrow 0$</td>
<td>384</td>
<td>0.18821 1:0</td>
<td>0.35032 34.4:1</td>
</tr>
<tr>
<td>$\Gamma^- \cdot \text{D}_2\text{O}$</td>
<td>$1^+ \leftarrow 0^+$</td>
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<td>4.07176 1:0</td>
</tr>
<tr>
<td></td>
<td>$1^+ \leftarrow 0^-$</td>
<td>160</td>
<td>1.84302 0:1</td>
<td>5.79381 0:1</td>
</tr>
<tr>
<td></td>
<td>$1^- \leftarrow 0^+$</td>
<td>179</td>
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<td>4.69716 0:1</td>
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<tr>
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<td>$1^- \leftarrow 0^-$</td>
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<td>4.56216 1:0</td>
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<tr>
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</tr>
<tr>
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<td>$2^+ \leftarrow 0^-$</td>
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<td>0.16720 0:1</td>
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<tr>
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<td>$2^- \leftarrow 0^+$</td>
<td>354</td>
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<td>0.00303 0:1</td>
</tr>
<tr>
<td></td>
<td>$2^- \leftarrow 0^-$</td>
<td>353</td>
<td>0.21032 1:0</td>
<td>0.34819 1:0</td>
</tr>
</tbody>
</table>
When the fixed charge model, described above, is used to model the dipole moments for the in-plane bend, we find that the intensities decrease by a larger factor (10–40 compared to 10–15), and the relative intensities of the $a$-type transitions are also much larger than those for the $b$-type transitions. Based on this, we conclude that electrical anharmonicity is not a major contributor to the intensity of this overtone, as it was for the out-of-plane bend, as any unexpected intensity patterns are captured by the fixed charge model. The difference in the behaviors of the in- and out-of-plane bends reflects the fact that large displacements along $\theta_{ip}$ lead to the formation of a different hydrogen bond. In contrast, large amplitude motion along the out-of-plane bend coordinate effectively destroys the hydrogen bond.

We have also calculated the fundamental and first overtone for the singly deuterated complexes. Partial deuteration breaks the symmetry of the zero point corrected potential along the in-plane bend coordinate, and this is illustrated in Figure 3.13(f). In all cases, once zero point energy in the other modes is included, the more stable isomer is the $X^-\cdot$DOH isomer, which has a deuterium in the $H_b$ position.\textsuperscript{75} This stability is reflected in the spectra in Figures 3.9 and 3.10 where both isomers are present, and the peaks attributed to the $X^-\cdot$DOH isomer are larger than those assigned to the $X^-\cdot$HOD isomer. Furthermore, analysis of the wave functions shows that although the barrier for isomerization is low, the wave functions can be characterized as having most of their amplitude in either the $X^-\cdot$DOH or the $X^-\cdot$HOD potential minima.
This leads to two distinct progressions in the calculated spectra, as indicated in Tables 3.2, 3.4–3.6, and 3.8–3.10. Wave functions for the in-plane bend states of interest for the twelve molecular species considered are shown in Figures 3.14–3.16.

3.4.3.4 In-plane bend + water bend combination bands

While it is interesting to contrast the spectral signatures of the in- and out-of-plane bending motions, the transitions involving the in-plane bend discussed above are outside of the experimental frequency range, and there is consequently no way to compare these results directly with experiment. In considering where one might find signatures of the in-plane bend in the spectrum, we consider two observations. First, the OX\(^-\) stretch was only assigned in combination with the OH\(_b^\) stretch. A rationalization for this is that the two vibrational modes can be considered as unequal admixtures of the OH\(_b^\) and the X\(^-\)H\(_b^\) stretching motions. Such a description was discussed in more detail in the previous chapter. Likewise, as discussed above in the context of the HOD bend frequencies, the in-plane bend and water bend normal modes are actually unequal admixtures of these two zero-order modes. This is reflected in the isotope dependence of the in-plane bend harmonic frequencies. If \(\theta_{ip}\) were a pure in-plane rotation of the water molecule, one would expect the frequency to be highest for X\(^-\).H\(_2\)O, intermediate and identical for X\(^-\).HOD/X\(^-\).DOH, and lowest for X\(^-\).D\(_2\)O. In fact, the harmonic in-plane bend frequencies for X\(^-\).HOD and X\(^-\).DOH differ by as much as 13 cm\(^{-1}\), with the frequency for X\(^-\).DOH being the higher of the two.
Figure 3.14: The in-plane bend potentials (thick black curves) with zero and one quanta of excitation in the water bend for Cl\textsuperscript{−}·H\textsubscript{2}O: $V_{\text{nHOOH}=0}(\theta_{\text{ip}})$ and $V_{\text{nHOOH}=1}(\theta_{\text{ip}})$, respectively. Energy levels and wave functions for the six vibrational states that lead to the $\nu_{\text{ip}}$ and $2\nu_{\text{ip}}$ bands are also shown for each potential surface. Pairs of degenerate states are shown in similar colors: red/pink, dark/light blue, and dark/light green. For the HOD/DOH species, the color scheme is the same for comparison purposes, but these states are nondegenerate.
Figure 3.15: The in-plane bend potentials (thick black curves) with zero and one quanta of excitation in the water bend for Br·H₂O: $V_{\nu_{\text{ip}}=0}(\theta_{\text{ip}})$ and $V_{\nu_{\text{ip}}=1}(\theta_{\text{ip}})$, respectively. Energy levels and wave functions for the six vibrational states that lead to the $\nu_{\text{ip}}$ and $2\nu_{\text{ip}}$ bands are also shown for each potential surface. Pairs of degenerate states are shown in similar colors: red/pink, dark/light blue, and dark/light green. For the HOD/DOH species, the color scheme is the same for comparison purposes, but these states are nondegenerate.
Figure 3.16: The in-plane bend potentials (thick black curves) with zero and one quanta of excitation in the water bend for $\Gamma \cdot \text{H}_2\text{O}$: $V_{\text{HOH}}=0(\theta_{ip})$ and $V_{\text{HOH}}=1(\theta_{ip})$, respectively. Energy levels and wave functions for the six vibrational states that lead to the $\nu_{ip}$ and $2\nu_{ip}$ bands are also shown for each potential surface. Pairs of degenerate states are shown in similar colors: red/pink, dark/light blue, and dark/light green. For the HOD/DOH species, the color scheme is the same for comparison purposes, but these states are nondegenerate.
Based on this, we looked for patterns in the spectra that could be attributed to the $\nu_{\text{HOH}} + \nu_{\text{ip}}$ combination bands. Such a band has already been tentatively assigned in the Cl$^{-}\cdot$H$_2$O spectrum$^{18}$ and is found at 1962 cm$^{-1}$ in Figure 3.6. It was also assigned to a strong transition in the calculated Cl$^{-}\cdot$H$_2$O spectrum of Rheinecker and Bowman.$^{174}$ Taking the spacing between this combination band and the water bend fundamental (Figure 3.6), yields a value for $\nu_{\text{ip}}$ of 309 cm$^{-1}$. This value is in good agreement with the calculated fundamental frequency (333 cm$^{-1}$), reported in Table 3.4, and the line position is in even better agreement with the 1985 cm$^{-1}$ calculated for this transition. In their six-dimensional calculations, Rheinecker and Bowman report the Cl$^{-}\cdot$H$_2$O combination band at 2027 cm$^{-1}$, yielding an in-plane bend frequency that deviates from their calculated position for the fundamental band by only 5 cm$^{-1}$.$^{174}$ The similarity between the in-plane bend frequencies evaluated when $n_{\text{HOH}} = 0$ and 1 can be explained by Figure 3.4(c). Here the frequency of the water bend is plotted as a function of the in-plane bend coordinate, and it varies little over $15^\circ \leq \theta_{\text{ip}} \leq 60^\circ$, which is where the wave function has the most amplitude. This is exactly the region that is sampled by the vibrational wave functions when $n_{\text{HOH}} = 1$. As a result the effective potentials, wave functions, and transition frequencies are similar when $n_{\text{HOH}} = 0$ and $n_{\text{HOH}} = 1$, as shown in Figures 3.13(a), (c), and (d) and 3.14–3.16. Based on the above, it is not surprising that the shift of the $\nu_{\text{HOH}} + \nu_{\text{ip}}$ combination band from the $\nu_{\text{HOH}}$ fundamental provides a good approximation to the anharmonic frequency of the in-plane bend fundamental.
In analyzing the spectra in Figures 3.6–3.10, we find transitions that are assignable to this $\nu_{\text{HOH}} + \nu_{\text{ip}}$ combination band in many of the species and are indicated in orange. They are also labeled as band 3 in Figure 3.11. The experimental and calculated frequencies for these bands are reported in Tables 3.2 and 3.4–3.6, respectively. These transitions occur as quartets in the $X^-\cdot\text{H}_2\text{O}$ and $X^-\cdot\text{D}_2\text{O}$ complexes, and we report all four frequencies. The splitting between the two pairs of states is generally smaller than 1 cm$^{-1}$, reflecting the small splitting of the ground state tunneling doublet. The notable exception is $I^-\cdot\text{H}_2\text{O}$, where the splitting of the ground state levels exceeds 4 cm$^{-1}$.

Overall, the agreement between experiment and calculation is very good. As is predicted in the calculations, the tunneling splitting increases from $\text{Cl}^-\cdot\text{H}_2\text{O}$ to $I^-\cdot\text{H}_2\text{O}$. This is reflected in the spectra shown in Figures 3.6–3.8. While in $\text{Cl}^-\cdot\text{H}_2\text{O}$ the $\nu_{\text{HOH}} + \nu_{\text{ip}}$ combination band appears as a single broad peak, in $I^-\cdot\text{H}_2\text{O}$ there are two resolvable features of nearly equal intensity, spaced by 83 cm$^{-1}$, compared to a theoretical value of 74 cm$^{-1}$. Preliminary results of calculations of the combination band intensities are consistent with the magnitudes relative to the $\nu_{\text{HOH}}$ bands seen in experiment.

### 3.5 Conclusion

In this chapter, a complete set of spectra for the $\text{Cl}^-$, $\text{Br}^-$, and $I^-\cdot\text{H}_2\text{O}$ complexes has been presented, including partial and full deuteration of the water molecule. Spectra are reported for frequencies from $\sim$800 to 3800 cm$^{-1}$. Based on the assignment of
these spectra, transitions involving all six vibrational modes have been identified in the majority of the complexes. This provides a library with which one can investigate the role of anharmonicity, resonance interactions, and mode-mode coupling in these complexes.

Four-atom systems contain six vibrational degrees of freedom and are amenable to full-dimensional treatments of the molecular vibrations. On the other hand, generation of six-dimensional potential surfaces that encompass all relevant regions of the potential and that are generated at a level of theory that is expected to produce spectroscopic accuracy is a large undertaking.\textsuperscript{174,175} Furthermore, as one moves from four-atom systems to larger complexes, for example by introducing additional water molecules, generation of the potential surface as well as the calculations of the vibrational spectra in full-dimensionality become increasingly challenging tasks. Consequently, a second goal of this work was to investigate how well reduced-dimensional treatments capture the spectral signatures of two of the intermolecular modes in these systems, specifically the in- and out-of-plane bends. Finally we discussed the qualitative implications of these results on the character and behavior of the anionic hydrogen bond.

As illustrated by the agreement between the experimental and calculated transition frequencies, the reduced-dimensional treatments of the two intermolecular bending coordinates can recover the observed behavior of these large amplitude vibrational motions. In addition, by analyzing the results of our calculations, we were able to further probe the nature of the anomalously large electrical anharmonicities that are
responsible for the large intensity of the overtone in the out-of-plane bend. We also predicted, and later verified by spectral assignment, splittings between the $\nu_{\text{HOH}} + \nu_{\text{ip}}$ combination bands that increase in magnitude from chloride to bromide to iodide.

The larger goal of this work is to ask how the insights gained in these studies will aid in studies of spectra of larger complexes for which there are more vibrational modes and consequently the coupling among modes is necessarily stronger. This is an on-going endeavor in studies of ion-water complexes. One important insight is the unexpectedly large intensity of the overtone of the mode that corresponds to displacement of hydrogen atoms involved in hydrogen bonds between the ion and the water molecule perpendicular to the bond axis. Similar signatures have been tentatively assigned for the $\text{OH}^- \cdot \text{H}_2\text{O}$ complex, and we believe that they may be leading to previously unassigned transitions in spectra of other ion-water complexes. Likewise, the identification of the $\nu_{\text{HOH}} + \nu_{\text{ip}}$ and $\nu_{\text{OH}_b} + \nu_{\text{OX}}$ combination bands in these complexes provides other targets for assignments in larger species.
CHAPTER 4

Theoretical investigations of the time-resolved photodissociation dynamics of IBr⁻

4.1 Introduction

One central goal of molecular spectroscopy has been to probe the potential energy surface underlying molecular transitions while a second has been to use this knowledge to explore the dynamics that take place on these surfaces. An area where there has been much recent work is the photoinduced dissociation of homonuclear and heteronuclear dihalide anions (X₂⁻ and XY⁻), both in isolation and in the presence of a small number of solvating atoms or molecules. From an experimental standpoint, X⁻₂ and XY⁻ molecules have low-lying excited electronic states, accessible by visible or near UV light. Additionally, the high electron affinities of their neutral counterparts and large polarizabilities allow for attachment of excess electrons via standard experimental methods, which in turn enables the use of time-of-flight mass spectrometry techniques in the study of size-selected clusters that incorporate these species. From a theoretical point of view, X₂⁻ and XY⁻ species are small enough that high level ab initio calculations can be performed, and in many cases, high level calculations are necessary given the degree of coupling between electronic states and
strength of the spin-orbit coupling. In these systems it is also possible to perform full quantum dynamics. Despite the fact that these systems are small, they continue to prove challenging given the density and coupling of the electronic states. Moreover, they provide a testing ground for understanding chemical physics phenomena more generally. For example, several fundamental studies have utilized the I$_2$, Br$_2$, or IBr chromophore to probe energy and charge transfer, vibrational dynamics, and predissociation in rare gas matrices and gas-phase clusters.\textsuperscript{9,64,179,181–189}

The focus of the present study is on the time resolved photoelectron spectroscopy (TRPES) of IBr$^-$, specifically the work reported by Sanov and co-workers.\textsuperscript{8} In these experiments, an equilibrium ensemble of anions is generated at a temperature of $\approx$ 100 K.\textsuperscript{62,190} The system is then photoexcited (or “pumped”) to some higher-lying excited electronic state of the anion. In the case of this work, the system undergoes a transition to the so-called $A'$ state, which corresponds to a promotion of an electron from the anti-bonding $\pi^*$ molecular orbital to the $\sigma^*$ orbital. After a delay time of several hundred femtoseconds ($\Delta t$), the system is ionized with a second “probe” laser pulse. The velocity and angular distribution of the ejected electrons are recorded, and this data is analyzed. In Figure 4.1 we illustrate the pump-probe excitation scheme utilized in these experiments while Figure 4.2 provides the resulting spectra, plotted as a function of pump-probe delay time.\textsuperscript{8} Related studies have been performed on complexes of IBr$^-$ with a single CO$_2$ molecule and are reported by Lineberger and co-workers.\textsuperscript{9}
Figure 4.1: Qualitative representation of the pump-probe excitation scheme utilized in the experiment modeled here.
Figure 4.2: Representation of the experimental signal for the time-resolved photo-electron spectra of IBr⁻ for different pump-probe delay time slices. The spectra have been reproduced from Ref. 8 with permission.
In the study on the photodissociation of IBr$^-$ performed by Sanov and co-workers,$^8$ the resulting signal (shown in Figure 4.2) was analyzed using a classical picture. Specifically, examination of the photoelectron signal at each time delay shows that there is a time dependence to the shape of the spectral contour as well as the energy that corresponds to the maximum in the signal. At short delay times the distribution is broad, and the signal is low at all energies. After $\approx 300$ fs, a peak is observed at $\sim 0.08$ eV. This peak remains at a nearly constant position for several hundred femtoseconds before shifting to its asymptotic value ($\sim 0.12$ eV) after 1.2 ps. The shifts in position of the peak were related to the difference between the potential energy of the $A'$ state on which the dynamics occurs and the IBr potential energy surfaces to which the system is excited by the probe laser. These differences were related to the delay time by propagating a trajectory on the $A'$ surface and evaluating the difference between the potential energies as a function of $R(\Delta t)$. While the agreement was generally good, it was achieved by assuming an initial I-Br separation of 3.30 Å, which is quite a bit longer than the measured equilibrium bond length of 3.01 Å.$^{62}$ It is also surprising that graphs of the position of the maximum in the signal, plotted as a function of time, show a rise starting at $\sim 250$ fs. This contrasts with the picture that would be anticipated by taking the difference between the potentials plotted in Figure 4.1 in which there would be a decrease in the energy of the maximum in the signal at shorter times, followed by an increase at longer times.
In the present study, we take the analysis of this experiment, but also TRPES studies more generally, one step further and focus on what effects the quantum nature of the wave packet has on the dynamics of the system. We focus on how the classical picture, described above, should be modified to account for the fact that the experiments employ lasers with finite duration in time and consequently sample finite energy ranges. Finally, since the electronic structure of the states that are represented by these curves changes as the molecule or molecular ion dissociates, we ask if it is necessary to account for the changes in the excitation cross-sections to describe the dynamics of these processes, as it is reflected in the reported spectra.

In this work, we address this question by investigating how the temporal pulse width affects the TRPES for IBr$^{-}$. Specifically, we address three temporal pulse width regimes: an infinitesimally short pulse that places no constraints on the excitation energy, a pulse with a temporal width that is the same as that used in the experiment, and a pulse that has a duration three times longer than experiment and consequently will excite into states with a much narrower energy range.

4.2 Theory

The theoretical study described herein models the time-resolved photodissociation experiment of IBr$^{-}$ by Sanov and co-workers. While the complete details of the experimental study are discussed in Ref. 8, the information relevant to this study is reported here. IBr$^{-}$ ions are prepared in their ground electronic state whereupon they undergo a $\pi^*-\sigma^*$ photoinduced excitation to the $A'$ electronic state ($^2\Pi_{1/2}$) by a pump
pulse with a wavelength of 780 nm (1.59 eV). This excited wave packet then evolves on the \(A'\) surface for a given length of time before being ionized by a time-delayed probe pulse with a wavelength of 390 nm (3.18 eV) and most likely dissociating on the \(C (^1\Pi_1)\) and \(A (^3\Pi_1)\) states of IBr. The photoelectron spectra were collected for pump-probe delay times of approximately 50 – 1350 fs. The functional forms of the pulses are assumed to be Gaussian with an estimated full width at half maximum (FWHM) of 300 fs.

Our approach is based on electronic structure and vibrational energy calculations as well as on full quantum dynamics. Multireference configuration interaction calculations that include spin-orbit terms were used to obtain the six lowest energy electronic states of the anion, and a sinc-discrete variable representation (DVR)\(^{107,108}\) was used to obtain the vibrational eigenstates associated with the electronic states of IBr\(^-\) and IBr.

