Employing Diffusion Monte Carlo to Study Ro-vibrational Excited States
and Minimized Energy Paths of CH$_5^+$

DISSETATION

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By

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ABSTRACT

Using Diffusion Monte Carlo, vibrational and rotational excited states of CH$_5^+$ and its deuterated isotopologues are evaluated and analyzed. A method for evaluating anharmonic corrections to energies along a minimized energy path for the reaction CH$_3^+$ + H$_2$ → CH$_5^+$ → CH$_3^+$ + H$_2$ is also discussed. For the vibrational excited states, the $v = 1$ energies and wave functions for the five CH stretch modes for CH$_5^+$ and CD$_5^+$ are calculated. These states are generated by requiring that the wave functions change sign at specified values of the five Symmetry Adapted Linear Combinations (SALC’s) of the displacements of the CH or CD bonds. While the definitions of these modes are based on displacements of the CH or CD bond lengths, the frequencies are found to be low compared to previously calculated CH vibrational frequencies of CH$_5^+$. The totally symmetric mode, with $A_1^+$ symmetry, has a calculated frequency of 2164 and 1551 cm$^{-1}$ for CH$_5^+$ and CD$_5^+$. The frequencies of the four fundamentals that arise from excitation of the four SALC’s that transform under $G_1^+$ symmetry have frequencies that range from 1039 to 1383 and 628 to 893 cm$^{-1}$ in CH$_5^+$ and CD$_5^+$, respectively. The origins of the broken degeneracy are investigated and are found to reflect extensive coupling to the two low-frequency modes that lead to isomerization of CH$_5^+$. For the study of rotational excited states, the $J = 1, |K| = 0, 1$ rotationally excited states of CH$_5^+$ and its deuterated isotopologues are calculated. The calculated $J = 1, |K| = 0, 1$ rotationally excited state energies are higher in energy when compared to the rotational energies calculated from vibrationally averaged rotational constants. The energy of a low-lying inversion mode that corresponds to a low-energy tunneling doublet is also calculated. When the inversion energy is subtracted from that of the $J = 1, |K| = 0, 1$
rotational energy, the energies are in good agreement with those calculated from the vibrationally averaged rotational constants. The low-lying inversion mode cannot be removed from the calculations because of the extremely high symmetry of CH$_5^+$. The participation ratios are also calculated. These ratios are found to be reduced from those of the ground state, and similar for the inversion and rotationally excited states. The low-lying inversion mode may help with assigning the high resolution spectra of CH$_5^+$. By using Jacobi coordinates, the evaluation of anharmonic corrections to the energies along a minimum energy path are straightforward to implement using Diffusion Monte Carlo. The CH$_3^+ + H_2 \rightarrow$ CH$_5^+$ reaction and its deuterated and partially tritiated analogues are investigated. In addition to exploring how the energetics of this reaction change upon deuteration or partial tritiation, projections of the probability amplitude onto various internal coordinates are evaluated and used to provide a quantum mechanical description of how deuteration affects the orientation of the two fragments as they combine to form the molecular ion. Different regions of interaction are reported and analyzed. Regardless of deuteration or partial tritiation or location of deuterium or tritium atoms, the distances at which different regions of interaction are observed do not change. Comparisons between quantum mechanical and classical mechanical calculations are also discussed.
“The Caterpillar and Alice looked at each other for some time in silence: at last the Caterpillar took the hookah out of its mouth, and addressed her in a languid, sleepy voice.

‘Who are you?’ said the Caterpillar.

This was not an encouraging opening for a conversation. Alice replied, rather shyly, ‘I - I hardly know, sir, just at the present - at least I know who I was when I got up this morning, but I think I must have been changed several times since then.’

‘What do you mean by that?’ said the Caterpillar sternly.

‘Explain yourself!’

‘I can’t explain myself, I’m afraid, sir’ said Alice, ‘because I’m not myself you see.’

‘I don’t see,’ said the Caterpillar.

‘I’m afraid I can’t put it more clearly,’ Alice replied very politely, ‘for I can’t understand it myself to begin with; and being so many different sizes in a day is very confusing.’

-Excerpt From Lewis Carroll, Alice’s Adventures in Wonderland,(Macmillan, United Kingdom, 1865)
To Christina
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CHAPTER 1

Introduction

Protonated methane has intrigued and challenged theorists and spectroscopists since it was first detected by mass spectrometry.[1] It is of particular interest to astrochemists as it is believed to be an intermediate in the reaction of H$_2$ with CH$_3^+$. [2–4] This reaction is thought to be responsible for the non-statistical hydrogen/deuterium isotopic fractionation in partially deuterated CH$_3^+$ in the interstellar medium.[3] Whether CH$_5^+$ exists as a stable long-lived species in dense interstellar clouds remains an open issue. The challenge in answering this question comes from the absence of an assigned high resolution spectrum. Several spectra have been reported.[5–8] The first of these is a 300 K high-resolution spectrum that was measured by White et al. In that study, roughly 900 transitions in the CH stretch region (2700-3150 cm$^{-1}$) were reported. The spectral complexity has made assignment of the spectrum challenging, and it remains unassigned. A 10 K high-resolution spectrum covering the CH stretch region (2825 to 3050 cm$^{-1}$) was reported by Huang et al.[8] again without assignments. A third set of low resolution spectra of CH$_5^+$ and its deuterated analogues have been reported by Asvany et al.[6, 7] These spectra access larger spectral ranges (500 - 3250 cm$^{-1}$) and are not rotationally resolved. Only the gross features in these lower resolution spectra have been assigned.[7–10] An assigned high-resolution spectrum would provide the signatures of CH$_5^+$ that are required to identify its presence and abundance in interstellar spectra.
1.1 Vibrationally and Ro-vibrationally Excited States of CH$_5^+$

The absence of an assigned rotationally resolved high-resolution spectrum reflects challenges in assigning the peaks to transitions between specific rotation-vibration energy levels. The challenge in assigning the high-resolution spectra comes from the highly delocalized nature of the wave function for CH$_5^+$, even in its vibrational ground state.[11–16] Based on calculations performed at the CCSD(T)/aug-cc-pVTZ level of theory/basis set, the dissociation energy of CH$_5^+$ to form CH$_3^+$ + H$_2$ is 47 kcal/mol,[17] making CH$_5^+$ a reasonably strongly bound molecular ion. On the other hand, close examination of the potential surface below 350 cm$^{-1}$ reveals a surprisingly flat potential.

Based on the bond lengths and angles as well as the electronic structure,[18–21] CH$_5^+$ can be best described as a H$_2$ unit bound to a CH$_3^+$ unit through a three-center two-electron bond. By symmetry, the potential surface that describes CH$_5^+$ must have 120 energetically equivalent minima. These correspond to the 120 unique ways five identical atoms can be bound to a single central atom (5!). The minimum energy geometry of CH$_5^+$ is depicted in the left and right columns of Figure 1.1. At these stationary points, the molecule has C$_s$ symmetry and these minima are often collectively referred to as the C$_s$(I) minimum. The 120 equivalent minima are connected by a chain of saddle points that are represented by the structures in the central column Figure 1.1. The lower energy saddle point also has C$_s$ symmetry and is referred to as the C$_s$(II) saddle point. It has an energy of approximately 30 cm$^{-1}$ above the C$_s$(I) minimum.[17] There are 120 energetically equivalent saddle points with this structure.[22–25] The atoms in the two structures with C$_s$ symmetry shown in Figure 1.1(a) that are part of the CH$_3^+$ unit are identified with letters C, D or E, while those in the H$_2$ group are identified by the letters A and B. The other low-lying saddle point has C$_{2v}$ symmetry and an energy of approximately 340 cm$^{-1}$ above the global minimum.[17] In the transition state structure with C$_{2v}$ symmetry [Figure 1.1(b)], the hydrogen atoms labeled A and C are equivalent and motion across this saddle point leads to the exchange
of the identities of atoms A and C and of atoms D and E. There are 60 equivalent $C_{2v}$ saddle points\[22–25\] on the global surface for CH$_5^+$. Taking these 180 saddle points into account, one can find a path that connects any of the $C_s$(I) minima to any of the other 119 minima. To help illustrate these motions, the atoms are labeled consistently between the panels in Figure 1.1.

![Figure 1.1: Geometries of CH$_5^+$ at the three lowest-energy stationary points. In the left and right column, the $C_s$(I) minimum structure is shown. In the center column, the transition states with (a) $C_s$ and (b) $C_{2v}$ symmetry that connect these minima are depicted. The letters on each structure are used to identify the location of a particular hydrogen atom in the CH$_5^+$ molecular ion.](image)

The barrier to internal rotation of the CH$_5^+$ and H$_2$ units depends on the level of theory that is employed. At the CCSD(T)/aug-cc-pVTZ level of theory/basis the barrier is $37.7 \text{ cm}^{-1}$,[17] and the one-dimensional cut through the twelve-dimensional potential in this internal rotor coordinate ($\phi$) has six equivalent minima. The harmonic frequency of this mode is $227.4 \text{ cm}^{-1}$,[17] leading one to anticipate that the ground state probability amplitude is a weak function of $\phi$. 

3
If this were the only large amplitude motion displayed by CH$_5^+$, the theory that has been developed to describe the couplings between an internal rotor and the rotational angular momentum of molecules like methanol would apply to this system as well.[26] Bunker and co-workers applied this approach in a series of studies of CH$_5^+$ and CD$_5^+$ and found that the calculated levels formed groups of 20 or 40 nearly degenerate states (split by 1 to 1.5 cm$^{-1}$).[22–25, 27] This grouping of the energy levels is consistent with a model in which the 120 equivalent minima on the potential surface are divided into 20 groups containing six minima each. The six minima in each group are connected through the internal rotor coordinate, $\phi$, while the barriers that separate the 20 groups are assumed to be much higher in energy.

Recent full-dimensional calculations of the $J = 0$ vibrational energies of CH$_5^+$ by Wang and Carrington showed a very different energy progression.[28] Based on that study, the lowest energy vibrationally excited state has an energy that is 10.4 cm$^{-1}$ above the zero-point energy, and the clumping of levels into groups of 20 nearly degenerate states is not observed. This is not surprising in light of the fact that there is a second large amplitude motion in CH$_5^+$, corresponding to the motion across the $C_{2v}$ transition state. After crossing this transition state an atom that had been in the CH$_3^+$ subunit has been exchanged with one that was in the H$_2$ unit. The barrier for this transformation is 331.2 cm$^{-1}$,[17] which is comparable to half of the harmonic frequency of the normal mode in CH$_5^+$ that moves the molecule from the minimum toward this transition state. For other isotopologues, the barrier is higher than the zero-point energy in this mode.[10]

Since motion across these saddle points primarily involves the hydrogen atoms and the saddle points all have energies below 350 cm$^{-1}$, it is not surprising that the ground state wave function of CH$_5^+$ has significant amplitude in all 120 minima as well as the saddle points that connect the minima.[12–14, 29] This observation has been supported by the recent work of Wang and Carrington[28]. They found that the energy level patterns for
the modes that correspond to isomerization of CH$_5^+$ are not significantly affected if they replace the potential surface of Jin et al.[30] by one in which any electronic energy below 2000 cm$^{-1}$ was replaced with an energy value of 2000 cm$^{-1}$. This and earlier studies point to an image of CH$_5^+$ in which it freely isomerizes among the 120 equivalent minima in the potential.[11–13, 15, 16] This picture is consistent with the energy progression calculated by Wang and Carrington[28] and means that the rotational structure will be more complicated than was anticipated in the earlier studies of Bunker and co-workers.[22] To date, a model Hamiltonian that fully captures the large amplitude motions in CH$_5^+$ has not been developed. This makes the assignment of the high resolution spectrum a challenge.

To investigate how the delocalization of the wave function among such a large number of equivalent minima is affected by vibrational excitation, and how this is reflected in the spectrum, I have embarked on a series of studies in which vibrationally and rotationally excited states of CH$_5^+$ are probed using quantum Monte Carlo techniques discussed in Chapter 3.[10, 31] Within this approach, excited states are generated by requiring that the wave function changes sign at selected molecular geometries. This approach generally does not produce molecular eigenstates. Instead it produces the lowest energy zero-order state that has the required properties. For example, we use this approach to calculate states in which the wave function changes sign as the CH bond lengths are extended and states in which the wave function changes sign in conjunction with a rotation of CH$_5^+$. In Chapter 4 I employ this technique and the high symmetry of CH$_5^+$ to calculate vibrationally excited states of CH$_5^+$ and CD$_5^+$ that transform as G$_1^+$ or A$_1^+$ under the G$_{240}$ complete nuclear permutation inversion group. In Chapter 5 the energies and wave functions of the $J = 1$, $|K_C| = 0, 1$ ro-vibrationally excited states of CH$_5^+$ and its deuterated isotopologues and the energy and wave function $J = 0$ inversion excited state are calculated. By calculating these vibrational and ro-vibrational excited state energies one goal is to aid in the assignment of
the high-resolution spectra of \( \text{CH}_5^+ \) to see if its presence can be identified in the interstellar medium.

### 1.2 Minimized Energy Paths

In addition to studies of the vibrational and ro-vibrational excited states of \( \text{CH}_5^+ \) and its deuterated isotopologues, a method for calculating the minimized energy paths for the reaction,

\[
\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ \rightarrow \text{CH}_3^+ + \text{H}_2
\]  

and its deuterated an partially tritiated isotopologues is also reported. The reaction path formalism has seen considerable success in the development of statistical theories of reaction rates, reaction dynamics as well as in reduced-dimensional treatments of quantum dynamics.[32] While understanding the minimum energy path that takes a system from one configuration to another is useful, the associated zero-point energy can change dramatically along the path. Miller, Handy and Adams [33] developed a reaction path Hamiltonian in which the reaction coordinate has been projected out, and the remaining degrees of freedom are treated as normal modes. This formalism has been used in a variety of applications, often to obtain harmonic zero-point corrections to the minimum energy path. Such harmonic evaluations of the zero-point energy correction can be made using a variety of electronic structure packages.

In many systems the vibrations are highly anharmonic at some points along the reaction path and harmonic treatments cannot fully capture the zero-point correction to the minimum energy path. For example, in systems that dissociate into two polyatomic fragments, six of the vibrations evolve into six additional translations and rotations as the system
goes from one molecule with $3N - 6$ vibrations to two molecules with a total of $3N - 12$ vibrations.

There are many molecules for which the vibrations are highly anharmonic, even in their ground states. CH$_5^+$ is a particularly extreme example of this. When the anharmonic vibrational ground state wave function is evaluated, it is found that there is comparable amplitude at the 120 equivalent minima and at the 180 low-energy saddle points that connect these minima.[8, 15] The highly delocalized nature of CH$_5^+$ makes quantum approaches essential, while the number of atoms (6) makes full-dimensional quantum treatments of the dynamics challenging, if not prohibitive.[28] An alternative approach is to define the reaction coordinate, and investigate the evolution of the anharmonically corrected energy and the associated wave function as the reacting species are brought together. This will require a formalism for evaluating anharmonic zero-point energies as a function of a reaction coordinate.