### 4.2.1 Potential energy surfaces

We perform \textit{ab initio} calculations to obtain the electronic states of the anion using the electronic structure program package COLUMBUS.\(^{191-194}\) The anion surfaces were calculated as a function of the I–Br distance, \(R\), at 29 points between 3.5 – 25.0 \(a_0\), and a list of the absolute electronic energies as a function of \(R\) can be found in the Tables 4.1–4.6. These surfaces were calculated using multireference configuration interaction with single and double excitations, and spin-orbit coupling was included (MR-SO-CISD).\(^{195}\) We employ aug-cc-pVDZ basis sets\(^{196}\) and relativistic
core potentials (RECPs) for the atoms,\textsuperscript{197,198} where iodine has a [Kr]-like core and bromine an [Ar]-like core.

The molecular orbitals (MOs) used in the MRCI calculations were determined from a multiconfiguration self consistent field (MCSCF) calculation averaged over all states obtained from placing the 11 valence electrons in the six valence MOs: $\sigma$, $\pi$, $\pi^*$, and $\sigma^*$. The d-orbitals of iodine and bromine were included in the MCSCF as well. As a result six reference states were obtained, and the lower lying $\sigma$ and $\sigma^*$ orbitals were constrained to be doubly occupied in these references. All single and double excitations were then performed out of these six reference states, and the MOs corresponding to the d-atomic orbitals were frozen. These calculations made use of the $C_{2v}^*$ double group, but the CI wave functions retain their $C_{\infty v}^*$ double group symmetries.

The functional forms of the potential energy surfaces for the neutral IBr electronic states were obtained from a study by Ashfold and co-workers.\textsuperscript{199} In the experiment on IBr, the energies of the electronic states are reported relative to the dissociation energy of IBr, which is set to zero. Therefore, to ensure that the electronic states of IBr\textsuperscript{−} and IBr are on the same energy scale, the energies of the neutral electronic states were shifted by the electron affinity of iodine, $\sim 3.06$ eV.\textsuperscript{200} The relevant electronic states of IBr\textsuperscript{−} and IBr are shown in Figure 4.3.

4.2.2 DVR calculations

One-dimensional variational calculations were carried out in a discrete variable representation (DVR)\textsuperscript{107,108} for the four electronic states of interest: the $X$ and $A'$
Table 4.1: *Ab initio* data for the $X$ state potential energy surface of IBr$^-$. 

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Table 4.2: *Ab initio* data for the A state potential energy surface of IBr$^-$. 

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Table 4.3: *Ab initio* data for the $A'$ state potential energy surface of IBr$^-$. 

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Table 4.4: *Ab initio* data for the $a$ state potential energy surface of IBr$^-$. 

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Table 4.5: *Ab initio* data for the $d'$ state potential energy surface of IBr$^-$. 

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Table 4.6: *Ab initio* data for the $B$ state potential energy surface of IBr$^-$.  

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Figure 4.3: Electronic states of IBr$^-$ and IBr. The bold, black lines represent the four states relevant to the dissociation dynamics of IBr$^-$: $X$ and $A'$ states of IBr$^-$ and $C$ and $A$ states of IBr.
states of IBr$^-$ and the $C$ and $A$ states of IBr. For the IBr$^-$ distance coordinate, $R$, we used the reduced mass ($\mu$) of $^{79}$Br. The Hamiltonian for this system (in atomic units) is given by

$$\hat{H} = -\frac{1}{2\mu} \frac{d^2}{dR^2} + V(R). \quad (4.1)$$

The potential surfaces, $V(R)$, were acquired from spline interpolations of the energies obtained from either the electronic structure calculations or from the experimental potential fit parameters described above. The grid points used for the DVR calculations ranged from 1 to 95 $a_0$ with a grid spacing of 0.0294 $a_0$ (3200 points). In using DVR basis functions, we are approximating the continuum states; however, we have varied the DVR grid length (35, 55, and 75 $a_0$) and the number of grid points (2400), and these parameters do not impact the calculated spectra.

### 4.2.3 Time-dependent calculations

In this study, we assume a vibrational temperature of 75 K.$^{8,62,190}$ At this temperature, the first four vibrational states of the ground electronic state account for 99.99% of the total vibrational population with over 90% attributed to $v = 0$. Each of the thermally-populated $X$-vibrational states are propagated on the $A'$ excited potential surface by treating the evolving wave packet as a linear superposition of $A'$ vibrational states and will heretofore be referred to as $\psi(R, \Delta t)$:

$$\psi(R, \Delta t) = \sum_m c_m e^{-i\frac{\hbar}{\mu}E_m \Delta t} \phi_m(R). \quad (4.2)$$

Overlaps between the wave packet and eigenstates of the neutral surface are then evaluated. The results of this treatment will be presented as the infinitesimally short
pulse; however, there is no discrimination of accessible energies in this treatment and will be discussed in more detail below.

To account for the fact that the laser pulses have a finite time duration, and hence a finite spectral range, we follow an approach that is based on the study of I$_2$ photodissociation by Zanni et al. and Batista et al.$^{179,201}$ To aid in the description of the method presented here, the first three equations are identical to eqs. (2.5), (2.11), and (2.12) from Ref. 201. The probability distribution of electron kinetic energies, $P(\epsilon)$, in the long time limit is given by the expression

$$P(\epsilon) = \sum_K \int dE_K \left( \frac{-i}{\hbar} \right)^2 \int_{-\infty}^{t} dt \int_{-\infty}^{t'} dt' \left( \mu_{K,A'} \cdot \epsilon(t) \right) \times \left( \mu_{A',g} \cdot \epsilon(t') \right) e^{(i/h)(E_K+\epsilon)t} \times e^{-(i/h)E_A t'} \langle \chi_{E_K} | e^{-(i/h)\hat{H}_{A'}(t-t')} | \chi_{g} \rangle^2. \quad (4.3)$$

Here $P(\epsilon)$ is the sum of the manifold of IBr electronic states ($K$) that can be accessed upon photodetachment of the electron. The time variables, $t'$ and $t$, give the time evolution of the pump and probe pulses, respectively. The electronic transition moments, $\mu_{i,j}$, are treated within the Condon approximation and are therefore assumed to be independent of the nuclear coordinates and the kinetic energy of the detached electron.$^{201}$ The time-dependent electric field, $\epsilon(t)$, is given by

$$\epsilon(t) = \epsilon_{01} F_1(t)e^{-i\omega_1 t} + \epsilon_{02} F_2(t - \Delta t)e^{-i\omega_2(t-\Delta t)} + c.c. \quad (4.4)$$

and is the sum of the pump and probe pulses with functional forms $F_1$ and $F_2$ and characteristic frequencies $\omega_1$ and $\omega_2$, respectively. The matrix element in eq. (4.3)
accounts for the photodissociation dynamics in that the Boltzmann-populated vibra-
tional state of the ground electronic state, \( |\chi_g\rangle \), is propagated on the excited potential
surface of the anion \( (A') \), before being overlapped with eigenstates of the neutral ex-
cited electronic state, \( |\chi_{EK}\rangle \).^{201}

We can obtain an expression for the photoelectron signal that depends on the
pump-probe delay time \( (\Delta t) \) and on the electron kinetic energy \( (\epsilon) \) by substituting
eq (4.4) into eq. (4.3). We can then simplify the resulting expression by inserting the
identity operator twice, once on either side of exponential term containing \( \hat{H}_{A'} \). The
identity operator represents the manifold of vibrational eigenstates of the\n\( A' \) excited
electronic state: \( |\phi_m\rangle \). Making these substitutions, the matrix element presented in
eq (4.3) then becomes

\[
\sum_{m,m'} \langle \chi_{EK}|\phi_{m'} \rangle \left \langle \phi_{m'} | e^{- (i/\hbar) \hat{H}_{A'} (t-t')} | \phi_m \right \rangle \langle \phi_m | \chi_g \rangle. \tag{4.5}
\]

As noted in eq. (4.3), there is a sum over all accessible neutral electronic states
upon photodetachment. However, to our knowledge, the electron detachment cross-
sections that describe the electronic transition between the \( A' \) state of IBr\(^-\) and
electronic states of IBr have not been reported. Therefore, we remove the dependence
of the spectra on these parameters by calculating the dynamics that results from
excitation to each of the two neutral surfaces separately and by separately normalizing
the final signal. These changes make \( K = 1 \) and \( |\chi_{EK}\rangle = |\chi_n\rangle \) in eq. (4.3), where \( n \)
is the manifold of vibrational eigenstates of one of the IBr excited electronic states.
The final expression for the time-resolved photoelectron signal, $P(\epsilon, \Delta t)$, is given by

$$P(\epsilon, \Delta t) = \hbar^{-1} \sum_n \left| \sum_m c_m \langle \chi_n | \phi_m \rangle \int_{-\infty}^{\infty} dt F_2(t - \Delta t) e^{[i/\hbar(E_n + \epsilon - E_{probe} - E_m)t]} \right|^2 \times \left| \int_{t}^{t'} dt' F_1(t') e^{[i/\hbar(E_m - E_g - E_{pump})t']} \right|^2$$

(4.6)

where $c_m$ is $\langle \phi_m | \chi_g \rangle$ and $\hat{H}_A' \phi_m = E_m | \phi_m \rangle$. $E_{pump}$ represents the energy of the pump pulse and is equal to $\hbar \omega_1$ with a value of 1.58955 eV; likewise for the probe pulse, $E_{probe} = \hbar \omega_2$ and has a value of 3.17911 eV.$^8, 201$

As noted above for the infinitesimally short pulse, the electron kinetic energy ($\epsilon$) is not well-defined because there is no central frequency; however, we define the energy value, $\xi_n$, which is shifted to ensure that the maximum in the signal at long times is at the same energy as that obtained from the calculations that employed pulses with finite width. Thus, $\xi_n$ is defined as

$$\xi_n = (E_g + E_{pump} + E_{probe}) - E_n - E_{shift}$$

(4.7)

where $E_g$ is the energy of the Boltzmann-populated vibrational state of the $X$ potential surface, $E_n$ is the energy of the vibrational state of a given IBr surface, and $E_{shift} = 0.048$ eV. Subtraction of $E_{shift}$ ensures that the value of $\xi$ at long delay times is consistent with experiment. The spectra calculated using the short pulse were discretized into a series of $\Delta t$ cuts and normalized such that the integrated signal of the time slice $\Delta t = 800$ fs is unity.
4.2.3.1 Finite pulse widths

For the examination of the time-resolved photoelectron spectra as calculated using pulses with finite widths, we utilized the following functional form for the laser pulses

\[ F_j(t) = \text{sech}^2 \left( \frac{t}{f \delta_j} \right) \]  \hspace{1cm} (4.8)

where \( \delta_j \) is the FWHM and has a value of either 300 or 900 fs, and \( \cosh\left(\frac{1}{2f}\right) = \sqrt{2} \). The intermediate pulse, \( \delta_j = 300 \) fs, has the same FWHM as that determined in the experiment.

While equation (4.6) follows from the derivation presented in Ref. 201, there is an alternate form that is analytically equivalent to eq. (4.6) but is more computationally efficient. Equation (4.6) can be rewritten by rearranging the summations to give

\[ P(\epsilon, \Delta t) = \hbar^{-4} \sum_n \left| \int_{-\infty}^{\infty} dtF_2(t - \Delta t)e^{i/\hbar (E_n + \epsilon - E_{\text{probe}})t} \left[ \sum_m c_m \langle \chi_n | \phi_m \rangle e^{-i/\hbar (E_m t)} \times \int_{-\infty}^{t} dt' F_1(t')e^{i/\hbar (E_m - E_g - E_{\text{pump}})t'} \right]^2 \right|. \]  \hspace{1cm} (4.9)

From the form of eq. (4.9), it is can be easily seen how the calculation may be broken up into more efficient segments.

As a way to further understand how pulse width may impact the photoelectron signal, we examine how the wave packet is dressed by the pump pulse and define the quantity \( \Xi_d(R, \Delta t) \):

\[ \Xi_d(R, \Delta t) = \left| \sum_m c_m e^{-i/\hbar (E_m \Delta t)} \phi_m(R) \int_{-\infty}^{\Delta t} dt' F_1(t')e^{i/\hbar (E_m - E_g - E_{\text{pump}})t'} \right|^2. \]  \hspace{1cm} (4.10)

*While we follow the derivation discussed in Ref. 201 for the work presented here, our expression of \( F_j(t) \) and \( f \) differ slightly from those noted in Ref. 201 due to inconsistencies between these definitions in Ref. 201.*
The definition for $\Xi_d(R, \Delta t)$ is the expression for $P(\epsilon, \Delta t)$ when $F_2(t - \Delta t) = \delta(t - \Delta t)$ projected onto $R$. We can obtain a similar quantity by projecting $P(\epsilon, \Delta t)$ on to $m$ instead:

$$
\Xi_e(m, \Delta t) = \left| c_m e^{-i\hbar(E_m\Delta t)} \int_{-\infty}^{\Delta t} dt' F_1(t') e^{i\hbar(E_m - E_g - E_{\text{pump}})t'} \right|^2.
$$

(4.11)

The corresponding quantity of $\Xi_e(m, \Delta t)$ for the wave packet prepared by the infinitesimally short pulse is straightforward to obtain as this quantity is independent of time and is simply $c_m^2$ from eq. (4.2).

4.2.3.2 Numerical details

For the study presented here, the time-resolved photoelectron signal of IBr$^-$ was calculated over a range of electron kinetic energies from 0.00 to 0.31 eV in increments of 0.01 eV and over a range of pump-probe delay times from 0 to 1350 fs in increments of 10 fs. The time step for the numerical integration is 1.0 fs for the long pulse ($\delta_j = 900$ fs) and 0.2 fs for the intermediate pulse ($\delta_j = 300$ fs). The integral over $t$ is defined for $-14 000 \leq t \leq 14 000$ fs and for $-5 000 \leq t \leq 5 000$ fs, respectively. These time steps and $t$ ranges were chosen such that all of the oscillations were captured within the envelope of $F_j(t)$ and when the value of $F_j(t)$ became vanishingly small.

The spectra calculated with the finite pulse widths were normalized in two ways. First, the spectra were normalized such that the integrated signal for only a single time slice, $\Delta t = 800$ fs, is unity. Second, to aid in comparison with experiment, the spectra were discretized into a series of slices in $\Delta t$, convoluted with a Gaussian with a HWHM of 15 meV, and normalized such that the integrated area of each time slice
is unity. The spectra were convoluted to account for several sources of broadening in
the experiment that were not included in the calculations. Most notable of these are
the effects of velocity spread in the molecular beam, the fact that the laser pulses are
not Fourier-transform limited, and the energy resolution of the detector.190,202–205

4.3 Results and discussion

4.3.1 Potential energy surfaces of IBr− and IBr

The potential energy surfaces utilized here are presented in Figure 4.3. Of main
interest to the dynamics are the X and A′ states of IBr− and the C and A states of
IBr, as shown by the bold, black curves in Figure 4.3. However, before discussing
how the potential surfaces relate to the dynamics, we present the results from the
electronic structure calculations and compare properties derived from these surfaces
to those obtained from studies by Thompson et al.188 and Sheps et al.62 In the work
by Thompson et al.,188 they perform similar calculations as those presented here,
using the MR-SO-CISD level of theory. However, Thompson et al. utilized large core
potentials (a 46 e− core for iodine and a 28 e− core for bromine)206,207 compared to the
small cores used in the present study.197,198 The use of the large core necessitated the
inclusion of a core polarization potential (CPP) in their calculations. In addition, their
basis sets are nominally aug-cc-pVTZ in size,206,207 whereas we use aug-cc-pVDZ basis
sets. Finally, Thompson et al. also used the MOLPRO package of ab initio programs
by Werner and Knowles,208 whereas the potentials reported here were obtained using
the COLUMBUS electronic structure programs.191–194
4.3.1.1 Calculations of IBr⁻ electronic states

The electronic properties of IBr⁻ derived from the electronic structure calculations are given in Table 4.7. The equilibrium bond distances ($R_e$) and dissociation energies ($D_e$) were obtained from a cubic spline interpolation of the ab initio data presented above. The data were evaluated at the same values of $R$ that were in the DVR calculations. In Table 4.7 we can see that all six electronic states are bound, with the ground state of IBr⁻ being the most strongly bound by 0.86 eV. Incidentally the well depth of the $X$ state is under-bound by $\sim 0.1$ eV as compared to the most recent experimental and theoretical work, $D_0 = 0.966$ eV and $D_e \sim 0.96$ eV, respectively.$^{62,188}$ The calculated equilibrium IBr bond length for the $X$ state is 3.11 Å. This value is in reasonable agreement with the values determined by Thompson et al.$^{188}$ where they report values of 3.06 and 3.05 Å for the experimental and calculated bond lengths, respectively. However, the $R_e$ value calculated here is longer than the 3.01 Å value measured by Sheps et al.$^{62}$ We believe that differences between our calculated values and those reported by Thompson et al.$^{188}$ and Sheps et al.$^{62}$ are the result of our use of double-ζ rather than triple-ζ basis sets. Unfortunately triple-ζ basis sets corresponding to the RECPs for I and Br used here are not readily available.$^{209}$

Despite the discrepancies at small values of $R$, the energies of the electronic states relative to one another are quite good. The measured spin-orbit splitting of iodine is 0.94267 eV,$^{210}$ and our calculated value is 0.93303 eV. Likewise for bromine, the measured spin-orbit splitting is 0.45691 eV$^{210}$ with a calculated value of 0.46726 eV. In addition to the spin-orbit splittings, the calculated energy difference between $X$
Table 4.7: Calculated and derived parameters from the electronic structure calculations of the six IBr\(^-\) electronic states in order of increasing energy, where \(R_e\) is the equilibrium bond length, and \(D_e\) the dissociation energy. Relevant electronic properties, such as spin-orbit (SO) splittings and differences in electron affinities (\(\Delta\text{EA}\)) are also given.

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<th>(D_e) (eV)</th>
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</tr>
<tr>
<td>(a') 2(\Pi) (_{1/2})</td>
<td>4.8986</td>
<td>0.02660</td>
</tr>
<tr>
<td>(B) 2(\Sigma^+) (_{1/2})</td>
<td>4.9452</td>
<td>0.04044</td>
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</tbody>
</table>

SO splitting of I: 0.93303 eV.
SO splitting of Br: 0.46726 eV.
\(\Delta\text{EA}\) of I and Br: 0.33579 eV.

\(^a\) The data are obtained from a cubic spline interpolation of the \textit{ab initio} points.
and $A'$ dissociation limits, which is the difference in electron affinities between I and Br, is in good agreement with the previous theoretical work reported by Thompson et al.\textsuperscript{188} We obtain a value of 0.33579 eV as compared to 0.3156 eV from Thompson et al.\textsuperscript{188} and to the experimental value of 0.30455 eV.\textsuperscript{200} The good agreement between the calculated and accepted values of the spin-orbit splittings demonstrates that the spin-orbit parameters of the core potentials utilized here are good; however, the larger error in the calculated difference in electron affinities of I and Br could again be due to the use of double-$\zeta$ basis sets.

While the differences mentioned above may seem concerning, we are more interested in the qualitative shapes of the potential energy surfaces and the relative energies of the $X$ and $A'$ states, as these are the most relevant to the dynamics. Generally speaking, we have good agreement with previous calculations and with experiment. Also, we do not expect the aforementioned differences to have a significant effect on the dissociation dynamics because the wave packet is accessing mostly continuum states upon excitation for which the characteristics of the potential, such as $D_e$ and $R_e$, have little impact; however, as the parameters of the $X$ state will affect the dynamics upon initial excitation by the pump laser, we address our treatment of the $X$ state discrepancies next.

4.3.1.2 Use of potential surfaces in dynamics study

As mentioned above, the $X$ state of IBr$^-$ is under-bound by $\sim 0.1$ eV and has a calculated $R_e$ that is larger than experiment by $\sim 0.06$ Å.\textsuperscript{188} To account for these differences in our calculations, we have reduced the pump frequency by 0.102 eV
($E_{pump} = 1.48755 \text{ eV}$) and shifted the $X$ state potential minimum by 0.0474 Å such that it is more consistent with the experimental values reported by Thompson et al.\textsuperscript{188} We opted to decrease the excitation energy of the pump pulse rather than scaling the potentials because this scaling could have unforeseen effects on the five other calculated states. We also shifted the $A'$ state potential minimum by 0.2815 Å such that $E_{X,v=0} + E_{pump} \approx E_{A'}$ at $R_e$ for the $X$ state (3.0637 Å). While the shift of the $A'$ state may seem large, the magnitude of the shift is similar to that used by Sanov and co-workers.\textsuperscript{8} To check the effect of these changes to the potential surfaces on the results reported below, we have also calculated the time-resolved photoelectron spectra of IBr$^-$ using data derived from the unshifted potentials for the long pulse (900 fs) and find that the qualitative picture does not change from the results presented here. The spectra calculated using the unshifted data can be found in Figure 4.4.

Upon examination of the neutral surfaces presented in Figure 4.3, there are many states that dissociate to I + Br. Electronic states that correlate to I + Br represent the pertinent states that are energetically accessible upon photodetachment from the $A'$ state in the experiment. In our study, we only focus on the $C$ and $A$ states because the experimental fit parameters for the $Y$ state are “preliminary,”\textsuperscript{199} and the $X$ state, although dissociating to I + Br, would require a 2 e$^-$ transition, but in the experiment,\textsuperscript{8} only 1 e$^-$ detachment transitions are observed. Lastly, the $B$ neutral excited state will not contribute because it dissociates to I + Br*, which is higher in energy than is accessible at the probe photon energy.\textsuperscript{8}
Figure 4.4: Calculated time-resolved photoelectron spectra of IBr\(^-\) using data derived from the unshifted potentials. The calculated time-resolved photoelectron spectra of IBr\(^-\) using data derived from the shifted potentials is shown for comparison. Both calculations use pulses that have FWHM of 900 fs. Unshifted: (a) C state and (c) A state dynamics. Shifted: (b) C state and (d) A state dynamics. The color indicates signal strength: red (weakest signal) to blue (strongest signal).
The potential energy surfaces considered herein were also used to examine the ranges of possible electron kinetic energies that could be accessible by the probe laser pulse upon detachment. Based on the differences in the electronic energies of the \( A' \) and neutral surfaces, we utilize an energy quantity that is a function of the internuclear distance, \( \Delta E(R) \), and we use a spline interpolation to obtain the value of \( \Delta E(R) \) at all points on the DVR grid. Here \( \Delta E(R) \) is defined as

\[
\Delta E(R) = E_{\text{probe}} - [V_C(R) - V_{A'}(R)]
\]  

where \( V_i(R) \) is the potential energy surface described above for either the \( A' \) or \( C \) state, and a similar expression is obtained for the \( A \) state.

### 4.3.2 IBr\(^-\) time-resolved photoelectron spectra

In the experimental spectra obtained by Sanov and co-workers,\(^8\) shown as both a waterfall plot in Figure 4.2 and as a contour plot in Figure 4.5(a), several interesting features are present. In focusing on the first 150 fs of Figure 4.2, we see that the photoelectron spectrum for the first three time slices is rather broad in energy with no clear maximum in the signal. Generally speaking, the strongest feature of this broad distribution is between \( \sim 0.07 \) and \( 0.22 \) eV. Over the next 350 to 400 fs, there is a shift in the peak maxima and a distinct narrowing of the spectra. Furthermore there appears to be two distinct peaks in the experimental spectra with time rather than one continuous progression. For delay times between 250 and 500 fs, the spectra have maxima near 0.08 and 0.09 eV. After this the spectra have maxima at 0.12 eV, and the electron kinetic energy (eKE) value at these maxima does not change much.
past 800 fs. While these observations are more clearly shown by Figure 4.2, they are also evident in Figure 4.5(a), which will be the focus of the remainder of the discussion.

As a way to interpret the experimental signal, Sanov and co-workers\textsuperscript{8} used a classical model akin to the reflection principle\textsuperscript{211} in which they obtained a one-to-one correlation between time and internuclear distance. To do so, they obtained potential energy surfaces similar to the ones presented here\textsuperscript{188,199} and calculated three classical trajectories at different initial IBr distances. By superimposing $\Delta E(\Delta t)$ on top their spectra, they were able to correlate the time evolution of the spectra to features of the underlying potentials. However, it is unclear how well the classical picture survives when the spectra are evaluated using a completely quantum mechanical treatment, since a number of factors that are part of the reported signal are not included in the classical model, such as detachment cross-sections, pulse width, and other quantum effects.

The results of our time-dependent calculations are shown in Figure 4.5 where we give the time-resolved photoelectron spectra of IBr$^-$ for the $C$ and $A$ state dynamics in Figure 4.5(b) and (c), respectively. Waterfall plots of this data, similar to that presented in Figure 4.2, are shown in Figure 4.6 for comparison. Upon examination of Figure 4.5(b)-(c), many of the spectral features characteristic of the experimental spectra in Figure 4.5(a) are also present in the calculated spectra. For example, in Figure 4.5(b) there is a shift in the photoelectron signal with time. The calculated spectra also have the bimodal distribution observed in the experimental spectra with
Figure 4.5: Experimental and calculated time-resolved photoelectron spectra of IBr$^-$. (a) Experimental signal reproduced from Ref. 8 with permission. TRPES calculated using the FHWM = 300 fs pulse for (b) $C$ state and (c) $A$ dynamics. The color indicates signal strength: red (weakest signal) to blue (strongest signal).
one peak between electron kinetic energies of 0.05 and 0.10 eV for delay times between 50 and 250 fs. The second peak is between 0.10 and 0.15 eV for \( \Delta t > 500 \) fs. The shift in the photoelectron signal with time is also present in the \( A \) state dynamics, but it is much less pronounced. Overall the agreement between calculation and experiment is very good, and we obtain this level of agreement without introducing any adjustable parameters. There are small quantitative differences between the calculated and experimental spectra, which could be due to the fact that the \( C \) and \( A \) state dynamics are calculated separately whereas the experiment samples both surfaces considered here as well as possibly others, such as the \( Y \) state. In the absence of detachment cross-sections, we were not able to fully model the spectra; however, the fact that the calculated spectra for the \( C \) and \( A \) states each exhibit many of the features in the experimental spectra gives us confidence as we move to addressing the origin of these features.

4.3.3 Photodissociation dynamics of IBr$^-$

As we begin our discussion of the origins of the spectral features observed in the experiment, we revisit the classical model discussed above and investigate how we would expect the spectra to look if we assume that the signal is a convolution of the energy differences between the \( A' \) potential of IBr$^-$ and IBr neutral \( A \) and \( C \) state surfaces across the evolving wave packet (\( \Delta E(R) \) from eq. (4.12)). Figure 4.7(a) shows the value of eKE when the photoelectron signal is at a maximum for each measured (blue circles) and calculated \( C \) state (black curve) and \( A \) state (red curve) time slice. For Figure 4.7(a), the first point that is plotted for the experimental
Figure 4.6: Representations of the calculated signal for the time-resolved photoelectron spectra of IBr$^-$ for different pump-probe delay time slices: (a) $C$ state dynamics and (b) $A$ state dynamics (pulse FWHM = 300 fs).
results is for 200 fs. While the data were recorded for earlier times, there are low signal-to-noise ratios in the experiment,\textsuperscript{190,212} as evidenced most strongly by the plots in Figure 4.2, making identification of the maximum in the signal difficult to quantify.

In Figure 4.7(a), we can more clearly see the shift in the maximum of the eKE distribution with time as compared to Figure 4.5. In Figure 4.7(b) we show the time-dependent average of $\Delta E(R)$, $\langle \Delta E(\Delta t) \rangle$, where the average is over $|\psi(R,\Delta t)|^2$ as defined in eq. (4.2). The error bars in Figure 4.7(b) provide the width of the distribution. An important feature of Figure 4.7(b) is that at long delay times, $\Delta t > 500$ fs, $\langle \Delta E(\Delta t) \rangle$ for the $C$ and $A$ states are nearly identical. This delay time roughly corresponds to an IBr distance of $\sim 8 \text{ Å}$, indicating the asymptotic region of the potential where the $C$ and $A$ states are isoenergetic. This is also the approximate time after which the calculated and experimental maxima in eKE are the same in Figure 4.7(a). A second important feature of Figure 4.7(b) is the range of $\Delta E(R)$ sampled by the wave packet over time, and for delay times up to 300 fs, the range of $\langle \Delta E(\Delta t) \rangle$ is inconsistent with the experimental signal in Figure 4.7(a). Specifically, due to conservation of energy from the pulse frequencies, energies above $\sim 0.12$ eV are not accessible. However, all energies below $\sim 0.12$ eV should be energetically accessible by the pump and probe lasers used in the experiment. Comparisons of the energies of the maxima in the experimental and calculated peaks in Figure 4.7(a) to $\langle \Delta E(\Delta t) \rangle$ in Figure 4.7(b) show a large deviation for times smaller than $\approx 300$ fs. This difference leads us to conclude that some of the short time features of the spectra involve processes that are not accounted for by the classical model.
Figure 4.7: Illustration of estimated electron kinetic energy available to the system and that obtained from solving eq. (4.6) with a pulse width of 300 fs and from the experiment: (a) value of the electron kinetic energy (eKE) that corresponds to the maximum in signal for a given $\Delta t$ time slice, and (b) value of the average $\Delta E(\Delta t)$ (defined as $\Delta E(R)$ over $|\psi(R, \Delta t)|^2$ from eqs. (4.12) and (4.2), respectively) with error bars providing the width of the distribution. In (a) and (b) the black curves correspond to $C$ state dynamics; red, $A$ state dynamics; and the blue, open points correspond to the experimental data. Note that in (b) only every fifth point is shown for clarity.
Before looking for this, we examine what one would have to do from an experimental standpoint to obtain spectra that follow the curves plotted in Figure 4.7(a). Such a picture implies instantaneous excitation and does not include pulse information; this would be akin to using an infinitesimally short pulse in the experiment. The results of such a treatment are presented in Figure 4.8(a) and (d), and we also overlay the curves from Figure 4.7(b) for comparison. Note that the data presented in Figure 4.8 are truncated to $\Delta t = 800$ fs. This is because the spectra change very little past $\Delta t = 800$ fs. In comparing the spectra calculated with the infinitesimally short pulse to the experimental signal in Figure 4.5(a), probably the largest difference is the full width half maximum of the spectra at $\Delta t = 800$ fs. The increased width along the energy axis reflects the fact that no energy window has been imposed on the system, so a much broader range of $\xi$ will be accessible, where $\xi$ are the energies sampled upon detachment as shown in eq. (4.7).

In Figure 4.8(a) and (d), the signal is strongest for $\xi > 0.12$ eV at $\Delta t > 200$ fs. In panel (d) the strength of the signal for $\Delta t > 200$ fs is off the scale of the plot and extends to $\xi \sim 0.7$ eV, and the patterns in the signal in this energy region reflect the large overlap of the wave packet with the bound vibrational states of the $A$ potential surface. Plots similar to Figure 4.8(a) and (d) with a larger range in $\xi$ are given in Figure 4.9. Both of these observations reflect the range sampled by $\langle \Delta E(\Delta t) \rangle$ and will not contribute when the pulses are included. Again since the calculated spectra in Figure 4.8(a) and (d) do not look like the experimental spectra shown in Figure 4.5(a), the source of the underlying shape of the experimental signal at short times
Figure 4.8: Calculated time-resolved photoelectron spectra of IBr$^-$ for the (a)-(c) C state and (d)-(f) A state dynamics in the three pulse width regimes: (a) and (d) infinitesimally short pulse; (b) and (e) intermediate pulse with a FWHM of 300 fs; and (c) and (f) long pulse with a FWHM of 900 fs. The average $\Delta E(R)$ curves from Figure 4.7(b) are overlaid on the spectra in panels (a) and (d). The data presented in (b) and (e) are the same as that shown in Figure 4.5(a)-(b) but for a different normalization scheme, as discussed in the text. The color indicates signal strength: red (weakest signal) to blue (strongest signal).
requires knowledge of more than the energy differences between the $A'$ state of IBr$^{-}$ and $C$ or $A$ states of IBr.

Since we know that by utilizing a pulse width that is the same as experiment, we can obtain very good agreement with the experimental spectra, we then pose the question of how does pulse width impact the visualization of the dynamics through the spectra? To address this, we take the next step by calculating the time-resolved photoelectron spectra using a pulse that has a duration three times longer than experiment. Figure 4.8(c) and (f) shows the spectra calculated using a pulse with a FWHM of 900 fs. In similarity with Figure 4.8(b) and (e), which are the same as the data presented in Figure 4.5(b) and (c) but with a different normalization scheme and no convolution as mentioned above, Figure 4.8(c) and (f) also exhibits a bimodal distribution in the photoelectron spectra with time. However instead of remaining stationary for the first 200 fs before shifting to higher eKE, the peak between 0.05 and 0.10 eV persists for nearly 500 fs, although the strength of the signal in this region is substantially weaker than in Figure 4.8(b) and (e). In addition, the spectra in Figure 4.8(b), (c), (e), and (f) have very similar signals at long delay times, $\Delta t > 500$ fs.

To understand how and why the spectral features change with pulse width, we turn to an analysis of the wave packet that has been prepared by the pump pulse as described by eqs. (4.10) and (4.11) for $v = 0$. In Figure 4.10(b) and (c) we plot $\Xi_d(R, \Delta t)$ from eq. (4.10), and in panel (a) we show $|\psi(R, \Delta t)|^2$ evaluated using eq. (4.2) for comparison. The most notable difference between the three pulse widths (short, intermediate, and long) is how the width of $\Xi_d(R, \Delta t)$ changes with time. In
Figure 4.9: Photoelectron spectra of IBr\(^{-}\) as calculated using an infinitesimally short temporal pulse: (a) \(C\) state dynamics and (b) \(A\) state dynamics. The color indicates signal strength: red (weakest signal) to blue (strongest).
Figure 4.10(a) $|\psi(R, \Delta t)|^2$, which has no pulse information included, is symmetric and its amplitude broadens with time. For $\Xi_d(R, \Delta t)$ in panels (b) and (c) at $\Delta t = 0$ fs, $\Xi_d(R, \Delta t)$ is bimodal with a sharp rise at small values of $R$ and a slowly decaying tail as compared to $|\psi(R, \Delta t)|^2$. More specifically, as apparent by the insets in Figure 4.10(b) and (c), $\Xi_d(R, \Delta t)$ is bimodal for at least the first 100 fs, if not longer.

If one estimates the $R$ values that correlate to the centers of the two peaks at $\Delta t = 0$ fs for either the intermediate or long pulse, the maxima of the two peaks are located at $\sim 3.063$ Å ($R_e$ for the $X$ state) and at a slightly longer $R$ value, $\sim 3.193$ Å, respectively. As time increases, the bimodal character of $\Xi_d(R, \Delta t)$ is lost for the intermediate pulse after $\sim 300$ fs; however, this bimodality persists for the longer pulse, so amplitude continues to build up at small $R$ over the entire time range of interest. The times over which there is significant amplitude at small values of $R$ are the same as the times over which the low electron kinetic energy peak is seen in the spectra. Specifically, the low energy peak centered between 0.05 and 0.10 eV is seen for times less than $\approx 200$ fs for the 300 fs pulse and persists beyond 800 fs for the 900 fs pulse. Lastly the two sets of calculated spectra in Figure 4.8(b), (c), (e), and (f) look similar in the long time region, $\Delta t > 500$ fs, because the wave packet has reached the dissociation region of the potential, where eKE is constant, and has larger overlap with the continuum neutral eigenstates that are less affected by the characteristics of the potential surface. Both of these observations of the spectra calculated using finite pulse widths are consistent with the sharpening of the photoelectron spectra with time as shown in Figure 4.2.
Figure 4.10: Wave packet as dressed by the pump pulse as a function of the IBr distance. In (a) $|\psi(R, \Delta t)|^2$ for the infinitesimally short pulse from eq. (4.2). In (b) and (c) $\Xi_d(R, \Delta t)$ from eq. (4.10) for the finite pulse widths: (b) FWHM = 300 fs, and (c) FWHM = 900 fs. The main panels show the first 800 fs in increments of 100 fs, and the insets in each panel show the first 100 fs in increments of 20 fs. The colors show the progression of time, from red (shortest delay times) to blue (longest delay times). (d) $\Xi_e(m, \Delta t)$ from eq. (4.11) where the black curve ($c^2_m$ from eq. (4.2)) is for the infinitesimally short pulse, and the two red curves (solid and dashed) are for the 300 fs and 900 fs finite pulses, respectively, at $\Delta t = 0$ fs.
The correlation between the bimodal character of the spectra and the bimodal character of the dressed wave packets, plotted as functions of $R$, can be better illustrated by examining the range of $A'$ vibrational eigenstates accessed by the pump pulse, which is shown in Figure 4.10(d). The black curve in Figure 4.10(d) shows the broad distribution of contributing eigenstates when the infinitesimally short pulse is used ($c_m^2$ from eq. (4.2)). In the case of the finite pulse widths (red curves), we plot $\Xi_e(m, \Delta t)$ from eq. (4.11) where $m$ is the $A'$ vibrational state quantum number and is directly proportional to energy. Not surprisingly, the number of energetically accessible vibrational states decreases and the distribution narrows dramatically as pulse width increases. These different ranges of energetically accessible $A'$ vibrational states overlap with very different ranges of neutral eigenstates upon detachment, and this is manifested in the spectra, especially for short delay times.