In Chapter 6 and 7 I study the minimized energy paths of the CH$_3^+ +$ H$_2$ reaction and its deuterated and partially tritiated (CH$_4$T$^+$, CH$_3$T$_2^+$) analogues. These systems are of interest due to their potential importance in astrochemical reactions[2, 34] and for reactions within planetary ionspheres[35]. In kinetics studies, Gerlich and co-workers[3] determined that the reactions,

$$\text{CH}_3-\text{nD}_n^+ + \text{HD} \rightarrow \text{CH}_4-\text{nD}_{n+1}^+ \rightarrow \text{CH}_2-\text{nD}_{n+1}^+ + \text{H}_2$$

have net rate constants of $1.6 \times 10^{-9}$ cm$^3$ s$^{-1}$ at 15 K. These rate constants are independent of the value of n in eq 1. This value of the rate constant is slightly larger than the Langevin rate constant of $1.32 \times 10^{-9}$ cm$^3$ s$^{-1}$ and, after 3 seconds, more than 99% of the CH$_3^+$ has been converted to CD$_3^+$ at 15 K. While the efficiency of these reactions can be rationalized by the exothermicity of the reactions due to the smaller zero-point energy of the products of reaction 1 compared to that of the reactants, the question remains if other dynamical effects
are at play. Bowman and co-workers investigated the CH$_3^+$ + HD reaction using classical mechanical approaches, and obtained rates for the forward reaction that are consistent with experiment.[36] However, classical mechanics is not expected to provide a complete picture as it is not sensitive to the zero-point effects that are responsible for the exothermicity of the hydrogen/deuterium exchange reaction.
To better understand why it is difficult to understand the spectrum CH$_5^+$ and its isotopologues, it is useful to review some of the properties of CH$_5^+$. While the ground state has equal probability amplitude in all 120 minima, some of the excited states will not. This assertion reflects the fact that the full permutation/inversion symmetry of CH$_5^+$ ($G_{240}$) is much higher than the point group symmetry of any of the stationary points that are sampled by the ground state wave function ($C_{2v}$). Similar behavior is seen in molecules, like methanol[37] that have a three-fold torsion barrier. In Figure 2.1, a one-dimensional potential [$V(\phi) = \frac{V_3}{2}(1 - \cos(3\theta))$] is plotted as well as the probability amplitude associated with the three lowest energy eigenstates. As is seen, the ground state (plotted in red) has equal amplitude in all three wells, while the other two states (plotted in green dash-dot-dot and blue dash) have near equal amplitude in the two central wells but either zero or more amplitude in the outer wells. Similar behavior is expected for degenerate levels in CH$_5^+$. This being the case, it will also be useful to find methods for dividing the probability amplitude into 120 pieces, each of which is assigned to a single potential minimum.

As is mentioned in Chapter 1, there are three important low-energy stationary points on the CH$_5^+$ potential. All have calculated energies that are below 350 cm$^{-1}$, and are depicted in Figure 1.1.[17] On average, all five CH bonds are equivalent. In examining the CH bond lengths and HH distances at the three stationary points, the equivalence is less obvious. As the bond lengths reported in Table 2.1 indicate, in the two structures with $C_s$ symmetry,
Figure 2.1: Potential (thick black line) and probability amplitudes associated with the three lowest energy wave functions for a three-fold torsion barrier. The state plotted in red is the ground state. The other two states (blue dash and green dash-dot-dot) make up the doubly degenerate first excited state.
the shortest H-H distance is only 0.95 Å, based on the CCSD(T) calculations.[17, 19] These
two hydrogen atoms are also associated with CH distances that are longer than the other
three CH bond lengths by about 0.01 Å. Motion across the C₅(II) saddle point corresponds
to a 60° rotation of the CH₃⁺ subunit and is shown in Figure 1.1a. The motion across the
C₂ᵥ saddle point corresponds to exchange of a hydrogen atom between the two subunits
and is shown in Figure 1.1b.

Table 2.1: The CH bond lengths and HH distances at the three stationary points.ᵃ

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (in Å)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>C₅(I)</td>
</tr>
<tr>
<td>CH_A</td>
<td>1.20</td>
</tr>
<tr>
<td>CH_B</td>
<td>1.20</td>
</tr>
<tr>
<td>CH_C</td>
<td>1.11</td>
</tr>
<tr>
<td>CH_D</td>
<td>1.09</td>
</tr>
<tr>
<td>CH_E</td>
<td>1.09</td>
</tr>
<tr>
<td>H_AH_B</td>
<td>0.95</td>
</tr>
<tr>
<td>H_AH_C</td>
<td>2.04</td>
</tr>
<tr>
<td>H_AH_D</td>
<td>1.72</td>
</tr>
<tr>
<td>H_AH_E</td>
<td>1.72</td>
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<tr>
<td>H_BH_C</td>
<td>1.44</td>
</tr>
<tr>
<td>H_BH_D</td>
<td>1.94</td>
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<tr>
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<td>H_CH_D</td>
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<tr>
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<td>1.79</td>
</tr>
<tr>
<td>H_DH_E</td>
<td>1.88</td>
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</table>

ᵃ see Figure 1.1
ᵇ Ref. [17]

By employing the H₂ and CH₃⁺ subunits in these studies, an arbitrary molecular geo-
metry can be assigned to a specific minimum on the potential. To achieve this the five
hydrogen atoms must be labeled in an arbitrary structure of CH₅⁺ so that they correlate to
the labels in Figure 1.1. The hydrogen atoms that make up the H₂ subunit are identified
as H_A and H_B, while the hydrogen atoms labeled C through E make up the CH_3^+ subunit. The B and C labels have been chosen such that the distance between these two atoms be the shortest of the six possible hydrogen-hydrogen distances that involve one hydrogen atom from each subunit. The atoms labeled D and E are chosen to satisfy the requirement that the C, D, and E, hydrogen atoms contained within the CH_3^+ subunit are oriented in a clock-wise manner with respect to the plane containing the carbon atom and the hydrogen atoms labeled A and B in the +z-axis. While this is shown for the three stationary point geometries in Figure 1.1, this approach can be applied to any arbitrary molecular geometry.

The partially deuterated isotopologues of CH_5^+ are treated in an analogous manner. The addition of deuterium atoms results to a reduction in the symmetry of the molecule. This is because while five hydrogen atoms can be arranged in 120 unique ways (5!), four hydrogen atoms and one deuterium atom (or the reverse) can only be arranged 24 ways (4! × 1!). For two hydrogen atoms and three deuterium atoms (or the reverse) this drops to 12 ways (3! × 2!). For CH_4D^+ and CHD_4^+, the molecule is represented by the G_{48} Complete Nuclear Permutation Inversion (CNPI) group shown in table 2.2. CH_3D_2^+ and CH_2D_3^+, are represented by the G_{24} CNPI group shown in table 2.3. Due to quantum mechanical placement of the deuterium atom(s) into the CH_3^+ subunit and hydrogen atom(s) in to the H_2 group[9, 10], there is a reduction in the number of occupied minima. Probability amplitude for the C_s(II) and C_{2v} saddle points is still observed for all isotopologues, however the barrier to exchange may be increased. The same labeling system is applied.
Table 2.2: The $G_{48}$ character table for CH$_4$D$^+$ and CHD$_4^+$

<table>
<thead>
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<th>$G_{48}$</th>
<th>E</th>
<th>(12)*</th>
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<td>-1</td>
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Table 2.3: The $G_{24}$ character table for CH$_3$D$_2^+$ and CH$_2$D$_3^+$

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CHAPTER 3

Theory

First developed by Metropolis and Ulam, Monte Carlo is a statistical approach to solving differential equations. One of its original uses was to determine the distance neutrons would travel through materials. It has since been employed in many fields. In this work, Diffusion Monte Carlo (DMC) is employed. It was developed by Anderson based on the observation that the imaginary time time-dependent Schrödinger equation can be mapped onto a diffusion equation. Here, the Diffusion Monte Carlo method is discussed.

3.1 Diffusion Monte Carlo

Diffusion Monte Carlo is a statistical approach for solving the imaginary time time-dependent Schrödinger equation and is employed to obtain solutions to the imaginary time time-dependent Schrödinger equation that gives the energies and wave functions that are solutions to the time-independent Schrödinger equation. One way to start is to consider the time-dependent Schrödinger equation,

\[ i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H}\Psi(t) \]  (3.1)

where,

\[ |\Psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar}|n\rangle \]  (3.2)
\( c_n \) are the expansion coefficients at \( t = 0 \), \(|n\rangle\) is the \( n^{th} \) eigenstate and \( E_n \) are the corresponding energy eigenvalues. In implementing DMC one way to start is by transforming the time-dependent Schrödinger equation into imaginary time by substitution of the imaginary time variable \( \tau \) where,

\[
\tau = \frac{it}{\hbar}
\]

and equation 3.1 then becomes,

\[
|^\Psi(\tau)\rangle = \sum_n c_n e^{-E_n \tau} |n\rangle
\]

As equation 3.4 is propagated in imaginary time, the solution will go to the lowest energy state under any constraints that are imposed by the simulation. If no constraints are imposed the solution will go to the ground state.

How then can Diffusion Monte Carlo be employed to solve the set of equations above? First, the time-dependent Schrödinger equation is integrated so that it can be expressed in a propagator form,

\[
|^\Psi(\tau + \Delta \tau)\rangle = e^{-(\hat{H} - E_0)\Delta \tau} |\Psi(\tau)\rangle
\]

The Hamiltonian, \( \hat{H} \), can then be rewritten as \( \hat{H} = T + V \). When the time steps, \( \Delta \tau \) are small, the kinetic \( T \) and potential \( V \) energy portions of the propagator in equation 3.5 are approximately separable and,

\[
|\Psi(\tau + \Delta \tau)\rangle \approx e^{-(V - E_0)\Delta \tau} e^{-T \Delta \tau} |\Psi(\tau)\rangle
\]

This is the split-operator form of the time dependent Schrödinger equation that is commonly used in time-dependent quantum mechanics studies. Equation 3.6 has been shown to be accurate for small time steps[41] and errors within the statistical fluctuations in the Diffusion Monte Carlo simulations are accounted for.
The effect of the action of the kinetic and potential energy portions of the propagator in equation 3.6 on an arbitrary wave function is then evaluated. As Diffusion Monte Carlo is a statistical approach to solving the imaginary time time-dependent Schrödinger equation, the basis set is the ensemble of $\delta$—functions, where one $\delta$-function describes one CH$_5^+$ molecule. The $\delta$-functions are often referred to as walkers. At each time step, $\Delta \tau$, the size of the ensemble and the coordinates of each of the $\delta$—functions in the ensemble are allowed to change. For simplicity, each time step is divided into two portions, which corresponds to the action of the kinetic, and potential energy on each of the $\delta$-functions and each $\delta$-function is treated independently.

As I am employing Diffusion Monte Carlo to calculate the ground and excited state energies of CH$_5^+$, it is easiest to work in Cartesian Coordinates. As such the kinetic portion of the Hamiltonian takes the form:

$$\hat{T} = \sum_{i=1}^{18} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial q_i^2}$$

(3.7)

As there are six atoms in CH$_5^+$, there are 18 Cartesian coordinates, the mass of each atom is $m_i$, $q_i$ represents a cartesian coordinate of one of the six atoms. For each walker, when the exponential of equation 3.7 is applied to the $\delta$-function, a gaussian with a width of $\sqrt{\frac{2\Delta \tau}{m_i}}$, is obtained.[39] In order to retain the form of the wave function as an ensemble of $\delta$-functions, instead of allowing these functions to remain as Gaussian functions, each walker is displaced in each of the $3N$ Cartesian coordinates that define its position in space. The size of the displacement is obtain from a Gauss-random distribution with a width of $\sqrt{\frac{2\Delta \tau}{m_i}}$.

The Monte Carlo portion is also expressed as the position of each walker is displaced along each of its coordinates. After the displacements are made, the width of the $\delta$-function is reset to zero. The step size of each walker is determined by a random number generator that uses the central limit theorem to generate a Gaussian random number distribution. The mass also impacts the size of each step as Cartesian coordinates that represent hydrogen
atoms are lighter and will be displaced more than Cartesian coordinates that represent carbon atoms. Each coordinate of a given walker will take a slightly different sized step based on a Gaussian distribution. The potential energy portion of the calculation will also employ Monte Carlo statistics.

After the kinetic portion of the propagator is evaluated, the potential energy portion is applied. Since the walkers are diffusing over a potential surface, they could sample both classically allowed and classically forbidden regions of the potential. If a walker has moved into a region where the potential energy is less than $E_0$, the walker is in the classically allowed portion of the potential, $\exp[-(V - E_0)\Delta\tau] > 1$, and additional walkers may be added to the simulation; if the potential energy is now greater than $E_0$, the walker is in the classically forbidden region of the potential, $\exp[-(V - E_0)\Delta\tau] < 1$, and the walker may be removed from the simulation. In the classically forbidden region of the potential, $\exp[-(V - E_0)\Delta\tau]$, is compared to a survival probability generated from a uniform random distribution with a range of zero to one. If the value of the number generated from a random distribution is greater than the value of $\exp[-(V - E_0)\Delta\tau]$ then the walker will be removed from the ensemble. Likewise, if the walker is in a classically allowed portion of the potential the value of the exponential will determine the number of walkers added to the ensemble ($\exp[-(V - E_0)\Delta\tau] - 1$). The exponentials do not necessarily generate integers so often there is a partial walker left over. The probability of the partial walker being added to the ensemble is calculated by the same method used to calculate if a walker is removed from the potential. The individual energy of each walker is then averaged together to calculate the total energy of the system, the zero point energy, $E_0 = \langle V \rangle$. A cartoon of walkers being added to and removed from the ensemble is shown in Figure 3.1.
Figure 3.1: A cartoon showing walkers being added to and removed from a 1-dimensional potential surface. In frames a) and d) an initial walker, described by a red dot is shown. The location of the initial walker after the kinetic portion of the equation has been applied is shown in frames b) and e). In frame c), the walker is in a classically allowed portion of the potential and new walkers (blue circles) have been added to the ensemble. In frame f), the walker was in a classically forbidden portion of the potential and has been removed from the ensemble. The black horizontal line represents $E_0$.