In light of the results presented here, we conclude by commenting on the analysis of the time-resolved photoelectron spectra of IBr$^-$ using the classical model mentioned above. In general the observed signal increase in electron kinetic energy with time is dominated by the energy difference between the $A'$ state of IBr$^-$ and the $C$ or $A$ states of IBr, for times longer than $\approx 300$ fs. However, we do observe quantum effects that occur for shorter delay times. The quantum effects arise from the fact that the wave packet is prepared in a very specific manner by the pump pulse and leads to excitation of a small fraction of the states that have non-vanishing $c_m^2$ values. This leads to the bimodal character of the dressed wave packet when it is plotted as a function of $R$. This bimodality can persist for up to 800 fs for the long pulse and
leads to the two peaks seen in the experimental spectra. Once the calculated spectra are convoluted by a Gaussian to account for the experimental resolution, the two peaks become difficult to distinguish and appear as a shift in the signal for a single peak, as is seen in Figure 4.5.

4.4 Conclusions

In this study we have investigated the sources of the spectral shift in the TRPES of IBr\(^{-}\) that was reported by Sanov and co-workers\(^8\) by treating the system in a fully quantum mechanical manner. We have examined the effects of temporal pulse width on the photoelectron signal, particularly the effects of finite pulse width, using a width that is the same as in the experiment and one three times longer. In the limit of the infinitesimally short pulse, there are no constraints on the excitation energy, yielding a very broad distribution in the photoelectron spectra. For the other pulses, many of the features found in the spectra calculated with the short pulse disappear, and in particular, there is a shift in the signal of the photoelectron spectra from 0.05 to 0.15 eV over a time interval from 250 to 650 fs. This observation is derived from how the pulses prepare the time-evolving wave packet and to the features of the potential surfaces at various internuclear distances. We find that while there are some effects that can be rationalized by pulse width, especially for short delay times (\(\Delta t < 300\) fs), these effects are subtle, and the majority of the structure in the spectra reflects the difference in potential energies between the anion and neutral surfaces as described by the classical model that was proposed by Mabbs et al. Overall the calculated spectra...
are in very good agreement with experiment and give insights into the mechanism for the spectral structure.
CHAPTER 5

Solvent-mediated electron leapfrogging: Charge transfer in IBr$^-$\(\text{(CO}_2\text{)}\) photodissociation

5.1 Introduction

Chemical transformations involve the coupling of electronic and nuclear motions as reactants evolve into products, and a central goal of chemical physics is to obtain a molecular-level picture of the underlying fundamental rules that govern reaction dynamics. Such a detailed understanding requires knowledge of the potential energy surfaces, and many insights into chemical dynamics have come from experiments that characterized important regions of these surfaces.\textsuperscript{213–216} For example, photoelectron spectroscopy of stable anion precursors\textsuperscript{40,217} has been used to probe unbound regions of neutral potentials that correspond to transition states of unimolecular or bimolecular reactions.\textsuperscript{218,219} Yet, ideally we wish to characterize all areas of the potential along the reaction path, not simply those regions with configurations similar to the anion geometry. This task is best accomplished through time-domain experiments\textsuperscript{215,220} that use ultrafast laser pulses and allow for real-time dynamical studies, studies that could potentially involve multiple electronic states.\textsuperscript{221,222} One such technique, widely used to probe non-equilibrium dynamics, is time-resolved photoelectron spectroscopy
(TRPES), where a pump laser pulse prepares a non-equilibrium ensemble of reactants in an excited state and a time-delayed photodetachment (photoionization) probe pulse follows their evolution to products.\textsuperscript{223}

We also wish to understand how a molecule interacts with its environment in the condensed phase where the majority of chemical reactions take place. Thus, we want to know how solvent forces affect the nuclear motions and the flow of energy and charge in a reaction. However, the presence of a solvent adds enormous complexity to otherwise “simple” reaction dynamics, and this complexity makes real-time studies of chemistry in liquids especially challenging. Electron photodetachment from partially solvated ions offers a unique approach to investigate the transition from isolated to solvated reacting systems.\textsuperscript{223, 224} These gas-phase cluster ions can be size-selected by time-of-flight methods, which in turn provides access to well defined molecular environments,\textsuperscript{224} from one solvent molecule to multiple solvent shells. Several benchmark studies of cluster ions have begun to address the fundamental questions outlined above, such as solvent effects on caging dynamics,\textsuperscript{189, 225} vibrational energy transfer,\textsuperscript{226} and charge delocalization.\textsuperscript{183, 227, 228} Recent studies of the partially hydrated NO\textsuperscript{+} cation, NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n}, demonstrate that the configuration of the solvent can have a profound impact on the reactivity of small clusters with as few as two to four solvent molecules.\textsuperscript{16}

Charge transfer is another example of a process that is very sensitive to molecular interactions, as emphasized by Bragg \textit{et al.}, who examined solvent effects in atomic electron transfer reactions in liquids.\textsuperscript{229} Yet, photodissociation studies of IBr\textsuperscript{−}(CO\textsubscript{2})\textsubscript{n}
cluster anions show that solvent-driven electron transfer between atomic fragments can occur well before the completion of the first solvation shell.\textsuperscript{188} In the work presented in this chapter, we further reduce the problem by considering charge transfer that is mediated by a single solvent molecule. Sheps et al. report\textsuperscript{9} a TRPES study of the photodissociation of IBr$^-$\textsubscript{(CO$_2$)} excited to the $A'$ electronic state, which extends recent work on the breaking of isolated dihalide chemical bonds.\textsuperscript{8, 230} In these experiments, they directly probe the evolving electronic structure of IBr$^-$\textsubscript{(CO$_2$)} and find that the single CO$_2$ solvent molecule enables electron transfer from I$^-$ to Br approximately 350 fs after electronic excitation, corresponding to an IBr separation near 7 Å.

In this chapter, we characterize the time scale and IBr distance involved in the charge hop observed in the experiment by Sheps et al. clarify the crucial role of the CO$_2$ molecule, and propose a mechanism for the electron transfer. In particular, the experiment and accompanying analysis show that the electron transfer occurs in a configuration reminiscent of a solvent-separated pair and is made possible by charge delocalization from I$^-$ onto CO$_2$, as well as by intramolecular CO$_2$ vibrational excitation.

5.2 Experiment

5.2.1 Data collection

The experiments discussed herein were performed by Sheps, Miller, and Lineberger at JILA and the University of Colorado at Boulder and shall be referred to as Sheps et
al. The experiment combines a pulsed source of IBr\(^{-}\)(CO\(_2\)) cluster anions, a velocity-map imaging photoelectron spectrometer, and a 100-fs laser system for pump-probe TRPES. The experimental scheme, along with a qualitative representation of the \(X\) and \(A'\) potential energy surfaces of IBr\(^{-}\)(CO\(_2\)), are shown in Figure 5.1.\(^9\) The pump laser pulse, \(h\nu_{\text{pump}}\) (790 nm), initiates the dissociation of IBr\(^{-}\)(CO\(_2\)) on the \(A'\) state. After a delay time, \(\Delta t\), a probe laser pulse with energy \(h\nu_{\text{probe}}\) (313 nm) acquires the transient photoelectron spectrum. The application of this method to IBr\(^{-}\)(CO\(_2\))\(_n\) has been described elsewhere.\(^9,13,62,202,203,231,232\)

### 5.2.2 Previous results

The dynamics of IBr\(^{-}\)(CO\(_2\)) dissociation process involves the four lowest energy electronic states of IBr\(^{-}\) (labeled \(X\), \(A\), \(A'\), and \(a\)) shown by the solid curves in the right backplane of Figure 5.1. In its ground electronic state IBr\(^{-}\) dissociates adiabatically to I + Br\(^-\). In contrast, the only optically accessible excited state in this energy range, the \(A'\) state, owes its oscillator strength to its partial \(\sigma \rightarrow \sigma^*\) charge transfer character, and correlates to I\(^-\) + Br products. Consistent with the molecular orbital description of these states, bare IBr\(^-\) was shown to promptly dissociate on the \(A'\) state to form exclusively I\(^-\) + Br.\(^8,13\) Yet the presence of just one CO\(_2\) solvent molecule changes the product distribution dramatically.\(^{13}\)

\[
\text{IBr}^-(\text{CO}_2)\ (X) + h\nu_{\text{pump}} \rightarrow \text{IBr}^-(\text{CO}_2)\ (A') \rightarrow \text{I}^- + \text{Br} + \text{CO}_2 \sim 36\% \ [1] \\
\rightarrow \text{I}^- (\text{CO}_2) + \text{Br} \sim 61\% \ [2] \\
\rightarrow \text{I} + \text{Br}^- + \text{CO}_2 \sim 3\% \ [3]
\]
Figure 5.1: Cartoon of the $X\left(2\Sigma_{1/2}^{+}\right)$ and $A'\left(2\Pi_{1/2}\right)$ potential surfaces of IBr$^-$ (CO$_2$). The “CO$_2$ coordinate” indicates the location of the CO$_2$ molecule relative to I (purple spheres) or Br (green spheres). The arrows $h\nu_{pump}$ and $h\nu_{probe}$ show the pump and probe laser pulses, respectively. The three dissociation channels are labeled 1 to 3. Solid curves (right) are the four calculated lowest energy ($X$, $A$, $A'$, and $a$) electronic states of IBr$^-$. Dotted curves illustrate the minimum energy paths taken from the two-dimensional $X$ and $A'$ surfaces of IBr$^-$(CO$_2$). Reproduced from Ref. 9.
These three possible reaction channels are depicted by the arrows labeled 1, 2, and 3 in Figure 5.1.

5.2.3 Time-resolved spectra

The transient photoelectron spectra of dissociating IBr−(CO₂) following excitation to the A’ state obtained by Sheps et al. are shown in Figure 5.2. The photoelectron intensity is plotted versus the electron binding energy, eBE, defined as the difference between the probe photon energy and the electron kinetic energy. Background photoelectron signals have been removed, and these transient spectra reflect the time evolution of the dissociating ensemble created by the pump laser pulse. The transient spectrum gains intensity at very early pump-probe delays and shifts to higher eBE up to ∆t ≈ 300 fs. Within the next 200 fs, the spectrum splits into three components that continue to shift for another 500 fs, although the integrated transient intensity stays constant. After ∆t ≈ 1 ps the transient signal is invariant out to ∆t ≈ 50 ps, the longest delay time surveyed by Sheps et al. The asymptotic product distribution, shown in the top panel of Figure 5.2, is consistent with earlier photofragmentation studies by Lineberger and co-workers.

The transient spectra at ∆t ≥ 300 fs were fit to a sum of three Gaussian functions, and their center eBE values (shown as filled white circles in Figure 5.2) reflect the identity of the evolving dissociation products. The photoelectron peak at the lowest energy (3.06 eV) arises from the I− product (channel [1]), and the peak at highest
Figure 5.2: Time-resolved transient photoelectron spectra of the photodissociation of IBr$^-$($\text{CO}_2$) as a function of pump-probe delay. The false color scale indicates the photoelectron intensity. The filled white circles show the centers of spectral fit components. The right vertical scale shows the approximate IBr separation at each delay time, assuming evolution in exit channel [2], I$^-$($\text{CO}_2$) + Br. Top panel: Transient photoelectron spectrum at $\Delta t = 50$ ps and spectral fit (dashed line). I$^-$, “cold” I$^-$($\text{CO}_2$), and Br$^-$ are photoproduct reference eBE values. Spectra were recorded by Sheps et al. and are reproduced from Ref. 9.
energy (3.36 eV) is attributed to Br$^-$ (channel [3]). The broad feature at eBE $\approx$ 3.2 eV corresponds to reaction channel [2], I$^-$ (CO$_2$) products, but is redshifted by about 0.05 eV from the value measured for cold I$^-$ (CO$_2$). The width and redshift of this feature provide direct evidence that the I$^-$ (CO$_2$) photodissociation products have a broad distribution of vibrational excitation, averaging 0.05 eV, about 25% of the I$^-$ (CO$_2$) well depth.

The time evolution of the photoelectron signal is also presented in the two top panels of Figure 5.11. Panel (b) contains a plot of the total integrated spectral intensity as a function of $\Delta t$, which shows that the transient population of excited IBr$^-$ (CO$_2$) appears much faster than the experimental resolution (300 fs). After the initial rise, the constant transient signal confirms that the entire excited population is monitored en route to product formation. The transient photoelectron signal slice at eBE = 3.36 eV is plotted in Figure 5.11(a) along with a fit to an instrument-limited rise centered at $\Delta t = 350$ fs. Because this signal reflects the formation of Br$, Sheps et al. conclude that charge transfer from I$^-$ to Br, i.e. the transition to the X or A potential energy surface, occurs over a 200-fs time window centered at $\Delta t = 350$ fs.

5.3 Theory

To understand the origins of the observed experimental branching into the product channels (see Figure 5.1) and, in particular, to understand the mechanism for the non-adiabatic charge transfer from I$^-$ to Br at $\sim$ 350 fs, we discuss two sets of calculations. The first is a set of nonadiabatic molecular dynamics (MD) simulations where 5000
classical trajectories are run starting from an equilibrated ensemble of IBr\(^-\)(CO\(_2\))
cluster anions at internal energies ranging from 200 to 1400 cm\(^{-1}\). These trajectories
are run in groups of 1000, and the initial conditions reflect five cluster temperatures
ranging from 80 to 250 K. In the second set of calculations, we take the geometries
from several of these trajectories and perform high-level ab initio calculations\(^{10}\) of
the electronic energies of IBr\(^-\)(CO\(_2\)) and dipole moments for IBr\(^-\), I\(^-\)(CO\(_2\)), and
IBr\(^-\)(CO\(_2\)). In order to assess the effect of the CO\(_2\) bending motion, calculations
are performed for OCO bend angles of 175\(^\circ\) as well as the 180\(^\circ\) value used in the
trajectory simulations.

5.3.1 Molecular dynamics simulations

The MD simulations presented here were completed by Thompson\(^{9,207}\) and are
based on the effective Hamiltonian approach developed by Parson and co-workers,\(^{235,236}\)
which has been shown to successfully reproduce the results of a variety of experimen-
tal studies of photodissociation and recombination in solvated dihalide ions.\(^{237}\) The
application of this method to IBr\(^-\)(CO\(_2\))\(_n\) has been described elsewhere,\(^{9,188}\) and we
summarize only the relevant details here.

A set of nonadiabatic MD simulations are calculated in which potential energy
surfaces for the solvent-solute system are generated “on the fly” from an effective
Hamiltonian that takes into account the interaction between the solute charge distri-
bution, which is treated quantum mechanically, and the solvent charge distribution,
which is treated classically. Nonadiabatic transitions among the potential surfaces
are described by a variant of the surface-hopping algorithm developed by Tully and
Hammes-Schiffer.\textsuperscript{238,239} Strictly speaking, the individual trajectories calculated by this algorithm have no objective significance – physical reality resides in the ensemble as a whole. In practice, one commonly finds that the trajectories within the ensemble fall into recognizable patterns, within which it is not difficult to find single trajectories that provide a reasonably accurate qualitative description of the overall behavior. Such details as the exact moment when a nonadiabatic transition occurs in a particular trajectory are arbitrary, but the range of configuration space within which such transitions occur are not – one can find a number of trajectories that behave in a broadly similar way when they enter a region where the calculated nonadiabatic transition probability is large.

In the simulations, which use a rigid CO$_2$ molecule, the calculated energies correspond roughly to IBr$^-(CO_2)$ vibrational temperatures of 80, 120, 160, 200, and 250 K. These five ensembles were obtained by initiating a trajectory on the ground electronic state with the appropriate energy, propagating it for 5 ns, and sampling it at 5 ps intervals. These ensembles were then promoted to the excited $A'$ state, subject to conservation of the internal kinetic energy. To ensure the correct kinetic energy release, the IBr$^-$ bond length was adjusted slightly such that the energy gap between the $X$ and $A'$ electronic states matched the experimental excitation energy ($h\nu_{\text{pump}} = 1.57$ eV (790 nm)). The model accounts for polarization of the solute charge distribution by the solvent but not for charge transfer to the solvent or for solvent intramolecular vibrations.\textsuperscript{9,188,207}
5.3.2 Electronic energies, dipole moments, and frequencies of IBr\(^{-}\) related species

To assess the role that the solvent plays in facilitating the charge transfer from I to Br, we perform additional \textit{ab initio} calculations, using molecular configurations taken from individual MD trajectories. Unless otherwise noted, all of the electronic structure calculations use the MOLPRO package of \textit{ab initio} programs.\textsuperscript{10,240}

5.3.2.1 Electronic structure calculations

The electronic energies and dipole moments for the six lowest energy electronic states of IBr\(^{-}\) and IBr\(^{-}\)(CO\(_2\)) are calculated at the MR-SO-CISD level of theory. The dipole moments are also calculated for the ground electronic states of I\(^{-}\)(CO\(_2\)) and bare CO\(_2\) at the CISD level of theory. We employ an augmented Dunning basis set for C and O, aug-cc-pVTZ, and the related pseudopotential, aug-cc-pVTZ-PP, from Peterson \textit{et al.}\textsuperscript{166,167} for I and Br. With these pseudopotentials, iodine has a 28-electron core, and bromine has a 10-electron core. These pseudopotentials were chosen for their reliability and accuracy. We note that these calculations use two later versions of MOLPRO\textsuperscript{10,240} than the one used to construct the effective Hamiltonian used in the MD simulations.\textsuperscript{208} The overall level of theory (MR-SO-CISD) is the same, but the calculations described here use more recent pseudopotentials that were not available when the codes used to perform the MD simulations were developed. All reported results use version 2008.1 of MOLPRO.\textsuperscript{10}

State-averaged complete active space self-consistent field (CASSCF) calculations were carried out for IBr\(^{-}\) and IBr\(^{-}\)(CO\(_2\)) in the \(C_{2v}\) and \(C_1\) point groups, respectively.
The active space consisted of the six highest occupied molecular orbitals of IBr\(^-\) (\(\sigma, \pi, \pi^*, \sigma^*\)) with 11 valence electrons and is shown in Figure 5.3. All other occupied molecular orbitals were constrained to be doubly occupied. A total of six doublet states were averaged in each case, and the relevant electronic states are shown in Figure 5.4. The orbitals from the CASSCF calculations were used in subsequent internally contracted MRCI calculations of these same six states. Spin-orbit coupling was then included via the state-interacting approach both at the CASSCF and MRCI levels of theory using the spin-orbit parameters of the pseudopotentials. It should be mentioned that the occupied, valence molecular orbitals of CO\(_2\) lie energetically below the occupied, valence molecular orbitals of IBr\(^-\), so the active space and excitation scheme described above are valid for both IBr\(^-\) and IBr\(^-\)(CO\(_2\)).

![IBr\(^-\) MOs](image)

Figure 5.3: Molecular orbital (MO) diagram for the valence MOs of IBr\(^-\).