While a Monte Carlo sampling of the wave function ia obtained, it requires a value for $E_0$. $E_0$ can be approximated by employing the formula,[39, 42]

$$E_0 \approx W(\tau) = \bar{V} - \alpha \left( \frac{N(\tau) - N(0)}{N(0)} \right)$$

(3.8)

$W(\tau)$ is an estimate of the zero point energy, and $\bar{V}$ is the average energy of the ensemble of walkers. $N(\tau)$ is the number of walkers at time $\tau$ and if it is greater than the initial
number of walkers, $N(0)$, $W(\tau)$ will be smaller than the average potential energy, so at the next time step, more walkers will be in configurations where the potential energy is larger than $E_0$. This will lead to more walkers being removed from the simulation. The value $\alpha$ is constant and in this work is set to 0.1 Hartree. If there are fewer walkers at time $\tau$, then $W(\tau)$ will become larger than the average potential energy. The value of $\alpha$ is approximately $1/\Delta \tau$.

While Diffusion Monte Carlo is a ground state method, various techniques can be employed to transform it into a method for calculating excited states. These methods involve placing a node in the wave function. Fixed-node DMC works by placing a node at a specific value in a chosen coordinate of the wave function $\Psi$.[40] Adiabatic Diffusion Monte Carlo (ADMC) relies on changing the position of the node along this chosen coordinate to determine the location of a node.[43, 44] Specific examples of these techniques will be discussed in chapters 4, 5 and 6.

### 3.2 Analysis Techniques

One-dimensional probability distributions, rotational constants and participation ratios are quantities generated from the calculated probability amplitudes. The descendant weighting technique is used to obtain the probability amplitude from the DMC wave function,[42, 45] which can be projected onto any coordinate or coordinates of interest. These quantities give information that is essential for generating a picture of the structures that are sampled by $\text{CH}_5^+$ in the ground and various excited states. As such, analysis of these quantities aids in the overall understanding of the dynamics of $\text{CH}_5^+$. When analyzing the wave functions several techniques are used.
3.2.1 Projections of the Probability Amplitude

To assess changes in the probability amplitude with rotational and/or vibrational excitation, various projections of the probability amplitude are investigated. One-dimensional probability distributions are evaluated by projecting the probability amplitude onto a single coordinate. I will focus on the coordinates that are the CH bond lengths and HH distances, and the two isomerization coordinates, $\phi$, and $q$.\[10,31] Here $q$ is the coordinate that connects two adjacent minima through a $C_{2v}$ saddle point.

$$|q| = |r_{H_B H_C} - r_{H_A H_B}| \quad (3.9)$$

While motion along $\phi$ corresponds to motion across a $C_s$(II) saddle point. Specifically, $\phi$ is defined as the angle between the vector along CH$_C$, CH$_D$, or CH$_E$ bond axis and the plane that contains H$_A$, H$_B$ and the carbon atom.\[31] These coordinates give a statistical sampling of the structural properties of the excited states of CH$_5^+$. Other coordinates may be calculated for specific studies and will be discussed as they are employed.

3.2.2 Participation Ratios

In addition to projections onto internal coordinates, the participation ratios provide a useful measure of the delocalization of the wave function among the 120 equivalent minima. The more delocalized the wave function is, the more minima will be sampled. The participation ratio, $\rho$, provides a measure of how many minima are populated in a given excited state. This quantity is defined as:\[46,47]

$$\rho = \frac{1}{\sum_{i=1}^{120} \frac{P_i^2}{P_i}} \quad (3.10)$$
where $p_i$ represents the ratio of the probability amplitude associated with the walkers that is assigned to the $i$th minimum to the total number of walkers in the simulation. To obtain these populations, each walker is assigned to one of the 120 minima on the potential based on the discussion of hydrogen atom labeling in Chapter 2. In the ground state, all the $p_i = 1/120$ and $\rho = 120$. For excited states, the minima will not necessarily contain equal probability amplitude and $\rho$ provides a measure of how many minima are sampled in these states. $\rho$ provides a good approximation to the number of minima in the potential where the wave function has amplitude. Specifically, if $n$ minima contain equal probability amplitude of $1/n$ and the others have zero probability, $\rho = n$. 
CHAPTER 4

Theoretical Investigations of Mode Mixing in Vibrationally Excited states of CH$_5^+$

In this Chapter, I draw from the high symmetry of CH$_5^+$ and investigate the nature of vibrationally excited states obtained by putting one quantum of excitation in the vibrational modes that are generated by taking the linear combinations of the CH bond lengths that transform as $A_1^+$ or $G_1^+$ under the $G_{240}$ permutation inversion symmetry group for CH$_5^+$.\[48\]

For comparison, I have also studied how complete deuteration affects these results by calculating the same set of excited states for CD$_5^+$. It should be noted that while the nodal structure that has been chosen depends on the values of the CH or CD distances, the fact that DMC will generate the lowest energy state with the chosen symmetry properties does not ensure that the states accessed will be CH stretch fundamentals. Rather, by analyzing the delocalization (or localization) of the probability amplitudes associated the ground and excited states among the 120 equivalent minima on the potential surface, insights are gained into the nature of the couplings within in CH$_5^+$.

4.1 Theory

4.1.1 Diffusion Monte Carlo

Diffusion Monte Carlo (DMC) is used to obtain both the energy and wave functions for the ground and selected excited states of CH$_5^+$. In this study, the global potential surface for CH$_5^+$, developed by Bowman and co-workers is used.[17] To account for the equivalence of the minima, the DMC algorithm has been modified slightly to ensure that the wave function has the proper symmetry. Specifically, at each time step the coordinates of a randomly selected pair of fungible hydrogen atoms are exchanged. In principle this should not be necessary, but it has been found that when there is an effective barrier between minima that is large enough that there is zero-probability amplitude in the classically forbidden region of the potential, the distribution of walkers can become localized in a subset of the minima.[49] This addition to the algorithm prevents this from happening and has no effect on the resulting energies, within the statistical uncertainties of the simulation. Within the simulations, a time step of $\delta \tau = 10$ a.u. is employed.

The focus of the present study is on vibrationally excited states of CH$_5^+$ and the fixed-node treatment, originally described by Anderson, to evaluate these energies and wave functions is used.[40] Nodal surfaces divide the wave function into two pieces for which its amplitude is either positive or negative throughout. Near the node, the wave function approaches zero with a finite slope. This behavior is identical to that of a wave function near an infinite potential barrier. As such, within the fixed node treatment, configuration space is divided into two parts, using the nodal surface as the dividing surface. The region of space in which the amplitude of the wave function is positive is denoted $r_+$ and the remaining region of space is denoted $r_-$. As such, the fixed-node calculations are performed in two parts. In one, the global potential for CH$_5^+$ is used for $r_+$, while the potential is made to be infinite in $r_-$. In the second, the regions are reversed. Since the
amplitude of the wave function must be zero in regions of infinite potential energy, any 
walker that attempts to cross from $r_+$ to $r_-$ will be removed from the ensemble. Further, 
since $\Delta \tau$ is finite, a recrossing correction needs to be introduced.[40] This correction depends 
exponentially on the ratio of the product of the distance of the walker from the node before 
and after a displacement to the mass associated with this motion. Since nodal surfaces that 
depend on a single coordinate are being considered, the appropriate mass is given by the 
reciprocal of the Wilson $G-$matrix element associated with the nodal coordinate.[50] As 
the energies associated with the two simulations should be equal, a check on the functional 
form of the nodal surface is provided by calculating the differences between these two 
energies. If it is statistically non-zero the node has not been properly placed. A total of four 
independent DMC simulations are performed on each side of the node. Each independent 
simulation has a unique set of starting parameters. The energies reported are an average 
of these independent simulations. An $\alpha$ parameter of 0.1 Hartree is sufficient to control the 
fluctuations of the number of walkers within a given simulation.

A challenge in implementing the fixed-node treatment comes in the definition of the 
nodal surface. For the present study, it is a requirement that the wave function changes 
sign at a specified value of the various symmetry adapted linear combinations of the CH or 
CD bond lengths, described below. This is straightforward to implement when the value of 
the coordinate at the node can be determined to be zero, by symmetry. Complications arise 
for determining the position of the node in excitations along totally symmetric coordinates. 
In this case, a modified version of the fixed-node approach in the form of Adiabatic Diffusion 
Monte Carlo (ADMC) is implemented.[43, 44] This approach provides a way to determine 
the optimal position of the nodal surface as well as the associated excited state energy.

Once the simulations have been run, two separate wave functions are obtained, one with 
positive amplitude and one with negative amplitude. The full wave function is obtained by
splicing these two pieces together. This introduces an additional challenge. Since the simulations that generated the two parts of the wave function were performed independently, one must determine the relative weights of the two pieces. Several approaches have been proposed for doing this.[51] One possibility is to require that the excited state is orthogonal to the ground state.[52] A second approach, discussed by Buch and co-workers,[53] introduces the requirement that the slope be continuous across the node. A modification of the second approach is employed, requiring the second derivative of the probability amplitude be continuous across the node. The challenge in this approach is that the wave function has a $3N$ dimensional representation, while the nodal surface is $3N - 1$ dimensional. If the probability amplitude is projected along a coordinate in which the wave function changes sign, the problem becomes tractable.

4.1.2 Symmetry Coordinates

As alluded to above, in this Chapter, the vibrationally excited states of CH$_5^+$, defined as the Symmetry Adapted Linear Combinations (SALC’s) of the CH bond lengths that transform as $A_1^+$ or $G_1^+$ under the G$_{240}$ Complete Nuclear Permutation Inversion (CNPI) group are examined. A CNPI group is defined by all of the permutations of a given set of like nuclei. The group is of order $\prod_i n_i!$ to account for all of the permutations of each of the sets of $n_i$ identical nuclei in the molecule.[48] The number of permutations is then multiplied by two to account for inversion. In the case of CH$_5^+$, there are five hydrogen atoms, and one carbon atom, so the CNPI group has $240 = 5!1!2$ elements. The character table for the G$_{240}$ group is shown in Table 4.1.

Based on this character table, the Symmetry Adapted Linear Combinations of the five CH or CD stretches transform under $G_1^+$ and $A_1^+$ and are defined as
Table 4.1: The G_{240} character table for CH_{5}^+ 

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<td>0</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>-4</td>
<td>2</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>H_1^-</td>
<td>5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-5</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>H_2^-</td>
<td>5</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>-5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>I^-</td>
<td>6</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-6</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
\[ q_{A_1^+} = \sqrt{\frac{1}{5}} [r_1 + r_2 + r_3 + r_4 + r_5] \]  
\[ q_{G_1^+;1} = \sqrt{\frac{1}{2}} [r_4 - r_5] \]  
\[ q_{G_1^+;2} = \sqrt{\frac{1}{6}} [2r_3 - r_4 - r_5] \]  
\[ q_{G_1^+;3} = \sqrt{\frac{1}{12}} [3r_2 - r_3 - r_4 - r_5] \]  
\[ q_{G_1^+;4} = \sqrt{\frac{1}{20}} [4r_1 - r_2 - r_3 - r_4 - r_5] \]  

where \( r_j \) represents the distance between the carbon atom and the \( j \)th hydrogen atom.

In these definitions of the excited states of \( G_1^+ \) symmetry, the five hydrogen atoms are no longer equivalent, and in the permutation algorithm, described above, only equivalent hydrogen atoms are permuted. For example, in the case of the state with excitation in \( q_{G_1^+;1} \), the hydrogen atoms labeled four and five are not equivalent to any of the others, but the three remaining hydrogen atoms, those labeled 1, 2 and 3, remain equivalent. As such, only permutations among the three equivalent hydrogen atoms are considered. As a result the 120 equivalent minima can be subdivided into 20 groups of 6. The probability amplitude in minima in the same group must be equal.

The above discussion implies a loss of symmetry in some excited states and this may be surprising. If one considers the plots of the eigenstates of the one-dimensional potential, plotted in Figure 2.1, one immediately sees that the probability amplitudes that arise from the two states with \( E \) symmetry, plotted in red and blue, do not have equal amplitude in all three wells. It is this factor that is being captured in the permutation algorithm. Even in the absence of the permutation different populations of walkers are found in different potential minima. The permutation approach attempts to remove differences in the populations that are due to statistics as opposed to differences that reflect the physics of the system.
In the end, the energies of the calculated states are not affected by the introduction of permutation.

In the discussion that follows, minima are identified based on the locations of the unique atoms using a five character string indicating which of the five hydrogen atoms is in the positions labeled A, B, C, D, and E. When a hydrogen atom is unique by symmetry, its atom number is used to denote its position, as in the case of H_4 and H_5 in the example above. When two or more hydrogen atoms are equivalent by symmetry, their identities are represented by the letter X or Y. In the example above, X could represent H_1, H_2 or H_3. Table 4.2 provides a list of all distinct minima, based on the definition of the four modes that transform under $G^+_1$ in eqs 4.2 - 4.5.

### 4.1.3 Rotational Constants

Rotational constants for the various excited states are calculated by first transforming the geometries of each of the walkers in the ensemble into an Eckart frame.[10, 54, 55] The precise definition of this frame depends on the choice of the static molecular model. With the high symmetry of CH$_5^+$ and the existence of three classes low-energy stationary points, there are a number of structures that could be used. For example, there are 120 geometries that correspond to each of the C$_s$(I) minima, 120 for each of the C$_s$(II) saddle points, and 60 for each of the C$_{2v}$ saddle points. Following earlier work in our group on isotopologues of CH$_5^+$,[10] the rotational constants are evaluated, using each of the 240 C$_s$(I) and C$_s$(II) stationary points, enumerated above, to define the static molecular model. Once the static molecular model is chosen, all the walkers are rotated into an Eckart frame based on that choice. The rotational constants are evaluated as the expectation values of the elements of the inverse of the moment of inertia tensor, multiplied by the appropriate constants.

As described above, for some of the excited states, the probability amplitudes at the minima that correspond to the 120 C$_s$(I) static molecular models will not be equal. In
Table 4.2: Identification of the unique sets of minima for each of the four excited states along the $G_1^+$ modes.$^a$

<table>
<thead>
<tr>
<th>mode</th>
<th>number of equiv. min.</th>
<th>positive$^b$</th>
<th>negative$^c$</th>
<th>near zero$^d$</th>
<th>zero probability$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{G_1^+1}$</td>
<td>6</td>
<td>4xxx5; 4xx5x; xx4xx; x5x4x</td>
<td>5xx4x; x4xx</td>
<td>xx4x5; x5x4x</td>
<td>45xx5; 54xx4</td>
</tr>
<tr>
<td>$q_{G_1^+2}$</td>
<td>4</td>
<td>3xyxx; x3yyx</td>
<td>yyyxx; y5xx</td>
<td>y3xyx; y3yyx</td>
<td>yyxxy; yxyx3</td>
</tr>
<tr>
<td>$q_{G_1^+3}$</td>
<td>6</td>
<td>12xxx, 21xxx</td>
<td>xx1x2; xxx2</td>
<td>x21xx, 1xxx2</td>
<td>2xxx1; x1x2</td>
</tr>
<tr>
<td>$q_{G_1^+4}$</td>
<td>24</td>
<td>x1xxx, 1xxxx</td>
<td>x1xxx, xxxx1</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ the number labels identify the position of the unique hydrogen atoms with the five positions corresponding to ABCDE, as described in the text.

$^b$ Populated minima in the region where $q_{G_1^+n} > 0$; $^c$ Populated minima in the region where $q_{G_1^+n} < 0$; $^d$ Minima less than 10% the amplitude of the most populated minimum; $^e$ Minima less than 1% the amplitude of the most populated minimum; $^f$ X = H$_1$, H$_2$, or H$_3$; $^g$ X = H$_1$ or H$_2$ and Y = H$_4$ or H$_5$; $^h$ X = H$_3$, H$_4$ or H$_5$; $^i$ X = H$_2$, H$_3$, H$_4$ or H$_5$

collecting this data, the weighted averages of the 120 calculated rotational constants are reported, weighting the values by $p_i$ in eq. 3.10. When a C$_s$(II) saddle point structure is used for the static molecular model, the individual rotational constants are weighted by the average populations in the minima that are connected by that saddle point. Again, the reported rotational constants represent the weighted average of the results of the 120 separate calculations.
Table 4.3: Excited state energies (in cm\(^{-1}\)) for CH\(_5^+\) and CD\(_5^+\).\(^a\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Node(^b)</th>
<th>Energy</th>
<th>(\rho)^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_5^+)</td>
<td>(q_{G_1^+;2} = 0)</td>
<td>1039 ± 5</td>
<td>32 ± 1</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;3} = 0.01527 ± 0.00005) Å</td>
<td>1150 ± 5</td>
<td>36 ± 1</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;1} = 0)</td>
<td>1172 ± 5</td>
<td>65 ± 5</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;4} = 0.01435 ± 0.00004) Å</td>
<td>1383 ± 5</td>
<td>108 ± 2</td>
</tr>
<tr>
<td></td>
<td>(q_{A_1^+} = 2.58790 ± 0.00005) Å</td>
<td>2160 ± 5</td>
<td>120</td>
</tr>
<tr>
<td>CD(_5^+)</td>
<td>(q_{G_1^+;2} = 0)</td>
<td>628 ± 5</td>
<td>24 ± 1</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;3} = 0.01401 ± 0.00007) Å</td>
<td>716 ± 5</td>
<td>34 ± 1</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;1} = 0)</td>
<td>729 ± 5</td>
<td>60 ± 3</td>
</tr>
<tr>
<td></td>
<td>(q_{G_1^+;4} = 0.01328 ± 0.00004) Å</td>
<td>893 ± 5</td>
<td>104 ± 2</td>
</tr>
<tr>
<td></td>
<td>(q_{A_1^+} = 2.57435 ± 0.00003) Å</td>
<td>1551 ± 5</td>
<td>120</td>
</tr>
</tbody>
</table>

\(^a\) Energies are reported relative to a zero-point energy of 10 916±5 cm\(^{-1}\) for CH\(_5^+\) and 8045 ± 5 cm\(^{-1}\) for CD\(_5^+\).

\(^b\) Definition of the node used for the fixed-node DMC calculation

\(^c\) Defined in eq 3.10.

4.2 Results

DMC is used to evaluate the energies, wave functions and probability amplitudes of the lowest energy states that have a single node along each of the five coordinates, defined in eqs 4.1 - 4.5. The resulting energies are reported in the third column of Table 4.3. There are two surprising features of these results.

First, the calculated energies are too low for these calculated states to be fundamentals in the CH stretching vibrations. This is particularly notable for the four states with nodes in the four \(q_{G_1^+;n}\) coordinates. Even the fifth state, the one in which the wave function is constrained to change sign at a specified value of the sum of the five CH distances, has an energy that is on the very low end of the CH stretch frequency range. In contrast, based on converged variational approaches, Wang and Carrington obtained frequencies for the two stretch fundamentals of CH\(_5^+\) of 2467 cm\(^{-1}\) \((G_1^+)\) and 2969 cm\(^{-1}\) \((A_1^+)\).\(^{[28]}\) Based on
the large frequency differences, it appears that the fixed-node DMC calculations are not
generating the CH stretch fundamentals. Rather I have found the lowest energy state that
has the property that the wave function changes sign at a specified value of one of the these
linear combinations of the internal coordinates. Based on the frequencies, I believe that
the states that are being sampled can be better described as combinations of HCH bends
and the two low-frequency isomerization coordinates than as CH stretches.

This leads to the second observation. While one can construct the set of four coordi-
nates, given in eqs 4.2 - 4.5, that transform under the $G^+$ irreducible representation, the
calculated energies of the states that have nodes when each of these coordinates is zero
are not equal. The lack of degeneracy of these states is further illustrated by the fact that
each state has a different value of the participation ration, $\rho$, given in the fourth column of
Table 4.3.

Before continuing to a discussion of the states that were evaluated in this study, it is
useful to consider how a calculation that imposes a node based on a linear combination of
CH bond lengths could produce states whose energies are too low to be CH or CD stretch
fundamentals. It is also appropriate to ask if the calculated states are relevant to a fuller
understanding of the spectroscopy and dynamics of CH$_5^+$ and CD$_5^+$.

The fact that the calculated frequencies are too low to be CH or CD stretch fundamen-
tals was, at first, surprising, but not without precedent. In our previous study of excited
states of CH$_3^+$ an excited state was generated for which it was required the wave function
to change sign when $r_{12} - r_{23} = 0$ where $r_{ij}$ represented the distance between the $i$th and
$j$th hydrogen atom.[31] Such an excited state would, at first, be thought to correspond
to putting a node at the $C_{2v}$ saddle point, shown in Figure 1.1a. In fact the frequency
that was obtained and the projections of the probability amplitude led us to conclude that
the excited state contained a node at the $C_s$(II) saddle point, shown in Figure 1.1b. The
difference between the expected and actual excited state that was calculated reflects the
fact that the DMC simulation will provide the lowest energy state that has the requisite symmetry properties. Unexpected excited states have also been encountered in studies of Ne$_2$OH[55], H$_5$O$_2^+$[56] and H$_3$O$_2^-$. [57]

The situations encountered in H$_5$O$_2^+$ and H$_3$O$_2^-$ are most similar to the present study. These systems can be thought of as either a pair of water molecules or hydroxide ions with an excess proton whose average position is on the OO axis, equidistant from the two oxygen atoms. In these systems, fixed-node DMC provided frequencies for the excited states that correspond to displacement of the central proton along the OO axis that was in good agreement with other calculations and experiment.[56–58] On the other hand, the frequency that corresponded to displacement of the shared proton perpendicular OO axis was calculated to be close to 1000 cm$^{-1}$ in the DMC studies, while other approaches placed these frequencies between 1300 and 1500 cm$^{-1}$.[56, 57, 59] Interestingly, the frequencies calculated from DMC corresponded to transitions in the spectra of these species, while little intensity is seen at the frequencies calculated by other methods. Further analysis of the DMC wave functions in combination with comparison to states with similar energies in variational calculations led us to conclude that the DMC calculations were generating excited states that involved combination bands of lower frequency modes. More recent multi-configurational time-dependent Hartree calculations of H$_5$O$_2^+$ made similar assignments to the observed bands near 1000 cm$^{-1}$.[60, 61]

The insights gained from these studies lead us to expect that while the states that are evaluated in the present study are not CH stretch excitations, the identification of this set of five states provides us with an opportunity to investigate the nature of the coupling between the high and low frequency vibrational modes as well as obtaining an initial look at rotation-vibration mixing in CH$_5^+$. 
4.2.1 The $A_1^+$ state

The excited state with $A_1^+$ symmetry has an energy of $2160\pm 5\ \text{cm}^{-1}$. This frequency is about $800\ \text{cm}^{-1}$ lower than the value of this fundamental calculated variationally by Wang and Carrington\[28]\ and calculated by vibrational configuration interaction approaches by Huang et al.\[8]\ It is also to the red of the CH stretch band in the spectrum, reported by Schlemmer and co-workers.\[6]\ Based on this, it is anticipated that the calculated state is not the CH stretch fundamental, but rather a lower energy combination band, that, due to stretch/bend couplings, has the property that the wave function changes sign at a specified value of the CH distances. Both a calculation of the spectrum of $\text{CD}_5^+$ and a low-resolution spectrum have been reported.\[7, 9]\ However, the calculated frequency of $1551\pm 5\ \text{cm}^{-1}$ is significantly below the calculated CD stretch fundamental band, and likely corresponds to a combination band within the $\text{CD}_5^+$ spectrum as well. In addition, the near factor of $1/\sqrt{2}$ between the frequency of the calculated frequency and the corresponding one in $\text{CH}_5^+$ leads one to expect that this calculated state is also a combination band, rather than representing a fundamental in the CD stretch.

To investigate further the nature of this excited state, in Figure 4.1 projections of the associated probability amplitude along four internal coordinates are plotted. For comparison, the corresponding ground state distributions are plotted with thin colored lines. In both $\text{CH}_5^+$ and $\text{CD}_5^+$, the projections of the probability amplitude onto $r_{\text{HH}}$ and $\phi$ are not changed significantly with vibrational excitation. This indicates that structurally this excitation does not change how the molecule samples the various potential minima that are connected by the $C_s$(II) saddle points. On the other hand, there is an increase in the widths of the distributions when they are projected along $q$ and the CH distance coordinates. The CH distance distribution also contains a shoulder at larger values of the CH bond lengths. The increased width is not unexpected as the introduction of a node at a specified value of the average CH distance will necessarily increase the width of the probability amplitude.
Figure 4.1: Projections of the probability amplitudes for the $A_1^+$ excited state of $CH_5^+$ are plotted as functions of the (a) CH distance, (b) HH distance, (c) methyl rotor coordinate, $\phi$, and (d) $C_{2v}$ isomerization coordinate, $q$, with thick black lines. The corresponding distributions for $CD_5^+$ are plotted in panels e-h. The thin red and green lines represent the corresponding projections for the corresponding ground state.

when it is projected onto $r_{CH}$. The increase in the width of the projection of the probability amplitude onto $q$ can be understood by the CH distances at the three stationary points, reported in Table 2.1. Here the value of $q_{A_1^+}$ is 0.03 Å shorter at the $C_{2v}$ saddle point than it is at either of the other stationary points. As the distribution of CH distances that are sampled by the wave function shifts to larger values of $r_{CH}$, one can anticipate that there will be more probability amplitude near the $C_s$(I) minimum, compared to the $C_{2v}$ saddle point, in this excited state than in the ground state. This is what is reflected in the projections, plotted in panels d and h. This effect is also seen in the shoulder in the CH distance distribution in panels a and e. Due to the lower vibrational frequencies in $CD_5^+$, the effect is even more dramatic.

To investigate coupling between this vibrational excitation and the overall rotation of the molecule, the vibrationally averaged rotational constants are calculated for $CH_5^+$ and $CD_5^+$ and compared to those for the ground state.[10] The results are reported in Tables
Table 4.4: Vibrationally averaged rotational constants for the ground and excited states of CH$_5^+$.

<table>
<thead>
<tr>
<th>state</th>
<th>symmetry</th>
<th>$B_a$</th>
<th>$B_b$</th>
<th>$B_c$</th>
<th>$d_{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td>C$_s$(I)</td>
<td>3.895±0.015</td>
<td>3.864±0.021</td>
<td>3.848±0.012</td>
<td>0.003±0.008</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>3.890±0.015</td>
<td>3.867±0.018</td>
<td>3.851±0.016</td>
<td>-0.001±0.009</td>
</tr>
<tr>
<td>$q_{A_1}^+$</td>
<td>C$_s$(I)</td>
<td>3.884±0.011</td>
<td>3.845±0.010</td>
<td>3.832±0.011</td>
<td>0.000±0.008</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>3.881±0.011</td>
<td>3.850±0.011</td>
<td>3.831±0.011</td>
<td>0.000±0.008</td>
</tr>
<tr>
<td>$q_{G_1}^+$,1</td>
<td>C$_s$(I)</td>
<td>3.864±0.016</td>
<td>3.746±0.013</td>
<td>3.708±0.014</td>
<td>-0.010±0.007</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>3.865±0.016</td>
<td>3.744±0.014</td>
<td>3.709±0.013</td>
<td>-0.003±0.007</td>
</tr>
<tr>
<td>$q_{G_1}^+$,2</td>
<td>C$_s$(I)</td>
<td>4.107±0.017</td>
<td>3.638±0.013</td>
<td>3.575±0.012</td>
<td>-0.056±0.012</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>4.111±0.017</td>
<td>3.612±0.013</td>
<td>3.597±0.013</td>
<td>0.038±0.010</td>
</tr>
<tr>
<td>$q_{G_1}^+$,3</td>
<td>C$_s$(I)</td>
<td>4.084±0.014</td>
<td>3.655±0.013</td>
<td>3.583±0.013</td>
<td>-0.049±0.008</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>4.082±0.014</td>
<td>3.632±0.013</td>
<td>3.608±0.013</td>
<td>0.032±0.008</td>
</tr>
<tr>
<td>$q_{G_1}^+$,4</td>
<td>C$_s$(I)</td>
<td>3.784±0.016</td>
<td>3.774±0.015</td>
<td>3.759±0.015</td>
<td>-0.006±0.008</td>
</tr>
<tr>
<td></td>
<td>C$_s$(II)</td>
<td>3.787±0.016</td>
<td>3.777±0.015</td>
<td>3.754±0.015</td>
<td>-0.015±0.007</td>
</tr>
</tbody>
</table>

$^a$ State with a node in $q_{A_1}^+$.

4.4 and 4.5. It is found that at most four of the rotational constants are non-zero, within the statistical uncertainties of the calculations. Only these four rotational constants are reported in Tables 4.4 and 4.5. Following the notation of Ernesti and Hutson,[62] the constants represent the coefficients in

$$\hat{H}_{\text{rot}} = B_a\hat{J}_a^2 + B_b\hat{J}_b^2 + B_c\hat{J}_c^2 + d_{ab}\left[\hat{J}_a\hat{J}_b + \hat{J}_b\hat{J}_a\right]$$ (4.6)

As in the ground state, the three calculated diagonal rotational constants are nearly equal and $d_{ab} = 0$. This indicates that this excitation does not break the rotational symmetry of CH$_5^+$.

Upon comparison, of the ground and excited state rotational constants, the excited state ones are slightly smaller. This is consistent with an overall extension of the average CH bond lengths, depicted in Figure 4.1. Analogous trends are seen for CD$_5^+$.
Table 4.5: Vibrationally averaged rotational constants for the ground and excited states of \( \text{CD}_5^+ \).