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Here, we focus on nine of the classical trajectories: eight from the $T = 80$ K ensemble and one from the $T = 120$ K ensemble. These nine trajectories were selected based on characteristics that made them likely to undergo electron transfer. In other words, they have small classical $A' - X$ energy gaps of $< 1000 \text{ cm}^{-1}$ and IBr distances between 6 and 8 Å at propagation times between 200 and 500 fs. This set of criteria characterizes 21% of all trajectories from the $T = 80$ K ensemble and 7% from the $T = 250$ K ensemble. In obtaining these percentages, we consider only the trajectories that remain on the $a$ or $A'$ state until at least 500 fs. The nine trajectories differ from one another quantitatively, but qualitatively they are very similar and display similar dynamics. For this reason, we focus on the results from a single trajectory from the $T = 80$ K ensemble.

### 5.3.2.2 Franck-Condon calculations of CO$_2$ bend excitation

To ascertain the probability of electronic to vibrational energy transfer from the electronic degrees of freedom of IBr$^-$ to the CO$_2$ bending vibration, we calculate Franck-Condon overlaps between the ground vibrational state of CO$_2$ in I$^-(\text{CO}_2)$ and bend states of bare CO$_2$ with up to two quanta of excitation. Based on the analysis of the trajectories, it is anticipated that the charge hop occurs at an IBr distance of $\sim 7$ Å, an IC distance of $\sim 3.5$ Å, and a BrC distance of $\sim 6$ Å. At this I$^- \cdots \text{CO}_2$ distance, previous work suggests that the minimum energy configuration of the CO$_2$ will be bent by $\sim 5^\circ$.\textsuperscript{241} Using this information, along with the CO$_2$ bend frequencies for bare CO$_2$ and CO$_2$ in I$^-(\text{CO}_2)$ calculated at the CI$\text{SD}/\text{aug-cc-pVTZ(-PP)}$ level of theory/basis using Gaussian 03,\textsuperscript{242} we obtain the probabilities for
Figure 5.4: Electronic states of IBr$^-$ where (a) spin-orbit coupling is not included and (b) where spin-orbit coupling is included. Note that in (b), the Hund’s case (a) notation is given, which holds well near the equilibrium value of $R_{\text{IBr}}$; however, in the dissociation region, Hund’s case (c) is more appropriate as $\Omega$ is the only good quantum number.
vibrational excitation of CO\textsubscript{2} reported in Table 5.1. Relevant geometric parameters and harmonic frequencies are also given in Table 5.1.

Table 5.1: Franck-Condon overlaps between the ground CO\textsubscript{2} bend state in I\textsuperscript{−}(CO\textsubscript{2}) with the first three bend states of bare CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>bend state of bare CO\textsubscript{2}\textsuperscript{a}</th>
<th>% overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu = 0)</td>
<td>79%</td>
</tr>
<tr>
<td>(\nu = 1)</td>
<td>18%</td>
</tr>
<tr>
<td>(\nu = 2)</td>
<td>2%</td>
</tr>
<tr>
<td>total % excitation</td>
<td>20%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} CO\textsubscript{2} equilibrium structure: \(r_{\text{CO}} = 1.151\ \text{Å}, \theta_{\text{OCO}} = 180.0^\circ, \omega_e = 718\ \text{cm}^{-1}\). I\textsuperscript{−}(CO\textsubscript{2}) equilibrium structure: \(r_{\text{CO}} = 1.149\ \text{Å}, R_{\text{IC}} = 3.572\ \text{Å}, \theta_{\text{OCO}} = 174.9^\circ, \omega_e = 691\ \text{cm}^{-1}\).

It should be noted that complexation with I\textsuperscript{−} will break the degeneracy of the CO\textsubscript{2} bend. The CO\textsubscript{2} bend now has two (non-degenerate) components, an in-plane and an out-of-plane component; however, only the in-plane motion is considered here because it is more strongly coupled to the I\textsuperscript{−}···CO\textsubscript{2} dissociation coordinate. While it is clear that approximations were introduced in this model, we have varied the bend frequencies over a range of \(\sim 30\ \text{cm}^{-1}\) and find that the numerical values reported in Table 5.1 are insensitive to these changes at the level of accuracy reported here.
5.3.2.3 Dipole moments determination

To investigate how the solvent affects the charge distribution of IBr\(^-\), we calculate the dipole moments of IBr\(^-\), IBr\(^-\)(CO\(_2\)), I\(^-\)(CO\(_2\)), and CO\(_2\), as mentioned above. We have defined the axes, so the iodine and bromine atoms lie along the z-axis, and the carbon atom is in the yz-plane. For these calculations, the atoms are in the same positions in space in the four complexes with iodine at the origin. This orientation was necessary to ensure a proper comparison of the dipole moments among the four species because dipole moments are origin-dependent for charged systems;\(^{243}\) therefore, our dipole moment comparison is only valid when the molecular origin and orientation are the same. The dipole moment components of IBr\(^-\)(CO\(_2\)) and comparison of the dipole moments between IBr\(^-\)(CO\(_2\)), IBr\(^-\), I\(^-\)(CO\(_2\)), and CO\(_2\) are shown in Figure 5.5.

5.3.2.4 OCO angle and minimum IC distance

In the MD trajectories, the CO\(_2\) angle in IBr\(^-\)(CO\(_2\)) is constrained to be linear; however, the CO\(_2\) angle is most probably bent due to delocalization of the excess electron. Moreover, the proposed mechanism is based on electronic to vibrational energy transfer and a bent CO\(_2\) molecule in the proximity of I\(^-\). To further investigate the interdependence of the IC distance and the OCO angle, we calculate electronic energies for a range of IC distances at fixed values of the OCO angle while all other parameters were held constant: 3.0 Å < R\(_{IC}\) < 5.0 Å in increments of 0.1 Å, 170° < \(\theta_{OCO}\) < 180° in increments of 2.5°, and the OO axis was constrained to be perpendicular to the IC axis. The resulting data are given in Figure 5.6.
Figure 5.5: Dipole moment components for (a)–(c) IBr$^-(CO_2)$ and the values of $\Delta \mu$ in the two limits for a single trajectory: (d)–(f) $\Delta \mu$ in the $[IBr^- + CO_2]$ limit and (g)–(i) $\Delta \mu$ in the $[I^- (CO_2) + Br]$ limit. The black, solid and red, dashed lines represent bent (OCO = 175°) and linear CO$_2$ (OCO = 180°), respectively.
Figure 5.6: Minimum value of the OCO angle as a function of the IC distance. The data were fit to a linear function with a $R^2$ value of 0.9952: $\theta_{OCO} = 48.0078^\circ \cdot Å^{-1} \cdot R_IÇ - 3.8332^\circ$. 
5.4 Results and discussion

5.4.1 Impact of electronic states on dissociation dynamics

The initial excitation of IBr\(^-\)(CO\(_2\)) is solely to the \(A'\) state;\(^{188}\) the dynamical simulations indicate that during dissociation the wave packet also occasionally samples the \(a\) state, but only at times when the two surfaces are experimentally indistinguishable. Dissociation on the \(A'\) or \(a\) state results in pathways [1] and [2], and the branching ratio between the two pathways depends on the initial geometry of the complex and vibrational energy redistribution during dissociation. However, the third exit channel must arise from a solvent-driven non-adiabatic transition to one of the lower energy electronic states (\(X\) or \(A\)) that correlates asymptotically to I + Br\(^-\). The simulations reveal that transitions to both of these states indeed take place, albeit at large IBr separations where the \(X\) and \(A\) states are nearly isoenergetic. Recent experiments have shown that the electronic structure of the atomic fragments develops very early in photodissociation of dihalides, within about 200 fs after the excitation.\(^{8,230}\) Thus, the third exit channel physically corresponds to electron transfer between two atomic fragments partway through the dissociation, enabled by a single solvent molecule.

The CO\(_2\) coordinate in Figure 5.1 represents the CO\(_2\) position relative to I or Br. As shown by these plots, solvation of I\(^-\), Br\(^-\), or IBr\(^-\) by one CO\(_2\) molecule lowers the energy by roughly 0.2 eV.\(^{188,233,234}\) This shift is shown schematically by the dotted curves in the right backplane of Figure 5.1. Stabilization of the anions by CO\(_2\) is largely due to the strong attraction between the negative charge and the large quadrupole moment of the solvent. This stabilization is indicated by the well on the
left side of the IBr\textsuperscript{−}(CO\textsubscript{2}) \textit{A′} surface and on the right side of the \textit{X} surface. Upon examination of Figure 5.1, it should be noted that equilibrium solvation by a single CO\textsubscript{2} molecule is insufficient to lower the energy of the \textit{A′} or \textit{a} state below that of the \textit{X} or \textit{A} state.

### 5.4.2 Analysis of MD simulations

In Table 5.2, we summarize the results of the MD simulations based on the number of trajectories that sample reaction channels [2] and [3]. For all but the 80 K ensemble, a small number of the trajectories (between one and nine) exhibit charge transfer from I\textsuperscript{−} to Br, although the numbers remain smaller than are observed in the experiment. The number of trajectories that show three-body dissociation (channel [1]) increases with increasing internal energy, and by 250 K the fraction is 30%.

Analysis of correlations between the initial, \(\tau = 0\) CIBr angle (\(\theta_{\text{CIBr}}\)) distributions and the fraction of the trajectories that follow channel [2] shows that the range of \(\theta_{\text{CIBr}}\) that is sampled increases with increasing internal energy, with the 200 K and 250 K ensembles sampling the full range of CIBr angles from the collinear IBrC (0\(^{\circ}\)) to the collinear CIBr (180\(^{\circ}\)) configurations. The plots in Figure 5.7 show that for the complexes where CO\textsubscript{2} is initially closer to Br (\(\theta_{\text{CIBr}} < 50^{\circ}\)), the dissociating molecules generally form I\textsuperscript{−} + Br + CO\textsubscript{2} products (Figure 5.7(b)), while at larger values of \(\theta_{\text{CIBr}}\), I\textsuperscript{−}(CO\textsubscript{2}) + Br products are also seen. This leads to the temperature-dependent ratio of I\textsuperscript{−} to bound I\textsuperscript{−}(CO\textsubscript{2}) photoproducts reported in Table 5.2. The fraction that dissociate to I\textsuperscript{−} + Br + CO\textsubscript{2} are expected to increase if, rather than using a rigid model for CO\textsubscript{2}, energy had been allowed to transfer to internal vibrations in CO\textsubscript{2}. 

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Table 5.2: Summary of the results of the classical simulations.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>% of trajectories that follow channel [2]</th>
<th>% of trajectories that follow channel [3]</th>
<th>% of the trajectories in which the inner turning point of the IC vibration occurs between 200 and 500 fs</th>
<th>average internal energy of $\Gamma^-(\text{CO}_2)$ as a fraction of its binding energy&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>100%</td>
<td>0</td>
<td>68%</td>
<td>17%</td>
</tr>
<tr>
<td>120</td>
<td>98%</td>
<td>1</td>
<td>52%</td>
<td>25%</td>
</tr>
<tr>
<td>160</td>
<td>93%</td>
<td>9</td>
<td>46%</td>
<td>27%</td>
</tr>
<tr>
<td>200</td>
<td>78%</td>
<td>3</td>
<td>34%</td>
<td>29%</td>
</tr>
<tr>
<td>250</td>
<td>69%</td>
<td>8</td>
<td>28%</td>
<td>33%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Evaluated using the calculated average maximum IC distance (from Figure 5.8) in the expression for the $\Gamma^-(\text{CO}_2)$ potential reported in Ref. 234.
Figure 5.7: (a) The calculated range of CO$_2$ positions from the MD simulations of IBr$^-$(CO$_2$). (b) The dependence of the I$^-$(CO$_2$) product fraction on the initial distribution of CIBr angles. The angles of 0° and 180° correspond to a collinear geometry with the CO$_2$ molecule located near Br or I, respectively. The colored lines correspond to the temperature of the ensembles: 80 K (blue), 120 K (green), 160 K (yellow), 200 K (brown) and 250 K (red). It should be noted that at large values of $\theta_{CIBr}$, variations in the plotted values reflect the statistical uncertainty of small numbers.
We have also analyzed the maximum IC distances that are sampled by the $\text{I}^-(\text{CO}_2)$ complex photoproducts (channel [2]), and the results are reported in Figure 5.8. To connect this value to an estimate of the fraction of the $\text{I}^-\cdots\text{CO}_2$ binding energy that is represented by this amplitude of motion, we use the $\text{I}^-\cdots\text{CO}_2$ potential developed by Neumark and co-workers$^{234}$ and report the average of this value as a fraction of the 212 meV binding energy in Table 5.2. Consistent with the experiment, the average internal energy in the $\text{I}^-(\text{CO}_2)$ complex is approximately 25% for all but the 80 K ensemble, and the distributions have long tails that slowly decay at the higher excitation energies.

In addition to investigating the product state distributions, we probe the time at which the excess electron localizes on the iodine atom. We plot the distribution of times when the charge on the iodine atom exceeds 0.9 e$^-$ for each of the five ensembles of trajectories in Figure 5.9. In these plots, charge localization occurs between 180 and 200 fs, independent of the temperature at which the simulation is run. Such prompt electron localization times are consistent with the results reported for Br$_2$ dissociation.$^{230}$

Finally, as the mechanism we describe for long-range charge transfer hinges on the minimum in the $\text{I}^-\cdots\text{CO}_2$ distance being achieved at times near the 350 fs delay time, we have also reported the fraction of the trajectories that reach the first inner turning point in the IC vibration between 200 and 500 fs (Table 5.2). While this fraction is significant at all temperatures, it clearly decreases with temperature. This is a reflection of the fact that other channels are available at the higher temperatures.
Figure 5.8: The maximum IC distance sampled by trajectories that follow channel [2] and form $\text{I}^- \text{(CO}_2\text{)} + \text{Br}$ photoproducts.
Figure 5.9: Times at which the charge on I exceeds 0.9 e\(^-\) for each of the five ensembles of trajectories.
In addition distributions of the IC distances that correspond to the inner turning point of the first \( \text{I}^- \cdots \text{CO}_2 \) vibration are plotted for the five ensembles and given in Figure 5.10. Here we consider only those trajectories for which the \( \text{I}^- \cdots \text{CO}_2 \) vibration samples the inner turning point of the vibration between 200 and 500 fs. As we increase the temperature, an increasing fraction either directly dissociates or does not sample an inner turning point by this time. This is reflected in the decreasing integrated area of the histograms with increasing temperature. As expected, the range of IC distances increases with increasing internal energy of the complex.

### 5.4.3 Charge hop mechanism

In light of the results presented here, we conclude by discussing the mechanism responsible for electron transfer, in particular how the solvent mediates the electron transfer process. The proposed mechanism relies on the information gleaned from both the aforementioned MD simulations and the high-level \textit{ab initio} calculations. Although the MD simulations do not include the electronic structure or internal vibrations of the \( \text{CO}_2 \), they capture much of the dynamics of the photodissociation of \( \text{IBr}^- \text{(CO}_2) \).

Notably, these trajectories undergo prompt localization of the excess electron on iodine and reproduce the experimental result of significant vibrational excitation of the \( \text{I}^- \text{(CO}_2) \) cluster anion products. We find that at 80 K all of the trajectories form \( \text{I}^- \text{(CO}_2) + \text{Br} \) products (channel [2]), whereas at 250 K, 30% dissociate to form \( \text{I}^- + \text{Br} + \text{CO}_2 \). This value is consistent with \( \sim 36\% \) of the experimental signal being associated with channel [1].\textsuperscript{13} Based on an analysis of the five sets of
Figure 5.10: Distribution of minimum IC distances for the five ensembles. Only trajectories that sample an inner turning point in the IC vibration between 200 and 500 fs are included in this analysis.
1000 trajectories, we find that the fraction of the ensemble that follows channel [1] increases with increasing internal energy of the anion prior to photoexcitation, a result that reflects a strong correlation between the geometry of the complex at the time of photoexcitation and the probability of three-body dissociation. Similarly, at the higher temperatures, a small number of trajectories (< 1%) form Br\(^-\) (channel [3]). The simulations show that channel [1] is a concerted three-body breakup, but channel [3] begins with a prompt departure of the neutral bromine atom, followed by electron transfer from I\(^-\) to Br and subsequent CO\(_2\) dissociation.

Figure 5.11 shows the properties derived from the representative trajectories for pathways [2] and [3]. Three snapshots of cluster geometries, at \(\Delta t = 0\) fs, 350 fs, and 800 fs taken from these trajectories, appear at the top of the figure. A trajectory that undergoes electron transfer is shown on the left-hand side. In panel (c), we plot the IC distance; in panel (e), the \(X-A'\) and \(A-A'\) energy gaps; and in (g), the charge on the iodine atom, based on the charge distribution for the adiabatic electronic state used to describe the classical system. Consistent with earlier studies\(^{230}\), the charge localizes on the iodine atom within the first 200 fs. After roughly 350 fs, the energy gap between the \(A'\) and \(A\) states is smaller than 0.01 eV. This reduction in the energy gap, which coincides with the I\(^-\)···CO\(_2\) vibration reaching its inner turning point, enables a surface hop between the \(A'\) and \(A\) states that results in charge transfer from I\(^-\) to Br after \(\sim 400\) fs. Even though the energy gaps between the electronic states of IBr\(^-\) are too large for electron transfer when the CO\(_2\) is in its minimum energy geometry, motion of the CO\(_2\) molecule reduces these energy gaps and promotes the
charge transfer process. This solvent motion is brought about by charge redistribution upon electronic excitation and is further enhanced by thermal excitation of the cluster anions prior to photoexcitation.

Although there are several trajectories in which the charge hop occurs, the MD simulations significantly underestimate the contribution of channel [3]. This discrepancy is likely due to the fact that neither vibrational excitation of CO$_2$ nor solvent-mediated charge transfer is included in the model. In the right panels of Figure 5.11, we plot the properties for a trajectory that does not undergo a charge hop. Consistent with the results plotted in panel (e), the curves in Figure 5.11(f) show that at the time when the IC distance is minimized, the $X-A'$ and $A-A'$ energy gaps are also minimized. In contrast to panel (e), these energy differences were evaluated using electronic structure theory$^{10}$ for an OCO angle of 175$^\circ$. Similar curves were evaluated for an OCO angle of 180$^\circ$ and yield larger energy gaps than those shown in panel (f).