<table>
<thead>
<tr>
<th>state</th>
<th>symmetry</th>
<th>( B_a )</th>
<th>( B_b )</th>
<th>( B_c )</th>
<th>( d_{ab} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground</td>
<td>( C_s(I) )</td>
<td>1.975±0.004</td>
<td>1.963±0.005</td>
<td>1.955±0.006</td>
<td>0.000±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>1.979±0.006</td>
<td>1.960±0.005</td>
<td>1.955±0.006</td>
<td>-0.001±0.004</td>
</tr>
<tr>
<td>( q_{A_1^+} )</td>
<td>( C_s(I) )</td>
<td>1.976±0.004</td>
<td>1.957±0.004</td>
<td>1.949±0.004</td>
<td>0.000±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>1.974±0.004</td>
<td>1.959±0.004</td>
<td>1.948±0.004</td>
<td>0.000±0.003</td>
</tr>
<tr>
<td>( q_{G_1^+;1} )</td>
<td>( C_s(I) )</td>
<td>1.973±0.006</td>
<td>1.920±0.005</td>
<td>1.899±0.006</td>
<td>-0.008±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>1.970±0.006</td>
<td>1.920±0.006</td>
<td>1.902±0.005</td>
<td>-0.003±0.003</td>
</tr>
<tr>
<td>( q_{G_1^+;2} )</td>
<td>( C_s(I) )</td>
<td>2.110±0.006</td>
<td>1.851±0.005</td>
<td>1.838±0.005</td>
<td>-0.012±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>2.100±0.005</td>
<td>1.859±0.005</td>
<td>1.840±0.005</td>
<td>0.015±0.003</td>
</tr>
<tr>
<td>( q_{G_1^+;3} )</td>
<td>( C_s(I) )</td>
<td>2.077±0.005</td>
<td>1.881±0.005</td>
<td>1.842±0.005</td>
<td>-0.013±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>2.075±0.005</td>
<td>1.870±0.005</td>
<td>1.855±0.005</td>
<td>0.014±0.003</td>
</tr>
<tr>
<td>( q_{G_1^+;4} )</td>
<td>( C_s(I) )</td>
<td>1.936±0.005</td>
<td>1.933±0.006</td>
<td>1.928±0.005</td>
<td>0.004±0.003</td>
</tr>
<tr>
<td></td>
<td>( C_s(II) )</td>
<td>1.937±0.006</td>
<td>1.935±0.006</td>
<td>1.925±0.005</td>
<td>-0.008±0.003</td>
</tr>
</tbody>
</table>

\(^a\) State with a node in \( q_{A_1^+} \).

4.2.2 \( G_1^+ \) States

The situation is more interesting for the four excited states that correspond to excitation along the coordinates defined in eqs 4.2 - 4.5. While, taken together, these four coordinates transform under the \( G_1^+ \) irreducible representation, the energies, reported in Table 4.3 span from 1039 to 1383 cm\(^{-1}\) in \( \text{CH}_5^+ \) and from 628 to 893 cm\(^{-1}\) in \( \text{CD}_5^+ \). In addition to not being degenerate, this range of energies spans the HCH bend region of the spectrum for \( \text{CH}_5^+ \), reported by Schlemmer and co-workers\cite{6} and the calculated spectra for \( \text{CH}_5^+ \) and \( \text{CD}_5^+ \) reported by Huang \textit{et al.}\cite{8, 9}

In Figure 4.2, the probability distributions are projected onto the four internal coordinates. While these four excited states have different energies, the four projections are essentially identical to within the statistical uncertainties of the calculations. There is a small difference in the probability distribution along \( q \) for the state in which the excitation is along \( q_{G_1^+;4} \). As with the excited state distribution with \( A_1^+ \) symmetry, the projection of
Figure 4.2: Projections of the probability amplitudes of the excited states of CH$_5^+$ with nodes in $q_{G_1^{1-1}}$ (solid black line), $q_{G_1^{1-2}}$ (dashed line), $q_{G_1^{1-3}}$ (dash-dot-dot line) and $q_{G_1^{1-4}}$ (dotted line) are plotted as functions of the (a) CH distance, (b) HH distance, (c) methyl rotor coordinate, $\phi$, and (d) C$_{2v}$ isomerization coordinate, $q$, with thick black lines. The corresponding distributions for CD$_5^+$ are plotted in panels e-h. The thin red and green lines represent the corresponding projections for the corresponding ground state.

The distribution onto the CH distance coordinate contains a shoulder at large values of $r_{\text{CH}}$. In addition, there is a well-defined peak near 0.98 Å in the projection along $r_{\text{HH}}$. This, along with the minimum in the projection of the probability amplitude along $q$ indicates that the nodal surfaces cross at least some of the C$_{2v}$ saddle points, giving the excited state wave functions more distinct CH$_3^+$ and H$_2$ subunits. In contrast, the projection of the probability amplitude along $\phi$ is nearly identical in the ground and excited states. The results for these four states in CD$_5^+$ is similar to that for CH$_5^+$.

While analysis of the distributions, plotted in Figure 4.2, clearly shows coupling between each of the four $q_{G_1^{1-n}}$ coordinates and those coordinates that lead to isomerization, they do not explain why the four excited states have different energies. In fact, based on the similarities among these projections, one might anticipate that the four excited states could be degenerate. In contrast, the participation ratios, which provide a measure of the number
of minima sampled by each of the excited states, are different and increase with increasing vibrational energy. Overall, the participation ratios for CD$_5^+$, reported in Table 4.3 are somewhat lower than those for CH$_5^+$. This reflects the smaller amplitude of the vibrations in CD$_5^+$, compared to those in CH$_5^+$.

While the correlation between participation ratios and energy is reassuring, the trend is non-linear. In addition, one might expect that the states that sample more minima, and consequently have larger participation ratios, would be lower in energy. In fact the opposite trend holds for these results.

The localization of the wave function in a subset of the minima is a manifestation of couplings between the four $q_{Gi',n}$ coordinates and the isomerization coordinates. To understand the implications of the correlation between $\rho$ and vibrational energy, focus is shifted to exactly which minima in the potential are sampled by the parts of the wave function with positive amplitude and which are sampled by the parts of the wave function with negative amplitude. Once this has been determined, the isomerization pathways that connect minima in a single region of space in which the wave function does not change sign can be mapped out. One can also look at the geometries at which the wave function changes sign.

To start, as the definition of positive and negative amplitude is arbitrary, the region of positive amplitude will be equated with the region for which $q_{Gi',n} > 0$. Following the notation, above, this region of space will be symbolized as $r_+^{(n)}$. Likewise, the region with negative amplitude, $r_-^{(n)}$, is the region for which $q_{Gi',n} < 0$. In Table 4.2, the various minima that are unique by symmetry, are categorized based on whether they are in $r_+^{(n)}$, $r_-^{(n)}$, or have amplitude that is less than 10% or 1% of the amplitude in the minimum with the greatest amplitude for that state. These results are also depicted graphically in Figures 4.3 and 4.4. When possible, the $x-$axes in these plots are arranged so that the adjacent minima are separated by a single saddle point. The exception is the state with a node in
for which one finds that the regions with amplitude in \( r_+^{(n)} \) and \( r_-^{(n)} \) are separated by a long string of saddle points.

Figure 4.3: Projections of the probability amplitudes of the four excited states of \( \text{CH}_5^+ \) with nodes in \( q_{G_i,n} \), onto the occupied minima, defined in Table 4.2. The red and blue sticks provide the results of the simulations with \( q_{G_i,n} > 0 \) (red: bars above zero line) and \( q_{G_i,n} < 0 \) (blue: bars below zero line). Specifically, \( n = 4 \) in (a), 3 in (b), 2 in (c) and 1 in (d).

Because each of the bins in Figures 4.3 and 4.4 contains contributions from as many as 24 minima, it is hard to connect these plots directly to the localization of the wave function
Figure 4.4: Projections of the probability amplitudes of the four excited states of CD$_5^+$ with nodes in $q_{G^+}$, onto the occupied minima, defined in Table 4.2. The red and blue sticks provide the results of the simulations with $q_{G^+} > 0$ (red: bars above zero line) and $q_{G^+} < 0$ (blue: bars below zero line). Specifically, $n = 4$ in (a), 3 in (b), 2 in (c) and 1 in (d).
among the 120 equivalent minima. To further our understanding of these states, focus is
shifted to the connectivity of the individual minima with population in $r_+^{(n)}$ and in $r_-^{(n)}$.

One can start by looking at the state with the highest energy, the one with the node
in $q_{G_4^{+,4}}$. In this case, there is one unique hydrogen atom, labeled $H_1$. When $q_{G_4^{+,4}} > 0$
the molecule will be localized in minima in which $r_1$ is larger than the other for CH bond
lengths. Based on the geometries of the stationary points, this would correspond to minima
in which $H_1$ is in position A or B. Likewise, when $q_{G_4^{+,4}} < 0$ the wave function will primarily
have amplitude near the minima in which $H_1$ is in position D or E, and, to a lesser extent,
in position C. Investigation of Table 4.2 indicates that this is indeed the case. This result
is also depicted graphically in Figure 4.3. While this shows the connectivity of the minima,
it does not guarantee that all 48 minima in which the wave function has positive amplitude
or all 72 minima that contain negative amplitude are connected to each other through the
$C_s(\Pi)$ or $C_{2v}$ saddle points.

Closer examination shows that the 48 minima that are sampled in the simulation for
which $q_{G_4^{+,4}} > 0$ divide into eight groups of six minima. Each set of minima is connected
through a set of six $C_s(\Pi)$ saddle points, and these groups of six minima are further con-
connected through $C_{2v}$ saddle points, yielding two sets of 24 connected minima. Likewise the
72 minima that are sampled in the simulation in which $q_{G_4^{+,4}} > 0$ can be divided into two
groups of 36 minima. These groups of minima can be further divided into 3 groups of 8
minima that are separated by the 12 minima in which $H_1$ is in position C and where the
amplitude of the wave function is smaller. Taken together, the $r_+$ and $r_-$ regions of space
are separated by 36 of the $C_{2v}$ saddle points, thereby explaining why the amplitude near
this stationary point is lower in this excited state is lower than for the ground state. In
the end, taking into account the 96 minima with the largest amplitude, the probability
amplitude for this state is divided into eight pieces, rather than two.
At the other extreme, the state with the lowest energy is the one in which the node is chosen to be in \( q_{G+1,2} \). In this case, when \( q_{G+1,2} > 0 \), \( 2r_3 > r_4 + r_5 \) and \( H_3 \) is preferentially located in positions A or B, while \( H_4 \) and \( H_5 \) are in positions C, D or E. Likewise, when \( q_{G+1,2} < 0 \), \( 2r_3 < r_4 + r_5 \) and \( H_3 \) is preferentially located in positions C, D or E, while \( H_4 \) and \( H_5 \) are in positions A and B. This is seen both in the data in Table 4.2 and the plot in Figure 4.3. In this case, each of the reported structures represents four minima.

When the pathways connecting minima in which the wave function retains its sign are evaluated, one finds that the 32 minima with the largest amplitude in \( r_+ \) are divided into two groups of 12 that are each connected through 12 \( C_2 \) (II) and 1 \( C_{2v} \) saddle points. The pathways connecting minima 12 minima with the largest amplitude in \( r_- \) are found to divide into two groups of 6 minima that are each connected through 6 \( C_2 \) (II) saddle points. These four sets of minima are connected to each other through path that contains the remaining 58 \( C_{2v} \) saddle points. In comparison to the excited state with a node in \( q_{G+1,4} \), many fewer of the \( C_{2v} \) saddle points are expected to have probability amplitude. This is consistent with the results reported in Figure 4.2. Further the wave function is subdivided into only four pieces, as compared to the eight for the state described above. This is consistent with the energy difference between these states, presented in Table 4.3. The remaining two excited states may be analyzed in a similar manner.

Finally, the rotational constants for each of these states have been evaluated, and the results are reported in Tables 4.4 and 4.5. When the node is place in \( q_{G+1,1} \) or \( q_{G+1,4} \), the molecule retains its spherical symmetry and \( d_{ab} \) is nearly zero. In the other two states, \( B_a > B_b \approx B_c \) and \( d_{ab} \neq 0 \). The loss of spherical symmetry in these states can be understood by examination of Table 4.2. Specifically, in the states in which the node is in \( q_{G+1,2} \) or \( q_{G+1,3} \), two of the distinct hydrogen atoms are in positions A and B on one side of the node, and in positions C, D or E on the other. This brings the vibrationally averaged structure closer to the two \( C_3 \) stationary point structures, shown in Figure 1.1, with less
amplitude in the region of the $C_{2v}$ saddle point. While similar behavior is seen for the other two excited states, only one of the hydrogen atom is involved, thereby making the distortion from spherical symmetry less pronounced. Analogous behavior is seen for $\text{CD}_5^+$. 

4.3 Conclusions

In this Chapter, I investigated the wave functions for several excited states of $\text{CH}_5^+$. While the initial motivation for this work was to study stretch excited states, the states that emerged from the calculation were somewhat lower in frequency and reflect combination bands that involve the HCH bends. Four of the five states contain nodes along coordinates that, taken together, transform under the $G_{1i}$ irreducible representation of the $G_{240}$ permutation-inversion group. Projections of the probability amplitudes associated with these states are nearly identical, but the calculated energies differ by several hundred cm$^{-1}$. This result was, at first, surprising. Further analysis of the wave functions showed that these four states sample the 120 minima on the $\text{CH}_5^+$ potential in different ways. Specifically, introducing constraints that one of the CH bond lengths must be larger or smaller than the sum of a subset of the remaining CH distances results in the wave function becoming localized in a subset of the minima on the potential. Further, the sampling of these minima is different for each of these four excited states. The structure of the nodal surface that separates the regions of space where the wave function has positive and negative amplitude is not a simple seventeen dimensional function of a single coordinate, but rather a complicated function of the collective isomerization coordinates.

The consequences of this in the spectroscopy are not straightforward, as is indicated by the changes in the vibrationally averaged rotational constants by as much as 10% and the reduction of the symmetry of the molecule. This reinforces the experimental observation that the rotation-vibration spectrum is complex. As I move forward, I explicitly calculate
rotation-vibration states with $J > 0$ directly by DMC approaches\cite{63} in order to gain further insights into the spectroscopy and dynamics of this complicated small molecule.
CHAPTER 5

Diffusion Monte Carlo Studies of Low Energy Ro-vibrational States of CH$_5^+$ and its Deuterated Isotopologues

In this Chapter, we consider the nature of several low-energy states of CH$_5^+$ and its five deuterated analogues with $J = 0$ and with $J = 1$. Unlike pure CH$_5^+$ and CD$_5^+$, the mixed isotopologues will not have equal probability amplitude at all 120 minima,[10] and the effect of the partitioning of the amplitude on the energy and the nature of these low-lying states is a focus of the present study. The calculations will be performed using Diffusion Monte Carlo, including extensions that were recently developed in the McCoy group[63] for evaluating rotationally excited states.

5.1 Theory

Diffusion Monte Carlo (DMC) is employed to calculate energies and wave functions for the two lowest energy vibrational levels with $J \geq 0$ of CH$_5^+$ and its deuterated analogues. The reported energies reflect the averages of the energies obtained from 4 independent simulations and in each case, the system is equilibrated for at least 30 000 time steps and the energy is obtained from an average over another 30 000 time steps. The global potential

energy surface developed for the ground electronic state of CH$_5^+$ by Jin and co-workers[17] is employed for all of the calculations on CH$_5^+$. Descendant weighting is used to generate the associated probability amplitudes.[45] In the present implementation, $\Delta \tau = 10$ a.u., and all DMC simulations are run for 30 000 time steps to equilibrate the ground state, before performing an excited state calculation, and at least 60 000 additional time steps to equilibrate the excited states. Once the ensemble has been equilibrated, descendant weighting is performed over 25 time steps with a gap of 20 000 time steps between each evaluation of the wave function. The precise number of time steps used in the equilibration process varied among the isotopologues, and the numbers that were used are provided in table 5.1. Quantities of interest are evaluated by taking the average of their values obtained from 16 evaluations, and the reported uncertainties reflect one standard deviation.

The above prescription provides only the lowest energy solution to the time-independent Schrödinger equation. Excited states are evaluated within the fixed-node approximation. In this treatment, I exploit the fact that the behavior of a wave function in the vicinity of a node is identical to its behavior in the region of an infinite potential barrier.[40] Details of this procedure and its implementation for rotational[63] or vibrational[31, 42, 64] excited
states can be found elsewhere. A key to the success of this approach is in the choice of
the functional form for the nodal surface. I have chosen to make the surface depend on a
single coordinate, \( \zeta \). While the functional form of \( \zeta \) is flexible, the nodal surface is defined
to correspond to the loci of points for which \( \zeta = 0 \).[31, 64]

5.1.1 Rotationally Excited States

To calculate rotationally excited state energies and wave functions I apply the fixed-node
approach to rotational, rather than vibrational, degrees of freedom.[63] Since the rotational
coordinates (e.g. Euler angles) define the transformation from the body- to the space-fixed
axis system, their definition requires an embedding of the body-fixed axis system. In spite of
being a highly fluxional molecule, the McCoy group has demonstrated that Eckart embed-
ding[54, 65] can be used to determine vibrationally averaged rotational constants for \( \text{CH}_5^+ \)
and its deuterated analogues.[10] More specifically, as long as the wave function has ampli-
tude near the reference structure that is used to define the static molecular model,[54, 65]
the vibrationally averaged rotational constants for \( \text{CH}_5^+ \) and its deuterated analogues are
independent of this choice. In the cases of \( \text{CH}_5^+ \) and \( \text{CD}_5^+ \), which are near spherical tops,
the rotational constants based on the Eckart embedding are in excellent agreement with
the constants evaluated in a space-fixed axis system.[10, 15] In the case of the mixed iso-
topologues, the calculated vibrationally averaged rotational constants, obtained using the
same Eckart embedding, are found to be independent of the choice of the static molecular
model used to define the body-fixed axis system.

Similar Eckart embeddings of the body-fixed axis system have been employed in recent
DMC simulations of rotationally excited states of \( \text{H}_3\text{O}^+ \) and \( \text{D}_3\text{O}^+ \)[63] as well as in a study
of the vibrational spectra of \( \text{H}_5\text{O}_2^+ \) and its deuterated analogues.[66] In the present work, I
follow the approach used by the McCoy group in the study of \( \text{H}_5\text{O}_2^+ \) in which we rotate the

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walker to the Eckart frame at each time-step in the simulation. This differs slightly from
the procedure used for evaluating rotationally excited states of H$_3$O$^+$. 

As in our study of H$_3$O$^+$, the rotational contribution to the wave function are treated
as linear combinations of Wigner rotation matrices with $J = 1$, $|K| = 0, 1$ and $M = 0$:

$$\langle \theta, \phi, \chi | 1, 0, 0 \rangle = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (5.1)$$

$$\langle \theta, \phi, \chi | 1, 1, 0 \rangle_+ = \sqrt{\frac{3}{4\pi}} \sin \theta \sin \chi \quad (5.2)$$

$$\langle \theta, \phi, \chi | 1, 1, 0 \rangle_- = \sqrt{\frac{3}{4\pi}} \sin \theta \cos \chi \quad (5.3)$$

where $\theta, \chi$ and $\phi$ are the Euler angles and the angular momentum is quantized in terms of
its magnitude and its projection onto one of the body-fixed axes. The sign $\kappa = (2B - A - C)/(A - C)$ for the static molecular model is used to determine which of the body-fixed
axes the angular momentum is projected onto. Since the final energies do not depend on
this choice, in the discussion that follows the states and the energies are labeled using the
quantum numbers $J$ and $K_C$.

The functions in Eqs. 5.1-5.3 were chosen because they are the eigenstates of the $J = 1$
levels for a rigid asymmetric rotor. The zeroes in these functions provide the definition of
the nodes used in the calculations of the $J = 1$ energies and wave functions. The functional
forms of the nodes that are used to generate the rotationally excited states are based on an
assumed separability of the rotational and vibrational contributions to the wave function.
In contrast, no constraints have been placed on the functional form of the vibrational
contribution to the wave function. Indeed, the vibrational component of the ro-vibrational
wave function depends on the values of $J$ and $K_C$, allowing the DMC methodology to
capture the effects of the rotation-vibration coupling in these states. In fact for H$_3$O$^+$
the McCoy group finds noticeable changes to the projections of the probability amplitude
onto the internal coordinate that corresponds to the umbrella inversion as $J$ and $K_C$ are increased.[63]

Because finite time-steps are used in the fixed-node simulations, it is possible for a member of the ensemble, or walker, to cross a node two or more times within a single time step. If an even number of crossings takes place, the walker will experience a finite potential energy both before and after the displacement, and may not be removed from the simulation. On the other hand, if a series of smaller time steps had been taken, the walker would have experienced a region of infinite potential energy at some point along its trajectory and would have been removed from the simulation. Expressions that allow us to account for this recrossing error have been developed for vibrational excited states.[40] The higher rotational symmetry of CH$_3^+$ makes calculation of the recrossing error more challenging and due to the longer time-scale required for complete sampling of the rotational, compared to vibrational, motions, the use of $\Delta \tau = 10$ a.u. has been found to be sufficiently small to make the recrossing correction negligible in this case. To test this, simulations with a smaller value of $\Delta \tau = 1$ a.u. have been run and it has been found that there is no statistically significant change in the calculated energies.

One of the challenges to the evaluation of rotationally excited states comes from the fact that certain types of large amplitude motions lead to an inversion of the coordinate system used to define the molecule-fixed axis system. This is most clearly seen in a molecule like H$_3$O$^+$ or NH$_3$, where the two C$_{3v}$ minima are connected through displacements of the out-of-plane bend coordinate, as is illustrated by the top arrow in Figure 5.1. When this occurs, no set of rotations can connect the new structure to the one that was used to define the Eckart frame. As a result, the algorithms that are designed to rotate the molecule back to its orientation in the reference geometry will treat the effects of this vibrational motion as a combination of the inversion of the body-fixed axis system and a 180° rotation of the molecule about its C$_3$ axis, as indicated by the arrows that connect the top two structures.
Figure 5.1: An illustration of how the Eckart rotation matrix between the body- and space-fixed axis systems develops a negative determinant when relating the two minima of the $\text{H}_3\text{O}^+$ potential (shown at the top). The same change in geometry can be achieved by a combination of a 180° rotation of the molecule about the C$_3$ axis, followed by an inversion of the body-fixed axis system. The corresponding transformation matrices are given next to the arrows.

in Figure 5.1 through the intermediate structure, drawn below. Multiplying the associated transformation matrices leads to an overall transformation matrix between the space- and body-fixed frames that has a determinant of $-1$, as is illustrated by the matrix above the top arrow in Figure 5.1. Another way to look at this is to recognize that if the barrier between the two structures at the top of Figure 5.1 was very high and the three hydrogen atoms were distinguishable, the two structures at the top would form a chiral pair, and no set of proper rotations can transform one member of a chiral pair to the other.
While the motions that lead to inversion of the axis system in CH$_5^+$ are more complicated, the problem exists here as well. The origins of this effect are explored further in the following section. This observation led to the calculation the of $J = 0$ state that has a wave function that changes sign when the determinant of the transformation matrix between the body- and space-fixed axis systems goes from $+1$ to $-1$. This corresponds to evaluating the lowest energy $J = 0$ state for which the phase of the wave function in one minimum has the opposite sign from that in the minimum of its mirror image.

In the calculations of the states with $J = 1$, walkers for which the determinant of the transformation matrix is negative are replaced by walkers for which the signs of the $z-$cartesian coordinates of all the atoms have been reversed. This corresponds to reflection of the molecule in the $xy$ plane in the body-fixed axis system, and allows the Euler angles to be calculated from a proper rotation matrix. Considering what symmetry operations generate one chiral pair from another when the molecule is in its equilibrium configuration and all of the atoms are either hydrogen or deuterium, it will be reflection in the plane that contains the carbon atom and the three hydrogen atoms that are labeled A, B, and C in the $C_s(I)$ and $C_{2v}$ structures in Figure 1.1. In none of the reference structures used for the Eckart embedding does this plane correspond to the $xy$ plane. As such the reflection moves the walker from a region of configuration space near an inversion node to one that is far away from any of them. In a typical simulation, fewer than 0.36% of walkers are moved in this way in a single time step and usually this number is closer to 0.1% or less.

This same procedure is used, in the absence of the rotational nodes, to calculate state energies and wave functions for the first vibrationally excited state. All of these excited state calculations are performed with the same parameters employed for the rotational excited state calculations, but with $J = 0$. 

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5.2 Results

5.2.1 Methodologies for $\text{H}_3\text{O}^+$

Before discussing the energies and wave functions for CH$_5^+$ and its deuterated analogues, it is instructional to consider the results of calculations on H$_3$O$^+$. In the case of CH$_5^+$, two large amplitude motions are responsible for the transformation of the molecule among 120 equivalent minima. In contrast, in H$_3$O$^+$ there is only one large amplitude motion that separates the two equivalent minima on the potential surface. This makes the interaction between the rotation and tunneling dynamics easier to visualize. In our earlier study of rotationally excited states of H$_3$O$^+$, the McCoy group found that when one of the C$_{3v}$ equilibrium geometries is used as the static reference model for the Eckart embedding, the energy of the $|1,0,0\rangle$ state was too high. Specifically, an energy of 7521.61±2.68 cm$^{-1}$ is calculated, whereas the reported $J = 1, K_C = 0$ energy is 7472.9 cm$^{-1}$.[67] While the agreement with the $J = 1, K_C = 0 \nu = 0$ level was poor, this energy is in good agreement with the reported $J = 1, K_C = 0$ energy for the higher energy component of the tunneling doublet, 7518.7 cm$^{-1}$. The tunneling splitting arises from the difference between the energies of the states with even and odd symmetry with respect to reflection of the molecule in the plane perpendicular to its C$_3$ axis. The fact that the calculated state is indeed the upper member of the tunneling doublet can be confirmed by projecting the probability amplitude onto the tunneling coordinate, $\Gamma$, as defined in Ref. [63]. In Fig. 5.2, the results are presented for the ground state, and when the $|1,0,0\rangle$ state is calculated using both the C$_{3v}$ equilibrium and the D$_{3h}$ transition state geometries as the reference geometries for the Eckart embedding. As can be seen, when the $|1,0,0\rangle$ state is calculated with the C$_{3v}$ equilibrium geometry as the static molecular model (plotted with the red dash-dot-dot line) it has a node at $\Gamma=0$. 
Figure 5.2: Projections of the probability amplitudes onto $\Gamma$ for the ground state (thick black solid line) of $\text{H}_3\text{O}^+$ as well as the $|1,0,0\rangle$ states that are obtained when the $C_{3\nu}$ (red dash dot-dot line) and $D_{3h}$ (thin blue dashed line) stationary point structures are used to provide the reference structure for the Eckart embedding. The inversion coordinate is defined\[62\] so that a value of 0 corresponds to a planar structure and the minimum energy structure has $\Gamma = 0.2887 \text{ \AA}$. This Figure is based on the work of Andrew S. Petit.

In the case of $\text{H}_3\text{O}^+$ the energies and wave functions can be calculated for purely rotationally excited states by using the $D_{3h}$ saddle point structure for the static molecular model. Since there is no single saddle point in $\text{CH}_5^+$ that clearly separates the corresponding pairs of minima, I have not been able to employ an analogous approach. In the present study, the possibility of using geometrical operations to calculate the $J = 1$ energies of the $v = 0$ state is investigated, but none of the choices of reflection planes or other symmetry operations that were considered proved to be effective.

As a test, Andrew Petit also tried using these geometric operations to calculate the $J = 1$ levels of $\text{H}_3\text{O}^+$ when one of the $C_{3\nu}$ equilibrium structures is used for the static molecular model. While some choices provided the energy and wave function for one of the $J = 1$ levels that corresponded to the vibrational ground state, no choice produced this
state for all three $J = 1$ levels. As a result, as will be demonstrated below, the states that are reported for CH$_5^+$ reflect the $J = 1$ levels for the first vibrationally excited state.