Although the calculated energy gaps are too large to generate a significant transition probability for a direct hop from the $A'$ state to the $X$ or $A$ state, these gaps would be closed by adding one or two quanta of bend excitation to the CO$_2$ molecule (shown by the horizontal dotted lines in Figure 5.11(e) and (f)). Further evidence for participation of the CO$_2$ bend comes from photoelectron spectroscopy of I$^-$ (CO$_2$),$^{233,244}$ which indicates that in these complexes the equilibrium value of the CO$_2$ bend angle is about 175$^\circ$. The distortion arises from partial delocalization of the excess electron into the lowest unoccupied molecular orbital$^{244}$ of CO$_2$ and is expected to be
Figure 5.11: Panel a: A cut through the time-resolved photoelectron spectrum at eBE = 3.36 eV, reflecting the Br⁻ signal. Panel b: Integrated transient intensity, reflecting the total excited state population. Data in a and b were smoothed with a 3-point filter. Dashed lines in a and b are fits to instrument-limited rises, centered at ∆t = 350 fs and ∆t = 0 fs, respectively. Data in a and b were obtained by Sheps et al.⁹ Panels c–h: Calculated properties from two MD trajectories, one that exhibits electron transfer (left column, channel [3]) and one that does not (right column, channel [2]). Vertical dashed lines mark ∆t = 0 fs, ∆t = 800 fs, and the time at which the charge hop is likely to occur. Panels c and d: Distance between the I and C atoms. Panels e and f: Energy gaps between the initially excited state, A', and the two lower-energy states, A (solid) and X (dashed). In e, the energies are obtained from the MD simulation while in f, the CO₂ molecule is bent and the energies are calculated using electronic structure theory.¹⁰ The horizontal dotted lines indicate the energies of one and two quanta of CO₂ bend excitation. Panels g and h: Amount of excess charge on the I atom. The red dashed line in g indicates a nonadiabatic transition to the A state.
even larger at the inner turning point of the \( \text{I}^- \cdots \text{CO}_2 \) vibration, as shown in Figure 5.10. As the IC distance decreases, the distortion of the OCO angle from linearity increases. Moreover, a large fraction of the trajectories have minimum IC distances < 3.6 Å at the inner turning point of the \( \text{I}^- \cdots \text{CO}_2 \) vibration. Together these results present a consistent picture for the proposed charge hop mechanism. Namely at the inner turning point, IBr\(^-\)(CO\(_2\)) can sample configurations that are favorable for energy transfer. We therefore infer that that the distortion of the OCO angle upon interaction with \( \text{I}^- \) facilitates the charge hop through electronic to vibrational energy transfer.

To further investigate this mechanism, we need to assess the influence of CO\(_2\) intramolecular vibrations and of charge transfer from IBr\(^-\) to CO\(_2\) on the IBr\(^-\) electronic structure. We focus on how the introduction of the CO\(_2\) molecule modifies the charge distribution of IBr\(^-\) by calculating the dipole moments of IBr\(^-\)(CO\(_2\)) as well as the sums of the dipole moments of the [IBr\(^-\) + CO\(_2\)] and [I\(^-\)(CO\(_2\)) + Br] fragments. The differences between IBr\(^-\)(CO\(_2\)) and the two limits (\(\Delta \mu\)) are shown in Figures 5.5 and 5.12. Here the change in the dipole moment component (\(\mu_i\)) is defined as

\[
\Delta \mu_i = \mu_{i,AB} - [\mu_{i,A} + \mu_{i,B}],
\]

where AB represents the full complex, IBr\(^-\)(CO\(_2\)), and A and B represent the constituent fragments.

As evidenced by Figure 5.12, after 200 fs the presence of the CO\(_2\) molecule leads to a shift of the excess charge away from the iodine atom and toward the bromine atom in the complex, compared to the charge distribution in IBr\(^-\). This shift in the charge distribution reflects both charge transfer to the bromine due to the presence
of the CO$_2$ molecule and to charge delocalization between I$^-$ and CO$_2$ in the I$^-$(CO$_2$) complex. The [I$^-$(CO$_2$) + Br] limit serves to separate these two effects as this curve reaches a near-zero value after $\sim$ 500 fs. Based on these results, we conclude that for times between 200 and 500 fs, the charge distribution of IBr$^-$(CO$_2$) is perturbed relative to both asymptotes with greater negative charge on the Br atom. This time range corresponds well to the time at which the I + Br$^-$ + CO$_2$ product channel is observed in the experiment and suggests that at the time of the charge hop the molecular dynamics simulations underestimate the coupling between the adiabatic potential curves.

5.5 Conclusion

Taken together, the results of the calculations lead us to a mechanism for long-range electron transfer between I and Br in the dissociation of IBr$^-$(CO$_2$) on the $A'$ electronic state. When the I$^-$···CO$_2$ vibration reaches its first inner turning point (typically near a time delay of $\sim$ 350 fs), the energy gap between the $A'$ and $X$ or $A$ states is minimized. A small number of trajectories sample regions of the potential where the gap between the $A'$ and $A$ states is $\sim$ 0.01 eV, and a significant fraction of the trajectories have an energy gap that is commensurate with one or two quanta of CO$_2$ bend excitation. At these short IC distances, the CO$_2$ molecule will be bent, and the distorted OCO angle projects favorably onto the bend excited states after the charge transfer. At the same time, the changes in the dipole moment along the IBr axis indicate that the presence of the CO$_2$ molecule shifts the excess charge density
Figure 5.12: Differences between the dipole moment component along the IBr bond axis ($\Delta \mu_z$) for the IBr$^-$ (CO$_2$) complex and either the sum of the dipole moments of IBr$^-$ and CO$_2$ (solid curve and circles) or the sum of the dipole moments of I$^-$ (CO$_2$) and Br (dashed curve and triangles). As indicated by the arrow, a negative value of these quantities indicates more charge transfer to the Br atom, resulting from the introduction of the CO$_2$ molecule with a 175° OCO angle. The calculations were performed for the same MD trajectory that was used to generate the plots in the right panels of Figure 5.11, and the vertical dashed lines are at the same times as those in the right panels of Figure 5.11 to aid in comparison.
toward the bromine atom, thereby providing a mechanism for the increased coupling between the $A'$ and $X$ or $A$ electronic states. The mechanism and timescales are consistent with the observed $\text{Br}^-$ products at $\sim 350$ fs in the TRPES experiment. It is likely that the intimate, essential involvement of solvent internal degrees of freedom, elucidated in this simple example of long-range electron transfer, will be a significant component in other electron transfer processes taking place through solvent bridges.
CHAPTER 6

Femtosecond dynamics of Cu\(^-\)(CD\(_3\)OD)

6.1 Introduction

Spectroscopy is a powerful tool in the investigation of many chemical phenomena. Combined with gas-phase complexes, spectroscopy has been used to probe the nature of solvation in charged solvent-solute systems.\(^{18,20,78,79,245–248}\) Dynamics occurring within these systems upon solute excitation\(^{249–253}\) can be difficult to characterize due to the large number of interacting species and the rapid changes in their configurations. Size selection of gas-phase solvent-solute complexes allows for detailed dynamical investigations of individual solvent perturbations on the solute.\(^{217,252,254–258}\)

In previous studies of Cu\(^-\)(H\(_2\)O),\(^{12,259}\) electron photodetachment was shown to lead to large-amplitude H\(_2\)O reorientation within and dissociation from Cu(H\(_2\)O), due to the difference in topology between the anion and neutral potential energy surfaces. The Cu\(^-\)(H\(_2\)O) complex has a hydrogen-bonded, Cu\(^-\)–HOH, minimum energy configuration, while in neutral Cu(H\(_2\)O) the stronger Cu–O interaction determines its minimum energy configuration. Electron photodetachment from Cu\(^-\)(H\(_2\)O) produces an ensemble of vibrationally excited Cu(H\(_2\)O) complexes with an average internal
energy near the dissociation threshold of the complex. For the Cu(H\(_2\)O) study, following electron photodetachment from Cu\(^–\)-HOH, dissociation of Cu(H\(_2\)O) occurred on three different timescales, each separated by an order of magnitude. Some 30\% of the nascent Cu(H\(_2\)O) complexes directly dissociated. The remaining bound complexes dissociated on a 10 ps timescale via coupling of the H\(_2\)O intermolecular rotation to the Cu–HOH dissociation coordinate and on a 100 ps timescale by coupling of the H\(_2\)O intramolecular bending vibration with the Cu–HOH dissociation coordinate.\(^1\)\(^2\)\(^3\)\(^9\)\(^{99}\)\(^{100}\)

Hydrogen and methyl substituents, and functional groups in general, play pivotal roles in a wide array of chemical reactions. Substitutions of CH\(_3\) for H, and vice versa, can influence reactivity, especially due to steric interactions. Methyl groups have been shown to affect the structure and binding energy in I\(^–\) (ROH) complexes, (R = H, CH\(_3\)),\(^{99}\) and have recently been part of an investigation of infrared spectral features in Cl\(^–\) (ROH) complexes, (R = H, CH\(_3\), CH\(_2\)CH\(_3\)).\(^{100}\) In this chapter we discuss on the effects of a methyl group addition on the dissociation dynamics of a metal-ligand complex. We are interested in determining how the methyl group affects the solvent reorientation and dissociation dynamics in a Cu\(^–\) (ROH) complex (R = H, CH\(_3\)). For experimental reasons, the spectroscopic studies were carried out using fully deuterated methanol. Reports from previous investigations\(^{99}\)\(^{99}\) on Cu\(^–\)(H\(_2\)O)\(_n\) show no significant difference in the time-evolution of the dissociating neutral complexes upon deuteration.
6.2 Experiment

6.3 Apparatus and data collection

The experiments on Cu\textsuperscript{−}(CD\textsubscript{3}OD) photoinduced dissociation were performed by Barbera, Dribinski, and Lineberger at JILA and the University of Colorado at Boulder and shall be referred to as Barbera et al. The charge-reversal instrument used in the time-resolved photodetachment photoionization study has been described previously,\textsuperscript{4,231,259,263} and the instrument used in these experiments is the same as the instrumental set-up presented in Figure 1.3 in Chapter 1. As was also mentioned in Chapter 1, the temperatures of the clusters obtained in these experiments are not well characterized and rely on the estimations from other similar studies. Previous anion cluster studies estimate the temperature of (H\textsubscript{2}O\textsubscript{18})\textsuperscript{−} and I\textsubscript{2}\textsuperscript{−}(CO\textsubscript{2})\textsubscript{16} cluster ions\textsuperscript{63,64} to be \(\sim\) 150 K and \(\sim\) 50 K, respectively. Using these studies, Barbera et al. estimated the temperature of the smaller Cu(CD\textsubscript{3}OD) clusters to be greater than 150 K. For the purpose of calculations in this study, a vibrational temperature of 200 K is used; however, the qualitative conclusions do not depend on the exact cluster temperature.

The potential energy curves, plotted as functions of the Cu–O distance in Figure 6.1, show how the neutral Cu(CD\textsubscript{3}OD) complexes were formed by electron photodetachment from Cu\textsuperscript{−}(CD\textsubscript{3}OD) using a 398 nm pulse. Monitoring the time evolution of the neutral cluster was accomplished by photoionizing Cu(CD\textsubscript{3}OD) and its fragments in various pump-probe schemes. Figure 6.1 shows the two different pump-probe schemes used to detect the cation photoproducts. Scheme 1 in Figure 6.1 was used
to monitor the Cu$^+$ evolution as a function of the delay between the photodetachment and the excitation/ionization pulses; similarly, scheme 2 in Figure 6.1 was used to monitor the Cu$^+$$(CD_3OD)$ evolution. Individual Cu$^+$ and Cu$^+$$(CD_3OD)$ product signals were acquired by scanning a range of pump and probe time-delays. Error bars for the experimental data were obtained by averaging multiple data sets, and this averaged cation time dependence was fit to the functional forms described below.

Figure 6.1: Potential energy curves, plotted as functions of the Cu–O distance, $R$, along with laser pump-probe schemes. The dashed curves represent cuts in the hydrogen-bonded orientation, while the solid curves represent the orientation in which the copper atom is closest to the oxygen atom. The vertical arrows represent various pump-probe processes employed in the experiments of Barbera et al. in Ref. 4.
6.3.1 Time evolution of the Cu$^+$ and Cu$^+$($\text{CD}_3\text{OD}$) signals

Figure 6.2 shows the initial rise of the Cu$^+$ and Cu$^+$($\text{CD}_3\text{OD}$) signals from the anion species, Cu$^-$($\text{CD}_3\text{OD}$), following pump and probe pulses.$^4$ As a point of reference, the instrument response, measured by the rise of Cu$^+$ from Cu$^-$, is plotted with grey triangles and fit to a tanh function (solid line). The Cu$^+$($\text{CD}_3\text{OD}$) signal rises at the same rate as the instrument response while the Cu$^+$ signal rises with increasing pump-probe delay. A longer time scan is plotted in Figure 6.3. This plot shows that both signals reach their respective asymptotic values by $\sim t = 100$ ps. If the two signals are summed, their sum is nearly constant. Similar rise and decay features were also observed in the Cu($\text{H}_2\text{O}$) studies.$^{12,231,259}$

In order to extract dynamical information from the experimental data, all data sets were summed to produce total Cu$^+$ and Cu$^+$($\text{CD}_3\text{OD}$) time-dependent signals. Individually scaled and background-corrected data sets were averaged to obtain the Cu$^+$ and Cu$^+$($\text{CD}_3\text{OD}$) data shown in Figure 6.3. Barbera et al. found that fitting the data to single-exponential rise [Cu$^+$] and decay [Cu$^+$($\text{CD}_3\text{OD}$)] did not produce a satisfactory fit. Consequently a two-component fit was employed. The solid lines in Figure 6.3 were obtained by fitting the data to a double-exponential rise/decay function with the following form:

\[
I[\text{Cu}^+] = a_1(1 - e^{-t/x_1}) + a_2(1 - e^{-t/x_2}), \quad (6.1)
\]

\[
I[\text{Cu}^+(\text{CD}_3\text{OD})] = b_1e^{-t/y_1} + b_2e^{-t/y_2}. \quad (6.2)
\]
Figure 6.2: Initial experimental time dependence of cation signals. The Cu\(^+\) signal rise from Cu\(^-\) (gray triangles) is fit to a tanh function (solid line) and used as an *in situ* measure of the instrument time resolution. The open circles represent Cu\(^+\) signal from Cu(CD\(_3\)OD), while the filled circles represent the Cu\(^+\)(CD\(_3\)OD) signal from Cu(CD\(_3\)OD). The data were collected by Barbera *et al.* and are reproduced from Ref. 4.
Figure 6.3: Experimental time dependence of cation signals resulting from the photodetachment photoionization of Cu$^-$ (CD$_3$OD). The rising Cu$^+$ signal (open circles) results from photodetachment (398 nm) followed by two-color (327 + 265 nm) resonant ionization. The decaying Cu$^+$(CD$_3$OD) signal (filled circles) results from photodetachment (398 nm) followed by one-color (265 nm) resonant multiphoton ionization. The solid lines represent the exponential fits to the data used to extract time components. The data were collected by Barbera et al. and are reproduced from Ref. 4.
This parameterization gave a satisfactory fit; the parameters so obtained are reported in Table 6.1. Although the fits to the Cu\(^+\) and Cu\(^{+}\)(CD\(_3\)OD) data were carried out independently, the corresponding derived parameters \((a_1, b_1), (a_2, b_2), (x_1, y_1),\) and \((x_2, y_2)\) are each within 1\(\sigma\) of their counterpart. This agreement strongly suggested that both Cu\(^+\) and Cu\(^{+}\)(CD\(_3\)OD) signals arose from a common physical process. The fit parameters also show that each component has roughly 50% contribution to the signal. The reported error in fitting was determined by the standard deviation of the exponential fit to the averaged data sets. These errors are represented graphically in Figure 6.3 and numerically in Table 6.1. The large uncertainty present in \(y_1\) came from the recurring oscillatory features present in the decaying signal, as can be seen in Figure 6.2.

Table 6.1: Parameters of double exponential fit to the functions given in eqs. (6.1) and (6.2); the indicated errors are \(\pm 1\sigma\) of the least squares fit parameters. Fit parameters were obtained by Barbera et al. and are reproduced from Ref. 4.

<table>
<thead>
<tr>
<th></th>
<th>Cu(^+)</th>
<th>Cu(^{+})(CD(_3)OD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_1)</td>
<td>2.9 (\pm) 0.7 ps</td>
<td>5 (\pm) 3 ps</td>
</tr>
<tr>
<td>(x_2)</td>
<td>29 (\pm) 4 ps</td>
<td>33 (\pm) 3 ps</td>
</tr>
<tr>
<td>(a_1)</td>
<td>0.48 (\pm) 0.10</td>
<td>0.52 (\pm) 0.07</td>
</tr>
<tr>
<td>(a_2)</td>
<td>0.52 (\pm) 0.08</td>
<td>0.48 (\pm) 0.08</td>
</tr>
</tbody>
</table>

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6.4 Theory

In an earlier study of Cu(H$_2$O)$_{12}$, Taylor et al. focused on a three-dimensional, fully-coupled treatment that included the three intermolecular degrees of freedom of the complex. Although the full-dimensional treatment gave useful information, they found that many of these insights were borne out in analyses of the three, separate one-dimensional slices. Since calculating Cu(CD$_3$OD) in full dimensionality is impractical, we draw from the findings of Taylor et al. and expect that the one-dimensional decoupled picture should also hold for Cu(CD$_3$OD).

The calculations used to characterize the Cu(CD$_3$OD) complex fall into two general categories. First the minimum energy configurations for the anion, neutral, and cation complexes are determined and then a series of one-dimensional slices through the potential energy surfaces, starting from these geometries, are evaluated. These one-dimensional potential energy surfaces are used to calculate vibrational wave functions and energies using a sinc-discrete variable representation (DVR). The resulting energies and wave functions are used to investigate the regions of the potential that are sampled by the Cu(CD$_3$OD) system upon electron photodetachment. In particular we focus on the partitioning of energy among the internal coordinates and how this is reflected in the time-dependent signal and Cu(CD$_3$OD) photoelectron spectrum.
6.4.1 *Ab initio* calculations

All electronic structure calculations are performed by Barbera using the Gaussian 98 or Gaussian 03 program packages. The basis sets and level of theory used in these calculations have been described in a previous study. The basis set used to represent the copper atom is an augmented form of the Stuttgart-Dresden-Bonn (SDB) relativistic core potential developed by Preuss and co-workers, referred to as aug-SDB. The aug-SDB basis was developed by Schwarz and co-workers during their investigation of anion and neutral CuX$_2$ (X = Cl, Br). Hydrogen, oxygen, and carbon are each represented by aug-cc-pVTZ basis sets. Second-order Möller-Plesset perturbation theory (MP2) was used to optimize all geometries as well as in calculations of several one-dimensional (1-d) potential energy surfaces. The minimum energy configurations for the anion, neutral, and cation complexes are shown in Figure 6.4(a), (b), and (c), respectively.

![Figure 6.4: Minimum energy structures of Cu(CD$_3$OD) complexes for the three charge states of Cu, where shows the structure of (a) the anion, (b) the neutral, and (c) the cation.](image-url)
Both radial and angular one-dimensional potential slices are calculated at the MP2 level of theory, beginning from the minimum energy configuration of the anion and neutral. Barbera also calculated one-dimensional cuts starting from the vertical detachment geometry (VDG), i.e. cuts through the Cu(CD$_3$OD) potential based on the minimum energy configuration of the anion. For example, the anion surface is calculated as a function of the Cu–O distance, $R$, ranging from 1.6–7.6 Å in increments of 0.1 Å. The neutral surface is calculated over a range of 1.5–7.0 Å while the VDG surface ranges from 1.8–7.2 Å; both are evaluated in increments of 0.2 Å. In all scans the O–D bond length and the angle between the plane containing Cu, C, and O and the plane containing D$_4$, C, and O are relaxed at every step, while all other bond lengths and angles are held constant.