5.2.2 Rotation-vibration energies

The rotational excited state energies and wave functions ($J = 1$, $|K_C| \leq 1$, $M = 0$) for CH$_5^+$ have been calculated. Separate calculations were performed using the $C_s$(I), $C_s$(II), and $C_{2v}$ structures depicted in Fig. 1.1 for the static molecular model for the Eckart embedding. The results, reported in Table 5.2, illustrate that within the statistical uncertainties of the calculations, all nine calculated energies are identical. This demonstrates that the results are independent of both the static molecular model that is used to define the Eckart frame and the value of $K_C$. This latter point is consistent with previous studies that indicated that on average CH$_5^+$ is a spherical top.[10, 15] Based on the insensitivity to the choice of static molecular model used in these calculations as well as the results of earlier studies that showed a similar insensitivity of the calculated values of the vibrationally averaged rotational constants to this choice, only energies obtained using the $C_s$(I) structure (Fig. 1.1) as the reference geometry will be reported for the remainder of the isotopologues.[10]

In the case of the partially deuterated isotopologues of CH$_5^+$, there are more choices for the static molecular model as the results can depend on the specific locations of the hydrogen and deuterium atoms in the reference structure. In the earlier study,[10] the calculated vibrationally averaged rotational constants were found to be insensitive to this choice so long as the ground state wave function has amplitude in the vicinity of the reference structure. To minimize the uncertainties in the reported values, weighted averages of the results obtained using all relevant reference geometries are taken. Here, the weights are based on the relative magnitude of the probability amplitude at each of the stationary points that are considered. The values of the excited state energies that are obtained from each simulation as well as the weighting factors are provided in table 5.3.
Table 5.2: Energies (in cm$^{-1}$) of the excited states of CH$_5^+$ evaluated using each of the three structures in Fig. 1.1 for the reference geometry and the zero-point energy (ZPE) of CH$_5^+$.a

<table>
<thead>
<tr>
<th>State</th>
<th>$E_{(a)}$ (cm$^{-1}$)</th>
<th>$E_{(b)}$ (cm$^{-1}$)</th>
<th>$E_{(c)}$ (cm$^{-1}$)</th>
<th>$E_{RR}^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>1,0,0\rangle$</td>
<td>19±1</td>
<td>19±2</td>
<td>19±1</td>
</tr>
<tr>
<td>$</td>
<td>1,1,0\rangle_-$</td>
<td>20±1</td>
<td>20±1</td>
<td>20±1</td>
</tr>
<tr>
<td>$</td>
<td>1,1,0\rangle_+$</td>
<td>11 ± 2</td>
<td>11 ± 2</td>
<td>11 ± 2</td>
</tr>
</tbody>
</table>

a The energies are identified by the panel in Fig. 1.1 that is used for the reference structure.

b Evaluated using the rigid-rotor Hamiltonian with the vibrationally vibrationally averaged rotational constants from Ref. [10]. In the case of the inversion state, this entry provides the zero-point energy.

Using fixed-node DMC, energies of three states with $J = 1$ for CH$_4$D$^+$, CH$_3$D$^+_2$, CH$_2$D$^+_3$, CHD$_4^+$, and CD$_5^+$ are calculated. These energies are reported in Table 5.4. The vibrationally averaged rotational constants have also been used to calculate the $J = 1$ rotational energies using energy level expressions based on a rigid rotor model. These energies are reported in the right columns of Tables 5.2 and 5.4. Comparison of the two sets of energies shows that the energies that are calculated using fixed node DMC are in most cases larger by several cm$^{-1}$ than those obtained using the vibrationally averaged rotational constants. In most cases, these differences are larger than the reported uncertainties for either set of values. It can be concluded that the states that are evaluated using the fixed-node DMC approach are not simply the $J = 1$ energies for the $v = 0$ levels of these molecules. Instead they must be the $J = 1$ energies of a vibrationally excited state that, for CH$_5^+$, has an energy of roughly 11 cm$^{-1}$. Based on the similar behavior observed when one of the C$_{3v}$ minima was used for the static molecular model for H$_3$O$^+$, it can therefore be concluded that the vibrational excitation is likely in the lowest energy mode that effectively inverts the molecule fixed axis system.
Table 5.3: Values of the energies for the $|1, 0, 0\rangle$ ($E_{100}$), $|1, 1, 0\rangle$ ($E_{110}$), $|1, 1, 0\rangle$ ($E_{110}$), and inversion ($E_{\text{inv}}$) states of the partially deuterated isotopologues of CH$_5^+$, evaluated using different reference structures as well as the associated weights. In all cases the C$_s$ (I) reference structure (shown in Fig. 1 of the main text) is used.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Position</th>
<th>Weight$^{(b)}$</th>
<th>Avg. $E_{100}$ (cm$^{-1}$)</th>
<th>Avg. $E_{110}$ (cm$^{-1}$)</th>
<th>Avg. $E_{110}$ (cm$^{-1}$)</th>
<th>Avg. $E_{110}$ (cm$^{-1}$)</th>
<th>Avg. $E_{\text{inv}}$ (cm$^{-1}$)</th>
<th>Avg. $E_{\text{inv}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$D$^+$</td>
<td>HHHHDH</td>
<td>0.82</td>
<td>$11\pm2$</td>
<td>$11\pm1$</td>
<td>$11\pm2$</td>
<td>$10\pm2$</td>
<td>$10\pm2$</td>
<td>$3\pm1$</td>
</tr>
<tr>
<td></td>
<td>HHDHHH</td>
<td>0.13</td>
<td>$12\pm1$</td>
<td>$11\pm1$</td>
<td>$10\pm2$</td>
<td>$5\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DHHHHH</td>
<td>0.05</td>
<td>$12\pm1$</td>
<td>$12\pm2$</td>
<td>$11\pm1$</td>
<td>$6\pm2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$D$_2^+$</td>
<td>HHHHH</td>
<td>0.43</td>
<td>$10\pm1$</td>
<td>$10\pm2$</td>
<td>$9\pm2$</td>
<td>$9\pm2$</td>
<td>$2\pm1$</td>
<td>$3\pm1$</td>
</tr>
<tr>
<td></td>
<td>HHDHH</td>
<td>0.40</td>
<td>$9\pm2$</td>
<td>$8\pm1$</td>
<td>$9\pm2$</td>
<td>$3\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DHDDH</td>
<td>0.11</td>
<td>$10\pm1$</td>
<td>$8\pm3$</td>
<td>$9\pm2$</td>
<td>$2\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HDHHH</td>
<td>0.06</td>
<td>$11\pm2$</td>
<td>$9\pm1$</td>
<td>$8\pm2$</td>
<td>$5\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$D$_3^+$</td>
<td>HHDHD</td>
<td>0.66</td>
<td>$5\pm2$</td>
<td>$5\pm2$</td>
<td>$5\pm1$</td>
<td>$5\pm2$</td>
<td>$5\pm2$</td>
<td>$0\pm2$</td>
</tr>
<tr>
<td></td>
<td>DHHDH</td>
<td>0.28</td>
<td>$5\pm1$</td>
<td>$5\pm2$</td>
<td>$6\pm1$</td>
<td>$0\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HHHDD</td>
<td>0.06</td>
<td>$6\pm2$</td>
<td>$6\pm1$</td>
<td>$6\pm1$</td>
<td>$0\pm2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHD$_4^+$</td>
<td>DHDDD</td>
<td>0.56</td>
<td>$5\pm2$</td>
<td>$6\pm2$</td>
<td>$7\pm1$</td>
<td>$6\pm2$</td>
<td>$7\pm2$</td>
<td>$2\pm1$</td>
</tr>
<tr>
<td></td>
<td>HHDHH</td>
<td>0.35</td>
<td>$8\pm1$</td>
<td>$7\pm1$</td>
<td>$7\pm1$</td>
<td>$2\pm1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DHHDD</td>
<td>0.07</td>
<td>$9\pm2$</td>
<td>$9\pm2$</td>
<td>$8\pm2$</td>
<td>$4\pm2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DDDHD</td>
<td>0.02</td>
<td>$8\pm1$</td>
<td>$14\pm1$</td>
<td>$14\pm1$</td>
<td>$7\pm2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{(a)}$ Notation is defined in Fig. 5. Positions D and E are equivalent, and one possible combination is listed.

Table 5.4: The energies (in cm$^{-1}$) for the four excited states of the isotopologues of CH$_3^+$ are compared to the energies obtained from a rigid-rotor Hamiltonian.$^{[10]}$ The zero-point energies are given.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>State</th>
<th>$E_{DMC}^a$ (cm$^{-1}$)</th>
<th>$E_{RR}^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$D$^+$</td>
<td>$</td>
<td>1, 0, 0\rangle$</td>
<td>11±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_-$</td>
<td>10±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_+$</td>
<td>11±2</td>
</tr>
<tr>
<td></td>
<td>Inversion</td>
<td>3±1</td>
<td>10304±5</td>
</tr>
<tr>
<td>CH$_3$D$_2^+$</td>
<td>$</td>
<td>1, 0, 0\rangle$</td>
<td>10±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_-$</td>
<td>9±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_+$</td>
<td>9±2</td>
</tr>
<tr>
<td></td>
<td>Inversion</td>
<td>3±1</td>
<td>9696±5</td>
</tr>
<tr>
<td>CH$_2$D$_3^+$</td>
<td>$</td>
<td>1, 0, 0\rangle$</td>
<td>5±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_-$</td>
<td>5±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_+$</td>
<td>5±1</td>
</tr>
<tr>
<td></td>
<td>Inversion</td>
<td>0±2</td>
<td>9094±5</td>
</tr>
<tr>
<td>CHD$_4^+$</td>
<td>$</td>
<td>1, 0, 0\rangle$</td>
<td>6±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_-$</td>
<td>7±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_+$</td>
<td>7±1</td>
</tr>
<tr>
<td></td>
<td>Inversion</td>
<td>2±2</td>
<td>8563±5</td>
</tr>
<tr>
<td>CD$_5^+$</td>
<td>$</td>
<td>1, 0, 0\rangle$</td>
<td>10±2</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_-$</td>
<td>9±1</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>1, 1, 0\rangle_+$</td>
<td>10±2</td>
</tr>
<tr>
<td></td>
<td>Inversion</td>
<td>6±1</td>
<td>8045±5</td>
</tr>
</tbody>
</table>

$^a$ The reported error bars reflect one standard deviation and are based on four independent DMC simulations for $E_{inv}$ and eight DMC simulations for the $J = 1$ energies.

$^b$ Evaluated using the rigid rotor Hamiltonian with the averaged rotational constants from Ref. [12]. In the case of the inversion state, this entry provides the zero-point energy.

To verify this vibrational assignment, the lowest energy ($J = 0$) excited state of CH$_3^+$ and its deuterated analogues that is antisymmetric with respect to inversion of the body-fixed axis system has been evaluated. This excited state will be referred to as the inversion state in the discussion that follows. The resulting energies are reported as the inversion energy in Table 5.2 for CH$_3^+$ and in Table 5.4 for the other isotopologues.

All four of these states have been analyzed, the three $J = 1$ states described above and the inversion state, by considering the relative populations of the various minima
on the potential surface. The procedure for assigning walkers to minima, and from that partitioning the probability amplitude in terms of the 120 minima on the potential surface, is described in Chapter 1. The results for the $|1, 0, 0\rangle$ and inversion excited states are plotted in Fig. 5.3. For these plots, the 120 possible minima are identified by five digit numbers. These provide the identity of the hydrogen atoms in positions A, B, C, D and E, as indicated in the $C_s(I)$ minimum energy structures of Fig. 1.1. For example, if hydrogen atoms 1-5 were in positions A, B, C, D and E, respectively, that minimum would be identified by 12345 in this notation. On the other hand if atom 1 were in position B, atom 2 in position D, atom 3 in position C, atom 4 in position E and atom 5 in position A, the minimum would be denoted as 51324. The plots in Figure 5.3 show the amplitudes for one side of the nodal surface. Within the uncertainties indicated by the error bars, the probability amplitude for the other side of the nodal surface can be obtained by exchanging the probability amplitude between chiral pairs, e.g. between the pairs of minima that have the last two digits flipped. For example, swapping the probability amplitude between minima 12345 and 12354 and between minima 51324 and 51342, etc. In considering these plots, the distributions for the two states that are shown are found to be nearly identical. Further, the pairs of minima, described above, are considered, at most one of these has statistically non-zero probability amplitude. While not plotted, these observations hold for the other five isotopologues as well as for the other two $J = 1$ states.

Based on this I conclude that the vibrationally excited state that is sampled in our calculations is the lowest energy state for which regions with positive and negative amplitude are related to each other through inversion of the axis system. In contrast to most molecular systems, the existence of the two low-energy saddle points means that any pair of minima that is represented in Fig. 5.3 can be connected via a series of low-energy saddle point structures with electronic energies that are no higher than 340.7 cm$^{-1}$. When the harmonic zero-point energy $[15]$ is added the barriers for $\text{CH}_5^+$ are reduced to a value of less
Figure 5.3: The distribution of the probability amplitude among the 120 minima for the $|1, 0, 0\rangle$ state (white bars pointing upward) and for the inversion state (black bars pointing downward). The five digit numbers refer to specific $C_s(I)$ minima (Fig. 1.1) on the potential surface, as described in the text. The minima are ordered so that chiral pairs appear next to each other. The magnitude of the bars reflect the values of $p_i$ in Eq. (4) when the results from 16 evaluations of the wave function are averaged, while the error bars provide one standard deviation. The corresponding plots for the other two excited states considered in this Chapter (not shown) are also virtually identical to the ones that are plotted here. The black bars have inverted for clarity.
than 15 \text{ cm}^{-1}. Extensive contortions of the molecule are required to transform it from one minimum energy configuration to another[68], which makes the equivalent minima well-separated spatially. This results in a frequency for this excited state that is large enough to be determined by the DMC simulations.

The assignment of this vibrationally excited state as the lowest energy state that is antisymmetric with respect to inversion of the axis system is further confirmed by comparing the calculated energy of the higher level of the inversion doublet with the $J = 0$ energies calculated by Wang and Carrington.[28] In their calculations, they identified the lowest energy excited state of CH$_5^+$ to have G$_2^-$ symmetry and an energy that is 10.4 \text{ cm}^{-1} above the ground state. This energy is in good agreement with the calculated energy of the inversion excited state (11 ± 2 \text{ cm}^{-1}), reported in Table 5.2.

The results for the five other isotopologues are reported in Table 5.4. The $J = 1$ energies evaluated using fixed-node DMC show good agreement with the sum of the energies of this inversion excited state and the $J = 1$ energies calculated using vibrationally averaged rotational constants for all six species. The energy of this vibrationally excited state is highly sensitive to the extent of deuteration and does not follow an immediately obvious pattern. It is largest for CH$_5^+$ and decreases by between a factor of 2 and a factor of $\sqrt{2}$ when the system is fully deuterated. Partial deuteration decreases this value from 11 \text{ cm}^{-1} or 6 \text{ cm}^{-1} for CH$_5^+$ or CD$_5^+$ to values between 0 and 3 \text{ cm}^{-1} for the four remaining isotopologues. The values are roughly equal, within the statistical uncertainties of the results, for the CH$_4$D$^+$, CH$_3$D$_2^+$ and CHD$_4^+$ ions and is roughly zero for CH$_2$D$_3^+$.