Three types of angular scans were carried out, and the molecular coordinates for these one-dimensional surfaces are based on the structures shown in Figure 6.4. The electronic energy is calculated as a function of out-of-plane (oop) motion by varying the angle between the plane that contains the Cu, O, and C atoms and the plane that contains the D$_4$, O, and C atoms. This dihedral angle was sampled over a range of ±60° for the anion and ±180° for the flatter, neutral, and VDG surfaces. For all three surfaces, the out-of-plane motion is evaluated in increments of 2°, and the O–D and Cu–O distances are allowed to relax at each step along the path. Variation of the Cu-O-C angle produces the in-plane (ip) motion. The electronic energy as a function of this motion is calculated over a ±60° range in 2° increments for the anion surface and from −180° to 180° in increments of 10° for the VDG surface; the
O–D and Cu–O bond lengths are optimized at each step. For all three complexes, the electronic energy is calculated as a function of methyl torsion (CD$_3$) over a ±60° range of the D$_1$-C-O-D$_4$ dihedral angle in 5° increments. In this cut all three C–D bond lengths and O-C-D bond angles are relaxed. The ranges for each of the one-dimensional potentials are chosen such that they span the radial and angular regions sampled by the vibrational wave functions for the states of interest.

### 6.4.2 Vibrational coordinates and hamiltonian

One-dimensional variational calculations were carried out in a DVR. For the Cu–CD$_3$OD distance coordinate, $R$, we use the reduced mass of the complex. The effective masses, $b_{eff}$, for the angular motions are derived from the rotational constants for the associated molecular motions. In the case of the out-of-plane motion, this corresponds to rotation of the O–D bond about the C–O bond axis. The in-plane motion corresponds to the rotation of CD$_3$OD about its $c$ rotation axis coupled to rotation of the complex about its center of mass, while the methyl torsion is simply the three-fold rotation of the CD$_3$ group about its symmetry axis. Based on the above definitions, the values of $b_{eff}$ for these three motions are 9.9512 cm$^{-1}$ (oop), 0.6687 cm$^{-1}$ (ip), and 4.5172 cm$^{-1}$(CD$_3$), and the effective Hamiltonians for the radial and angular motions (in atomic units) are

\[
\hat{H} = -\frac{1}{2\mu} \frac{d^2}{dR^2} + V(R),
\]

and

\[
\hat{H} = b_{eff} \hat{J}^2 + V(\theta),
\]

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respectively. Here $\hat{J}^2$ is the angular momentum operator associated with the one-dimensional motions, and as such it has eigenvalues that are proportional to $j^2$. The potential surfaces, $V$, are acquired using spline interpolations of the energies obtained from the electronic structure calculations described above. For the stretch coordinate, grid points used for the DVR calculations range from 0.5 to 15.0 Å with a grid spacing of 0.0181 Å. For the bend and torsion coordinates, the grid ranges from $-180^\circ$ to $180^\circ$ with a spacing of 0.5°. For the stretch coordinate, grid points beyond those from ab initio calculations were necessary, and the ab initio data are extrapolated to the calculated value at 25 Å using

$$V_{ex}(R) = C_6 \frac{R^6}{R^6} + C_8 \frac{R^8}{R^8}, \quad (6.5)$$

where the values of $C_6$ and $C_8$ are chosen to ensure that the potential and its first derivative are continuous.

Within the Condon approximation, the photoelectron spectrum can be generated from overlaps between eigenstates on the anion and neutral surfaces. Since the low-lying vibrational states on the anion surface are localized near the potential minimum, we focus on those eigenstates on the neutral surface that are evaluated using cuts near the equilibrium structure of the anion, e.g. the VDG surface. Within this treatment, the four-dimensional wave functions are approximated by products of one-dimensional functions. The overlap integrals between the eigenstates on the anion and VDG surfaces are evaluated for each thermally populated state of the anion using the 200 K vibrational temperature as was mentioned above. The resulting spectra are summed...
and convolved with a Gaussian with a full width at half maximum (FWHM) of 50 cm$^{-1}$ (0.0062 eV). This width is chosen to facilitate comparison with experiment.

6.5 Results and discussion

6.5.1 Initial state characterization

Electron photodetachment from Cu$^-$ (CD$_3$OD) produces an ensemble of neutral Cu(CD$_3$OD) complexes far from their equilibrium geometry, resulting in large amplitude solvent rearrangement and dissociation. In order to investigate the nature of this rearrangement and dissociation, we must characterize the initial state of the ion-molecule complex.

6.5.1.1 Calculations

The anion complex has a distinctly different minimum energy configuration than the neutral and cation complexes. This is illustrated in the variation of selected bond lengths and angles reported in Table 6.2. By analogy to Cu$^-$ (H$_2$O), where the Cu$^-$ is in a hydrogen-bonded configuration, the minimum energy structure of the Cu$^-$ (CD$_3$OD), shown in Figure 6.4(a), has the Cu$^-$ positioned closest to D$_4$ and lying in the plane that contains D$_4$OCD$_1$. This hydrogen-bonding interaction between Cu$^-$ (CD$_3$OD) and the OD group in methanol is reflected in the fact that the O–D bond length is 0.03 Å longer in Cu$^-$ (CD$_3$OD) than in an isolated methanol molecule. In addition the value of the C–O–D angle is decreased from 107.98° in methanol to 105.82° in the cluster. In the context of the present study, the most important change in methanol due to complexation with Cu$^-$ is that it lowers the CD$_3$ torsional barrier
by nearly 75%, from 406 cm\(^{-1}\) in an isolated methanol molecule to 110 cm\(^{-1}\) in the complex.

Table 6.2: Select geometric parameters of all species, calculated at the MP2 level of theory.

<table>
<thead>
<tr>
<th></th>
<th>CD(_3)OD</th>
<th>Cu(^{−})(CD(_3)OD)</th>
<th>Cu(CD(_3)OD)</th>
<th>Cu(^{+})(CD(_3)OD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R(\text{CuO}))</td>
<td>...</td>
<td>3.23 Å</td>
<td>2.04 Å</td>
<td>1.86 Å</td>
</tr>
<tr>
<td>(R(\text{OD}))</td>
<td>0.96 Å</td>
<td>0.99 Å</td>
<td>0.96 Å</td>
<td>0.96 Å</td>
</tr>
<tr>
<td>(R(\text{CO}))</td>
<td>1.42 Å</td>
<td>1.41 Å</td>
<td>1.44 Å</td>
<td>1.47 Å</td>
</tr>
<tr>
<td>(\theta_{\text{COD}})</td>
<td>107.98°</td>
<td>105.82°</td>
<td>108.85°</td>
<td>109.64°</td>
</tr>
</tbody>
</table>

Calculations of the neutral Cu(CD\(_3\)OD) cluster at the MP2 level result in a minimum energy structure with the Cu atom closest to the oxygen atom, on the opposite side of the OD group compared to the anion, as shown in Figure 6.4(b). In the minimum energy structure, the copper atom resides above the plane that contains D\(_4\)OCD\(_1\), and the Cu–O distance is 2.04 Å. In comparing this complex to an isolated methanol molecule, we see that the O–C bond length increases, the O–D bond length remains unchanged, and the C-O-D angle increases slightly. In addition, the barrier to rotation of the methyl group is nearly equal to that in methanol, with a value of 421 cm\(^{-1}\). This change in the barrier height will be important as we analyze the origins of the observed time dependence of the Cu\(^{+}\) and Cu\(^{+}\)(CD\(_3\)OD) signals. The large difference between the barrier heights on the anionic and neutral surfaces is surprising, but similar changes in barrier heights have been observed in studies of the methyl rotor in CH\(_3\)O\(_2\) in its ground and first excited electronic states.\(^{270}\)
Upon electron photodetachment of Cu\(^-\)(CD\(_3\)OD), the resulting neutral complex is produced with an initial geometry that is close to the minimum energy structure of the anion. Comparing Figure 6.4(a) and (b), we note that this configuration is far from the minimum energy geometry of the neutral complex. In Tables 6.3 and 6.4 we report the harmonic and anharmonic fundamental frequencies of several modes of interest for the anion complex as well as for the two geometries of the neutral complex. The anharmonic frequencies were obtained from the DVR calculations described above, while the one-dimensional harmonic frequencies were obtained by replacing the potential term in eqs. (6.3) and (6.4) with a quadratic expansion of the potential about a local minimum. In contrast the fifteen-dimensional (15-d) harmonic frequencies were obtained from a normal mode analysis at the potential minimum. There are obvious differences between the frequencies, and these frequency discrepancies arise from several sources. The contrast between the two, one-dimensional results reflects the anharmonicity of the potentials. As can be seen, the stretch, in-plane, and out-of-plane potentials are nearly harmonic, while anharmonicity plays a larger role in the torsion potential. The variation between the two sets of harmonic frequencies reflects the difference between the coordinates that are used to define the one-dimensional potential cuts and the normal mode coordinates.

It should also be noted that no fifteen-dimensional harmonic calculations are presented for the VDG. This stems from the fact that the vertical detachment geometry is not a stationary point on the neutral surface. However, the VDG manifests itself as local minima in the one-dimensional cuts through the neutral potential energy
Table 6.3: Calculated fundamental frequencies of the four vibrational modes corresponding to the one-dimensional (1-d) potential energy slices for Cu\(^-\)(CD\(_3\)OD) and Cu(CD\(_3\)OD), which is the neutral complex in the anion configuration, i.e. the vertical detachment geometry.

<table>
<thead>
<tr>
<th>vibration</th>
<th>Cu(^-)(CD(_3)OD)</th>
<th>Cu(CD(_3)OD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15-d harmonic (cm(^{-1}))</td>
<td>1-d anharmonic (cm(^{-1}))</td>
</tr>
<tr>
<td>Cu–O stretch</td>
<td>138</td>
<td>102</td>
</tr>
<tr>
<td>in-plane bend</td>
<td>83</td>
<td>119</td>
</tr>
<tr>
<td>out-of-plane bend</td>
<td>489</td>
<td>423</td>
</tr>
<tr>
<td>CD(_3) torsion(^a)</td>
<td>44</td>
<td>53</td>
</tr>
</tbody>
</table>

\(^a\) Due to the near degeneracy of the three lowest energy states of the torsion, the 1-d values reflect the energy difference between the third excited state and the ground state.
Table 6.4: Calculated fundamental frequencies for the three vibrational modes corresponding to the 1-d potential energy slices of Cu(CD₃OD), minimum energy neutral configuration.

<table>
<thead>
<tr>
<th>vibration</th>
<th>15-d harmonic (cm⁻¹)</th>
<th>1-d anharmonic (cm⁻¹)</th>
<th>1-d harmonic (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–O stretch</td>
<td>230</td>
<td>183</td>
<td>193</td>
</tr>
<tr>
<td>out-of-plane bend</td>
<td>298</td>
<td>246</td>
<td>265</td>
</tr>
<tr>
<td>CD₃ torsion</td>
<td>82</td>
<td>116</td>
<td>123</td>
</tr>
</tbody>
</table>

Due to the near degeneracy of the three lowest energy states of the torsion, the 1-d values reflect the energy difference between the third excited state and the ground state.

surfaces. Therefore the one-dimensional calculations are shown in Table 6.3 for comparison with the anion and neutral frequencies.

Since the VDG is not the global minimum on the neutral surface, determining which of the calculated vibrational energy levels correspond to the ground and first excited states of the complex in the VDG can be difficult. For the out-of-plane bend, the lowest energy state that is strongly localized in the VDG minimum is easily assigned, whereas the first excited state is more difficult to isolate. This complication reflects the fact that the barrier to free rotation of the copper atom around the OD group of methanol is only 70 cm⁻¹ above this lowest energy state. As the harmonic frequency for this mode is 212 cm⁻¹, it is not surprising that the state that we identify as the first excited state has a frequency much lower than the harmonic value. In fact its energy is close to the barrier to free rotation, and it is rather delocalized over the full range of the out-of-plane angle. The in-plane motion also exhibits similar difficulties, albeit to a lesser extent. We also calculated the minimum
energy structure of Cu\(^+\)(CD\(_3\)OD), shown in Figure 6.4(c); key structural parameters for all three charge states are summarized in Table 6.2.

### 6.5.1.2 Photoelectron spectra

The Cu\(^-\)(CD\(_3\)OD) photoelectron spectrum obtained by Barbera \textit{et al.} is displayed in Figure 6.5\textsuperscript{271}. For comparison, we also plot the calculated Cu\(^-\)(CD\(_3\)OD) photoelectron spectrum, shown as a solid line. The energy scale of the calculated spectrum has been shifted by 91 meV, such that the maxima of the calculated and experimental spectra coincide. The magnitude and direction of this shift are in line with the error found in the calculation of the electron affinity of Cu atom at the same level of theory\textsuperscript{12}.

The agreement between the experimental and calculated photoelectron spectra is remarkable. In particular the calculated spectrum reproduces the width and contour of the experimental spectrum. This provides us with confidence in our reduced dimensional model for the Cu(CD\(_3\)OD) complex. Analysis of the calculated spectrum shows that its shape and width are captured by a one-dimensional calculation that includes only the Cu–O stretch coordinate, although the methyl rotor motion must also be taken into account to achieve the level of agreement seen in Figure 6.5.

While we only report the spectrum that was calculated at 200 K, we also evaluated the photoelectron spectrum for temperatures ranging from 0 to 200 K. The differences between these spectra reflect hot band structure in the Cu–O stretch coordinate and sequence bands in the methyl rotor. The intensities of these features increase with temperature, leading to broadening of the calculated spectrum. Interestingly, the
Figure 6.5: Experimental and calculated Cu\textsuperscript{−}(CD\textsubscript{3}OD) photoelectron spectra. The experimental spectrum is shown as black points. The calculated spectrum is reported with a solid, black curve. For comparison we also calculated the photoelectron spectrum after shifting the potential energy curve for Cu\textsuperscript{−}(CD\textsubscript{3}OD) by \pm 0.18 Å along the Cu–O distance coordinate \( R \). The results of these calculations are plotted with gray curves; the dashed line represents the calculation when the potential minimum is shifted to 3.24 Å and the dash-dot line represents the results when the minimum is at 3.60 Å. Experimental spectra were obtained by Barbera et al. and are reproduced from Ref. 4.
difference between the spectrum at 100 K and that at 200 K are small and are found to be in comparable agreement with the experimental spectrum, shown in Figure 6.5. While this insensitivity of the photoelectron spectrum to the vibrational temperature may seem surprising, it reflects the fact that the largest contribution to the width comes from the ground state wave function on the anion surface and is seen at 0 K. Similar behavior was seen in previous calculations for Cu(H_2O) and Cu(D_2O).

6.5.2 Dissociation time components

In contrast to the experimental work discussed above, Muntean et al. found that three time scales were required to fit the Cu^+ signal in the Cu(H_2O) study and that the Cu^+(H_2O) signal displayed more structure than was observed for Cu^+(CD_3OD). In Cu(H_2O) the shortest timescale was ~ 1 ps. This was shown to correspond to direct dissociation of the Cu(H_2O) complex upon electron photodetachment. An intermediate timescale of ~ 10 ps was associated with coupling between the hindered rotation of H_2O in the complex to the Cu–H_2O dissociation channel. Finally the 100 ps component was attributed to vibrational predissociation driven by states with excitation in the water bend.

6.5.2.1 Direct dissociation

As can be seen in Figure 6.6, after photodetachment the neutral Cu(CD_3OD) complex is in the VDG, a configuration that is far from the minimum energy configuration on the potential surface. The motions that would take the complex to the minimum energy geometry involve a combination of methanol rotation and a shortening of the
Cu–O distance. At the equilibrium Cu–O distance in the VDG of Cu(CD$_3$OD), the potential is relatively flat along the coordinates corresponding to methanol rotation. If there is sufficient energy in the Cu–O stretch coordinate, the complex should have enough time to dissociate before getting trapped near the minimum energy configuration of the complex. This mechanism is responsible for the $< 1$ ps, fast rise signal for Cu$^+$ from Cu$^+$(H$_2$O).

![Potential energy surface cuts](image)

Figure 6.6: Cuts through the potential energy surfaces along the Cu–O distance coordinate $R$ for (i) Cu$^−$(CD$_3$OD), (ii) Cu(CD$_3$OD) with other coordinates frozen at the anion configuration, and (iii) fully relaxed Cu(CD$_3$OD). The insets show the various solvent orientations for the three minima.
As seen in the results reported in Table 6.1, the parameters that describe the Cu$^+$
rise do not contain the fast ($t < 1$ ps) Cu$^+$ component observed in the Cu(H$_2$O)
study. This direct dissociation component was also absent in the Cu(H$_2$O)$_2$
rearrangement studies. To understand this difference between the previous Cu(H$_2$O)
and current Cu(CD$_3$OD) dissociation dynamics, we turn to cuts through the poten-
tials for the anion and neutral species, plotted in Figure 6.7. Here the solid lines
represent the potentials for the Cu(CD$_3$OD) complexes, while dashed lines provide
the potentials for the Cu(H$_2$O) complexes. The vertical and horizontal dotted lines
represent the equilibrium Cu–O distance on the anionic surf ace and the dissociation
energy of the neutral complexes, respectively. As these plots show, upon photodetach-
ment the Cu(CD$_3$OD) complex will be in a configuration that is close to the potential
minimum in the VDG along the Cu–O stretch coordinate. Comparison of the well
depths shows that the interaction energy of copper in a hydrogen-bonded orientation
with methanol, Cu–DOCD$_3$, is much larger than the corresponding interaction energy
between copper and water in a similar configuration. These differences imply that
Cu(H$_2$O) will have more energy along the Cu–H$_2$O dissociation coordinate than will
be the case for Cu(CD$_3$OD).

The implications of the above analysis of the potential curves, plotted in Figure
6.7, can be quantified by considering the properties of the ground state wave functions,
calculated using the lower, anionic surfaces when they are projected onto the neutral
surfaces. If we consider the average energy of these states, we find that it is 148
$\text{cm}^{-1}$ below the dissociation threshold ($D_0(C_{2v}) = 265 \text{ cm}^{-1}$)$^{12}$ in Cu(H$_2$O), while for
Figure 6.7: Cuts through the potential energy surfaces along the Cu–O distance coordinate $R$ for (i) the anion and (ii) the neutral at the vertical detachment geometries of Cu(CD$_3$OD) and Cu(H$_2$O). The solid curves represent Cu(CD$_3$OD), while the dashed curves represent Cu(H$_2$O). The vertical line is drawn at the Cu–O distance corresponding to the minimum energy configuration of both anions. The horizontal line at 1.23 eV indicates the dissociation energy of the neutral complexes.
Cu(CD₃OD) the average energy is 568 cm⁻¹ below the dissociation threshold ($D_0 = 628$ cm⁻¹). While the greater relative energy of Cu(H₂O) compared to Cu(CD₃OD) supports the above observations, the complexes are initially at a finite temperature, and this should also be taken into account. This can be accomplished by considering the overlaps between the wave functions that correspond to the thermally populated states on the anion surface at 200 K and the vibrational wave functions at the VDG on the neutral surface. We find that 18% of the probability amplitude reflects overlaps with states with energies above the Cu(H₂O) dissociation threshold, while this value drops to less than 2% for Cu(CD₃OD). This final observation supports the inability of the experimental signal to be fit to a fast time-component, analogous to the < 1 ps rise time in Cu(H₂O).

The above arguments rely on the shift between the minimum energy geometries of the slices along the Cu–O coordinate of Cu⁻(CD₃OD) and Cu(CD₃OD) in the VDG. We can investigate the appropriateness of this picture by calculating the photoelectron spectrum, as described above, with the Cu–O distance dependence of the Cu⁻(CD₃OD) potential shifted by ± 0.18 Å. The results of these calculations are plotted with dashed lines in Figure 6.5. The best agreement in the width of the calculated and experimental spectra is obtained when the unshifted vertical detachment potential surface is used. This finding, along with the calculated overlaps between the radial wave functions and the anion and VDG potential energy surfaces, supports the fact that the direct dissociation channel that was reported for the Cu(H₂O) complex is not observed in Cu(CD₃OD).
6.5.2.2 Energy redistribution

While the above discussion shows that there is not enough energy directly deposited into the Cu–O coordinate of Cu(CD$_3$OD) to lead to direct dissociation, in most cases there is more than sufficient excitation in several of the other vibrational degrees of freedom to dissociate the complex. An investigation of cuts through the neutral potentials, corresponding to both the in-plane and out-of-plane motions, reveals a relatively flat landscape similar to that seen in Cu(H$_2$O). In the three-dimensional simulations of the dynamics of Cu(H$_2$O) on the neutral surface, Taylor et al. were able to attribute the 10 ps timescale obtained from the fits to the Cu$^+$ and Cu$^+$(H$_2$O) signals to energy transfer between the hindered rotation of the water molecule and the dissociation coordinate. When we compare the initial internal energy in the in-plane and out-of-plane rotation coordinates in these two systems, based on one-dimensional calculations, we find that they differ by less than 10%. This, coupled to the similarity between the 3 ps time scale obtained in the present study and the 10 ps time scale for Cu(H$_2$O), leads us to conclude that the motions responsible for the 3 ps rise and decay times reported in Table 6.1 are associated with energy transfer from the methanol hindered rotation to the dissociation of the complex. The shorter timescale for methanol compared to water likely reflects the smaller rotational constants for methanol leading to a larger density of states.

In the Cu(H$_2$O) study, the 100 ps dissociation component stemmed from pre-dissociation driven by vibrationally-excited bending modes of H$_2$O. Table 6.1 gives the longest dissociation component as 30 ps for Cu(CD$_3$OD). We believe that this
component arises from coupling of the methyl rotor rotation into the Cu–CD₃OD dissociation coordinate. When we calculate the overlap between the thermally populated torsional levels of the CD₃ group in Cu⁻(CD₃OD) and the states on the neutral surface, we find that, upon photodetachment, 65% of the probability amplitude ends up in states with energy in the methyl torsion. This value is within 2σ of the values for a₂ and b₂, reported in Table 6.1. Based on this, we attribute the 30 ps time scale to coupling of states with methyl rotor excitation to the dissociation coordinate. We ascribe the difference in the dissociation time, compared to the 100 ps component of Cu(H₂O), to the presence of the methyl rotor and its ability to accelerate intramolecular vibrational energy redistribution (IVR).²²–²⁴

6.6 Conclusions

We discuss the experimental and theoretical investigations of the time-dependent dissociation dynamics of the Cu(CD₃OD) complex. Experiments using photodetachment photoionization spectroscopy provide insight into the evolution of the nascent neutral complex formed via electron photodetachment from Cu⁻(CD₃OD). Ab initio calculations provide the minimum energy structures and one-dimensional potential energy surfaces used in determining the vibrational energies and wave functions of the complex.

The ab initio minimum energy structures show that both anion species of Cu(H₂O) and Cu(CD₃OD) have similar hydrogen-bonded orientations as well as similar neutral Cu–O orientations. However, the Cu(CD₃OD) complex does not exhibit the direct
dissociation \((t < 1 \text{ ps})\) observed in Cu(H\(_2\)O), due to the predominantly bound-to-bound transitions upon electron photodetachment of Cu\(^-\)(CD\(_3\)OD). The rising Cu\(^+\) and decaying Cu\(^+\)(CD\(_3\)OD) signals from Cu(CD\(_3\)OD) both exhibit time components of 3 ps and 30 ps. Models of the dissociation dynamics suggest that the 3 ps component arises from coupling of Cu(CD\(_3\)OD) hindered rotations to the Cu–CD\(_3\)OD dissociation coordinate; this time scale is comparable to the solvent reorientation coupling observed in Cu(H\(_2\)O). Angular one-dimensional potential energy slices and calculated excitation energies confirm the similarity of the two systems in the solvent reorientation coordinates. Further modeling of the dynamics suggests that the excited methyl rotations couple into the Cu–CD\(_3\)OD dissociation coordinate on a 30 ps time scale, slightly faster than the 100 ps timescale observed in Cu(H\(_2\)O).
In this dissertation we have investigated the structure, spectroscopy, and dynamics of a number of weakly-bound anionic systems. One goal of this work was to examine how reduced-dimensional models could be used to obtain a qualitative understanding of the chemical physics of these systems and at the same time achieving quantitative agreement with experiment. These reduced-dimensional approaches become important as the number of internal degrees of freedom grows with system size and generation of such potentials becomes prohibitively large. As such, we have shown that our models can capture sufficiently anharmonic, large-amplitude motion, such as that exhibited by $X^-(\text{H}_2\text{O})$ and $\text{Cu}^-(\text{CD}_3\text{OD})$ complexes. The second goal of this work was to investigate the dissociation dynamics of these anion systems by use of both reduced-dimensional and full quantum dynamical methods. We investigated how intermolecular motion and solvent effects can promote or hinder dissociation in these systems as well as how laser pulse width can change the qualitative picture. From all of these systems, it is clear that the strong hydrogen-bonding and electrostatic interactions that are present in anions can give very different qualitative pictures than are seen from the corresponding neutral or cation.
Our work began with examination of halide-water clusters and the applicability of utilizing reduced-dimensional models to described large-amplitude anharmonic motion, and in particular at what level mode-mode coupling should be taken into account. In $\text{F}^-(\text{H}_2\text{O})$ we found that although numerous one-dimensional studies of these systems are present in the literature,$^{119,124}$ we needed a two-dimensional model, one that included both the OF and OH$_b$ stretches, to obtain quantitative agreement with experiment. In the case of $\text{X}^-(\text{H}_2\text{O})$, we employed one-dimensional treatments, but also included coupling to the in-plane bend coordinate via a reaction path formalism.$^{168,169}$ Furthermore, we investigated the robustness of our treatments and our proposed mechanisms by looking at the effects of partial and full deuteration of the water molecule. For these halide-water systems, we have good agreement with experiment, and our calculations helped to identify a number of previously unassigned peaks in all regions of the vibrational spectra ($\sim 600 – 3800 \text{ cm}^{-1}$).

In addition to determining the veracity of our models through comparison with experiment, we utilized these models to understand the spectral signatures of H-bonding and anion structure in the vibrational spectra. In our study of these systems, we addressed three important modes, the bonded OH stretch in $\text{F}^-(\text{H}_2\text{O})$ and the two intermolecular bending modes of $\text{Cl}^-(\text{H}_2\text{O})$, $\text{Br}^-(\text{H}_2\text{O})$, and $\text{I}^-(\text{H}_2\text{O})$, namely the in-plane and out-of-plane bends. In $\text{F}^-(\text{H}_2\text{O})$ the attraction between $\text{F}^-$ and the shared hydrogen is so great that even one quantum of excitation in the OH$_b$ stretch is sufficient to promote proton transfer well over 50%. The H-bonding attraction in this system accounts for the extreme redshift of the OH$_b$ stretch relative to the free
OH stretch (1523 and 3687, respectively)\textsuperscript{18} and the broadness and intensity of this spectral band. These H-bonding effects are also present in the other \(X^-(\text{H}_2\text{O})\) species, albeit to a lesser degree, and these \(\text{OH}_b\) bands are not nearly so redshifted but are still broader than their corresponding free OH stretches: 3146 vs. 3697 for \(\text{Cl}^-(\text{H}_2\text{O})\), 3296 vs. 3695 for \(\text{Br}^-(\text{H}_2\text{O})\), and 3393 vs. 3692 cm\textsuperscript{-1} for \(\text{I}^-(\text{H}_2\text{O})\), respectively.\textsuperscript{7}

The reduced-dimensional treatments of the two intermolecular bending coordinates recovered the observed behavior of these large amplitude vibrational motions. In addition, we deduced that anomalously large electrical anharmonicities were responsible for the large intensity of the overtone in the out-of-plane bend. We have also predicted an even larger \(2\nu_{\text{oop}}\) band intensity in \(\text{F}^-(\text{H}_2\text{O})\); however, due to the intensity of the \(\text{OH}_b\) stretch in this system, experimental observation of this band is highly unlikely.\textsuperscript{6} Moreover, we cannot draw comparisons between the in-plane bend frequencies of \(\text{F}^-(\text{H}_2\text{O})\) with the other halides. This is because the barrier to isomerization is much larger in \(\text{F}^-(\text{H}_2\text{O})\) than in the other halides, on the order of 2700 cm\textsuperscript{-1} or so, and our model breaks down because of the strength of the mode-mode coupling in this system that is not well capture by a harmonic treatment of the other degrees of freedom. The significant increase in the isomerization barrier makes sense when we think back to a simple general chemistry picture of hydrogen bonding—hydrogen bonds only exist between N, O, and F with H. Thus, the hydrogen bond strength in \(\text{F}^-(\text{H}_2\text{O})\) is sufficiently stronger than in the other halides that the possibility of breaking the hydrogen bond is very energetically unfavorable.
While the transition frequencies of the in-plane and out-of-plane bends allowed us to draw comparisons across the halide series, neither fundamental band is observable in experiment. Therefore, we have also made predications of the magnitude of the splittings between the \( \nu_{\text{HOH}} + \nu_{\text{ip}} \) combination bands and saw that they increased from chloride to bromide to iodide, which were later verified by spectral assignment. We are looking to finish these studies by determining the intensities of these combination bands as well the combination bands between the two OH stretches and the in-plane bend. Preliminary results of calculations of the \( \nu_{\text{HOH}} + \nu_{\text{ip}} \) combination band intensities are consistent with the magnitudes relative to the \( \nu_{\text{HOH}} \) bands seen in experiment. Moreover, calculations of the \( \nu_{\text{OH}_b} + \nu_{\text{ip}} \) and \( \nu_{\text{OH}_f} + \nu_{\text{ip}} \) bands seem to reproduce, at least qualitatively, the peak splittings observed in the I\(^-\)(H\(_2\)O) spectrum: 3393/3422 and 3692/3706 cm\(^{-1}\), respectively.\(^7\)

While there are differences among the four halide-water complexes, they all give the same qualitative picture in that H-bonding is important, giving rise to the asymmetric (single ionic hydrogen-bonded) structure, which then leads to the concomitant effect that there is little interaction with the other, “free” hydrogen and the peak position of the OH\(_f\) stretch does not shift significantly from its frequency in bare water. While this appears to be the case for the purely deuterated or purely hydrogenated species, frequencies of the mixed isotopologues shift in unforeseen ways and reflect the importance of mode-mode coupling in these systems. Overall, through H/D isotopic substitution, we obtain an extensive database from which to explore both the nature of the shared proton potential surface and the extent to which its motion is coupled to
the motions of other atoms in the complex. Based on the assignment of these spectra, transitions involving all six vibrational modes have been identified in the majority of the complexes, and this work provides a library with which one can investigate the role of anharmonicity, resonance interactions, and mode-mode coupling in these complexes.

In addition to how structure and bonding are encoded in the vibrational spectra, we are interested in how dynamics are encoded in the photoelectron spectra of these negatively charged species. Our goal was to understand how solvent effects perturb the dynamics of the chromophore. Therefore, we first needed to understand the dynamics of the bare chromophore. For this study we applied a fully quantum mechanical treatment to the dynamics observed in the time-resolved photoelectron studies of IBr\(^-\). In this work we focused on the validity and applicability of previous interpretations of this spectra within a classical framework. In general, the observed signal increase in eKE with time was dominated by the energy difference between the \(A'\) and \(C\) or \(A\) states, which is consistent with the conclusions drawn by Sanov and co-workers.\(^8\) However, we did observe quantum mechanical effects that occurred for delay times less than 500 fs. The quantum effects arose from the fact that the wave packet was prepared in a very specific manner by the pump pulse. In the limit of the infinitesimally short pulse, there are no constraints on the excitation energy, yielding a very broad distribution in the photoelectron spectra. For the other pulses, many of the features found in the spectra calculated with the short pulse disappear, and in particular, there is a shift in the intensity of the photoelectron spectra from 0.05 to
0.15 eV over a time interval from 250 to 650 fs. Overall the calculated spectra are in very good agreement with experiment and give insights into the mechanism for the spectral structure. To further probe the dynamics of this heteronuclear system, we complicated matters by adding a CO$_2$ molecule and observed some interesting dissociation dynamics.

In IBr$^-$ (CO$_2$) we found that the presence of just one solvent molecule was enough to split the product channel into three. From studies of IBr$^-$ we knew that 100% of the molecules dissociated to I$^-$ + Br$^-$; however in IBr$^-$ (CO$_2$), three sets of dissociation products were observed: I$^-$ + Br + CO$_2$ (∼ 36%), I$^-$ (CO$_2$) + Br (∼ 61%), and I$^+$ + Br$^-$ + CO$_2$ (∼ 3%).$^{13}$ The results of our calculations led us to a mechanism for long-range electron transfer between I and Br in the dissociation of IBr$^-$ (CO$_2$) on the $A'$ electronic state, which relied heavily on the distorted molecular geometry of the CO$_2$ and the fact that the dissociating clusters are vibrationally hot, allowing for I$^-$···CO$_2$ vibrational excitation to promote reaction. The distorted molecular geometry is extremely important because it acts as a conduit to absorb excess energy into the intramolecular bend after electron transfer. The delocalization of the excess electron into the LUMO of the CO$_2$ also allowed for an “electron bridge” between the dissociating halide fragments, thus also promoting electron transfer. Here we also noted that equilibrium solvation could not shift the energies of the electronic states sufficiently to promote electron transfer.
We further studied the effects of dissociation in the study of Cu$^-$ (CD$_3$OD) where we have also utilized reduced-dimensional methods. Here, we calculated the photoionization photodetachment spectrum by focusing on only four of the 15 vibrational degrees of freedom and then treated this four-dimensional function as the product of four, one-dimensional functions. In all actuality, we obtained qualitative agreement with experiment with the inclusion of only one degree of freedom, the dissociation coordinate. We drew comparisons from our analysis of Cu(CD$_3$OD) with the previous work by Taylor et al. on Cu(H$_2$O).$^{12}$ In doing so we find that both anion complexes exhibit similar H-bonding configurations, and both configurations are similar to those observed in X$^-$ (H$_2$O). We further observed that there are differences in the dissociation time constants between Cu(CD$_3$OD) and Cu(H$_2$O). For Cu(CD$_3$OD) the complex did not directly dissociate, unlike that observed in Cu(H$_2$O). We attributed this to the predominantly bound-to-bound transitions upon electron photodetachment of Cu$^-$ (CD$_3$OD). Our models of the dynamics also suggested that the intermediate and long time components arose from coupling of Cu(CD$_3$OD) hindered rotations to the Cu–CD$_3$OD dissociation coordinate, and these time scales were consistent with the solvent reorientation coupling observed in Cu(H$_2$O). The presence of the CD$_3$ rotor was of great importance because its ability to promote intramolecular vibrational energy transfer decreased the long time component by a factor of three relative to Cu(H$_2$O). Thus subtle variations in the solvent structure can have a large impact on the solute dynamics in Cu$^-$ (HOR) systems, R = CH$_3$ or H. Just like in the work
on IBr$^-(\text{CO}_2)$, the orientation of the solvent plays a crucial role in promoting or hindering reaction.

Having discussed specific vibrational motions and dynamics of these ion-solvated complexes, the question becomes how general they are and what other insights they provide into anion-solvent interactions, more generally. From a theoretical prospective, a change in the charge distribution of the solvent upon formation or loss of a electrostatic interaction leads one to question the versatility of charge-centered models of solvents, and in particular water, as electron/proton transfer processes taking place through solvent bridges are ubiquitous. The use of simple point charge models cannot account for polarization effects between the solvent and solute, and therefore could not capture the anomalous intensity of the $2\nu_{\text{oop}}$ bands in $X^-(\text{H}_2\text{O})$ systems (nor the electron transfer mechanism in IBr$^-(\text{CO}_2)$), or presumably similar effects in other charged systems. The insights of how electrical and mechanical anharmonicities are related to vibrational band intensities in $X^-(\text{H}_2\text{O})$ systems can be used as a guide to better understand how charge orientation and charge redistribution$^{6,7,272,273}$ are reflected in the vibrational spectra of other species, such as in $M^+(\text{CH}_2\text{O})$ and $M^+(\text{NH}_2\text{CH}_2\text{COOH})$ systems ($M = \text{Li}, \text{Na}$, and $\text{K}$).$^{274}$ In these systems, orientation of the solute relative to the solvent can have profound effects on the relative intensity of vibrational bands, in particular the C=O stretch, while the band frequency appears to be insensitive to the solute position.

From an experimental viewpoint, photoelectron and rare-gas predissociation spectroscopies provide useful media by which to study weakly-bound ionic clusters and
reactive intermediates, and spectroscopic studies of these types of systems can probe a variety of behaviors, such as formation of and transfer between binding motifs and charge density and charge transfer information.\textsuperscript{16, 164} Moreover these types of species are important building blocks for larger systems, such as guest-host chemistry\textsuperscript{275} and transport of charged species through nanostructures for electronic and biological applications.\textsuperscript{276} These two examples are at the forefront of bio-organic and bio-inorganic chemistries because of their potential for novel drug design and transport. The information presented about the fundamental interactions in these systems could provide a basis for design of these molecules as system size increases.

To summarize examination of the structure, spectroscopy, and dynamics of these small anionic systems presents several studies that can provide rich structural, energetic, electronic, and dynamical information about these complexes. Moreover, much information can be gained by utilizing reduced-dimensional approaches that will become the norm as system size increases. These studies also show the importance of collaboration between experiment and theory, and as physical chemists, we will continue to work together to, as Prof. Mark Johnson so eloquently put it, “anchor the empirical rules of chemistry to the laws of physics ... to explain trends seen in reactivity and molecular structure.”\textsuperscript{42}
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