These differences can be understood by considering the localization of the vibrational ground state of CH$_5^+$ upon partial deuteration.[10,14,15] The results are plotted with the black bars in Fig. 5.4. A similar notation is adopted to describe the minima as is used in Fig. 5.3, but now is identified by the type of atom (H or D) rather than its number. The font-style scheme has been adopted from Fig. 1.1 to designate which atoms are in
the $H_2$ subunit and which are part of the $CH_3^+$ subunit. As can be seen, the greatest localization is obtained for $CH_2D_3^+$ where more than 63% of the probability amplitude is localized in the minima that correspond to having all three of the deuterium atoms in the $CH_3^+$ subunit and the hydrogen atoms in the $H_2$ subunit, as identified in Fig. 1.1(a). This can be seen to reflect both a much higher effective barrier for the $C_{2v}$ structure shown in Fig. 1.1(b) when zero-point energy is included and the ground state probability amplitude becoming nearly zero at points along the path that connects the pairs of minima that are related by the inversion of the axis system. This is reflected in the result that the reported energy difference between the ground state and inversion excited state for $CH_2D_3^+$ is 0 cm$^{-1}$. Similar behavior is seen in the other three isotopologues, but the localization is strongest in the $CH_2D_3^+$ case. As a result the frequencies of this excited state for the other three isotopologues are lower than for $CH_3^+$ and $CD_3^+$, but not zero.

These results can be compared to those obtained by the models used by Bunker and co-workers.[22, 24] While the models that underly the two sets of calculations differ, if the uncertainties in the calculated rotational energies are taken into account, the results are consistent. In addition, when the Hamiltonian that they use for the case of the ground state in the internal rotor are analyzed, I find that the couplings between rotation and vibration are anticipated to be primarily diagonal, with the terms that couple different eigenstates of the asymmetric top Hamiltonian expected to be smaller by an order of magnitude or more. To further investigate possible couplings in the $J = 1$ states of these systems and the nature of the vibrational excited state being accessed, the probability amplitudes are analyzed.
Figure 5.4: The distribution of probability amplitude among the distinct minima for the ground (black bars) [10] and $|1, 0, 0\rangle$ (white bars) states of CH$_3$D$^+$, CHD$_4^+$, CH$_2$D$_3^+$, CH$_2$D$_4^+$. In generating these plots the $p_i$ values [Eq. (4)] have been summed for all minima that are related by permutation of identical atoms. The resulting distributions reflect the averages of the values obtained from 16 evaluations of the wave function, and the error bars provide one standard deviation. To help in identifying which atoms are in the H$_2$ and CH$_3^+$ subunits, the corresponding letters are printed in bold red(A, B) and blue italics text(C, D, E).
5.2.3 Probability Distributions

To further explore the nature of these excited states, projections of the wave functions and probability amplitudes, obtained from DMC, onto a variety of coordinates are evaluated. I will focus on three different classes of distributions. Specifically, I look at projections of the probability amplitude onto the internal coordinates, projections of the amplitude of the wave function onto the Euler angles and the distribution of the probability amplitude among the 120 minima on the potential.

Projections the probability amplitude are obtained from the ground state, the inversion excited state and the $J = 1$ states onto a variety of internal coordinates. Here I will focus on its projection onto the distances between pairs of hydrogen atoms ($r_{HH}$). Other quantities that were also studied include projections onto the CH or CD distances and projections onto the coordinates that connect pairs of minimum energy structures through the $C_{s}(II)$ and $C_{2v}$ transition states shown in Fig. 1.1(a) and (b). As the differences between the distributions for the five states that are considered are small, only the projections onto the HH distance in CH$_5^+$ are plotted in Fig. 5.5. The indistinguishability of the distributions for these five states is also found for the other five isotopologues.

The indistinguishability of the projections of the probability amplitude onto $r_{HH}$ for the two $J = 0$ states is consistent with the results reported by Wang and Carrington.[28] In that study, they compared the projection of the probability amplitudes for the two lowest energy vibrational states onto HH distances and found the resulting distributions to be virtually indistinguishable. This observation, coupled with the fact that the excited state they considered is also the lowest energy state that is antisymmetric with respect to inversion, and the similarity of the energy they report for this state and the value obtained using DMC gives me confidence that I am looking at the same state. The similarity of the $J = 0$ and $J = 1$ projections provides an additional demonstration that the rotational and vibrational motions are relatively decoupled at this level of rotational excitation.
Figure 5.5: Projections of the probability amplitude onto the HH distances, $r_{HH}$, for the of the ground state (thick black solid line), the inversion excited state ($J = 0$) (medium dashed red line), and the $|1, 0, 0\rangle$ state (small blue dotted line) of CH$_5^+$. 

The rotational contributions to the wave function are characterized by projecting the absolute magnitude of the wave function onto the two Euler angles $\theta$ and $\chi$,[63] and the results for the $|1, 0, 0\rangle$ state are plotted in Fig. 5.6. For comparison, the distributions that are anticipated by Eq. 5.1 are also plotted. As can be seen the agreement is very good. To minimize the noise in these plots, I take advantage of the anticipated symmetry and average the distributions for $\theta$ and $180^\circ - \theta$ and for $\chi$ and $360^\circ - \chi$. Similar results are found for the other five isotopologues and for the other two $J = 1$ states.

In Table 5.5 the participation ratios for the ground state, inversion, $|1, 0, 0\rangle$ and $|1, 1, 0\rangle_\pm$ states for CH$_5^+$ and its deuterated isotopologues are reported. The value for $\rho$ for the ground states of CH$_5^+$ and CD$_5^+$ are both roughly 106 with an uncertainty (1$\sigma$) of approximately 6. This value for $\rho$ is lower than one would anticipate as the equivalence of the minima in these systems means that all 120 minima should be populated with equal probability amplitude. The deviation from the expected value of $\rho = 120$ reflects difficulties in converging these values. If the permutation symmetries of CH$_5^+$ and CD$_5^+$ are enforced by arbitrarily
Figure 5.6: Projection of $|\Psi|$ onto the (a) $\chi$ and (b) $\theta$ Euler angles for the $|1,0,0\rangle$ state of CH$_5^+$ (thick black line). For comparison, the analytical expression for the rotational function for a $|1,0,0\rangle$ state given in Eq. (1) is plotted (thin red dashed line).

Partial deuteration lowers the permutation symmetry of the system, and will lead to a reduction in the value of $\rho$.\[10, 14\] In these cases, the values of $\rho$ that are obtained with and without permutation of identical atoms either are the same (CH$_4$D$^+$ and CH$_3$D$_2^+$) or differ by a factor of two (CHD$_4^+$ and CH$_2$D$_3^+$). In the cases where there are differences of a factor of two, these differences reflect the fact that the minima are divided into two subsets and the barriers between these subsets of minima are sufficiently large that the amplitude of the wave function in the vicinity of the highest energy transition states is effectively zero. This may seem surprising since the barriers depend on the electronic energies, which cannot change upon deuteration. On the other hand, the relevant energy is not the absolute barrier height, but its size relative to the zero-point energy in the mode that takes the system from one of the minima toward the transition state. When the zero-point energy in the modes that are orthogonal to this coordinate are included, the relative energies of the transition
Table 5.5: Participation ratios, $\rho^a$ (defined in Eq. (4)), of CH$_5^+$ and its isotopologues for the ground state, inversion as well as the $|1,0,0\rangle$ and $|1,1,0\rangle\pm$ excited states.

| Isotopologue | Ground$^b$ | Ground$^c$ | Inversion | $|1,0,0\rangle$ | $|1,1,0\rangle_+$ | $|1,1,0\rangle_-$ |
|--------------|-----------|-----------|-----------|----------------|----------------|----------------|
| CH$_5^+$     | 107±5     | 118 ± 2   | 78±8      | 92±8           | 90±6           | 96±10          |
| CH$_4$D$^+$  | 69±7      | 74 ± 4    | 38±6      | 36±4           | 52±6           | 50±8           |
| CH$_3$D$_2^+$| 41±6      | 44 ± 3    | 32±6      | 42±6           | 34±4           | 34±4           |
| CH$_2$D$_3^+$| 13±1      | 25 ± 1    | 26±2      | 24±2           | 26±2           | 26±2           |
| CHD$_4^+$    | 27±4      | 56 ± 2    | 56±6      | 56±4           | 58±4           | 56±6           |
| CD$_5^+$     | 105±7     | 119 ± 1   | 84±8      | 96±6           | 86±8           | 94±12          |

$^a$ The reported error bars reflect one standard deviation and are based on sixteen independent evaluations of the wave function.

$^b$ Using the same algorithm as for the excited states.

$^c$ Enforcing permutation symmetry, see text for details.

states change dramatically with deuteration. The size of this effect will depend on the specific pair of isotopomers they separate.

When the various excited states are considered, the values of the participation ratios for CH$_5^+$, CD$_5^+$, CH$_3$D$^+$ and CH$_3$D$_2^+$ further decrease, and in all but the CH$_4$D$^+$ isotopologue, the four excited states have roughly equal values of $\rho$. This decrease reflects the inequality of the distribution of the probability amplitude among the minima, shown in Fig. 5.3. This decrease in the value of $\rho$ with rotational and/or vibrational excitation serves to illustrate that the calculated states with $J = 1$ also contain excitation of the inversion mode. The similarity of the probability amplitude in the individual minima and the similarity of the values of the participation ratios for the four states that are reported provides yet another illustration that at this level of rotational and vibrational excitation, the rotations are relatively decoupled from the vibrational motions of the molecule.

In the case of CH$_2$D$_3^+$ and CHD$_4^+$ the value of the participation ratios actually increases by a factor of two for the excited state when compared to the corresponding values for the ground states. These values of $\rho$ for the excited states are in good agreement with the values obtained when permutation symmetry is enforced in the ground state simulations.
This is a consequence of the way \( \rho \) is evaluated for excited states. To account for the symmetry of the total wave function, when the participation ratios are evaluated, it is a requirement that the values of \( p_i \) are equal for the two members of each chiral pair.

Finally, the average probability amplitude in the minima that are related by permutation of identical atoms, shown in Fig. 5.4 is considered. The distributions for \( J = 0 \) and \( J = 1 \) are now nearly identical, indicating that as with the internal coordinate distributions, the effect of the node is averaged out when I only focus on the type of atom in each position rather than identifying the locations of each of the atoms.

5.3 Conclusions

I have calculated \( J = 1, |K_C| = 0 \) or 1 and inversion excited states for CH\(_5^+\) and its isotopologues. Regardless of the structure that is used for the Eckart embedding of CH\(_5^+\), the energies for a given state are identical to each other to within statistical uncertainties. In the case of CH\(_5^+\) and CD\(_5^+\), the three \( J = 1 \) energies are the same, a result that is consistent with CH\(_5^+\) and CD\(_5^+\) being near-spherical top molecules. These energies are larger than one would anticipate if the excitation were purely rotational, and are assigned as the \( J = 1 \) levels of the lowest energy state that is antisymmetric with respect to inversion of the axis system. Similar behavior was seen in studies of H\(_3\)O\(^+\), but unlike H\(_3\)O\(^+\) the symmetry of the molecule cannot be employed to obtain the \( J = 1 \) energies for the \( v = 0 \) state.

The probability distributions were analyzed for all of the states that were calculated. The vibrational distributions are found to be identical for all states of the same chemical species. The rotational distributions have the functional forms expected for the three \( J = 1 \) states investigated in this study. Differences are seen in the calculated participation ratios between the ground and the set of excited states considered in this study. In particular, I find that all \( J = 0, J = 1, |K_C| = 0,1 \) rotational and inversion excited states for a given isotopologue sample the same number of minima on the potential surface, on
average, although in most cases this number is smaller than the number of minima that contain probability amplitude in the ground state. These results, along with the analysis of the energies, lead us to conclude that for the states studied here, the coupling between rotation and vibration in these highly fluxional molecules remains small, although it is anticipated that with vibrational excitation this coupling should increase, and it will be interesting to see if the apparently complex patterns observed in the high resolution spectra can be understood in terms of a model Hamiltonian, once the correct model Hamiltonian is identified.
CHAPTER 6

Minimized energy path Diffusion Monte Carlo approach for investigating anharmonic quantum effects: applications to the

$\text{CH}_3^+ + \text{H}_2$ reaction

In this Chapter, I investigate changes to the energy and wave functions of the $\text{CH}_5^+$ system as it is formed from the $\text{CH}_3^+$ and $\text{H}_2$ fragments. From earlier studies of $\text{CH}_5^+$, the McCoy group and others\cite{8, 10, 14, 15, 30, 69} found that the ground vibrational state has equal probability amplitude at each of the 120 equivalent minima and has approximately the same amplitude at these minima and at the 180 saddle points that connect the minima.\cite{8, 12} Despite the large fluxionality of $\text{CH}_5^+$, even in its vibrational ground state, projections of the ground state probability amplitude indicate that, on average, $\text{CH}_5^+$ can be described by a $\text{CH}_3^+$ subunit, connected to $\text{H}_2$ by a two electron, three centered bond.\cite{12, 15, 20, 21, 69} While all of the hydrogen atoms are equivalent in $\text{CH}_5^+$, the introduction of a single deuterium atom lowers the symmetry. Specifically, the quantum mechanical ground state of $\text{CH}_4\text{D}^+$ has the deuterium atom preferentially located in the $\text{CH}_2\text{D}^+$ subunit.\cite{14}

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6.1 Theory

To evaluate the anharmonic zero-point energies as a function of a reaction coordinate, the Diffusion Monte Carlo (DMC) approach is used. This method can be traced to Fermi, Metropolis and Ulam,[38] and our implementation is based on the work of Anderson[39, 40] and of Buch.[70] DMC has been shown to be an extremely effective approach for studying molecules,[42] including CH\textsubscript{5}+[14, 69] and H\textsubscript{5}+,71] that undergo large amplitude motions. Several years ago Clary and co-workers[72] used DMC to perform reaction path studies for the OH + H\textsubscript{2} reaction. In their implementation, they used the Miller, Handy and Adams reaction path formalism to obtain a reaction coordinate \(s\), and evaluated anharmonic corrections by performing the DMC simulation at fixed values of \(s\). In that work, they only allowed displacements of coordinates orthogonal to the reaction coordinate. In the present study, a different approach is pursued in which I use the adiabatic DMC formalism, developed in the McCoy group,[43] to evaluate the anharmonic zero-point corrected energy as a function of the center of mass separation of the two fragments.

One of the strengths of the DMC approach is that it provides a way to obtain a Monte Carlo sampling of the ground state wave function, and by extension, a statistical sampling of the ground state probability amplitude that can be readily projected onto any coordinate, or coordinates of interest. As the formation of CH\textsubscript{5}+ from CH\textsubscript{3}+ and H\textsubscript{2} is considered, I focus on several projections of the probability amplitude. More specifically, the probability amplitude is projected onto the CH and HH distances as well as the Euler angles that describe the orientations of the two subunits relative to the vector that connects their centers of mass, \(R\), as depicted in 6.1. As the molecular fragments are brought together, the Euler angles evolve from rotational coordinates into two bends and a torsion. It should be noted that, unlike earlier studies, the five hydrogen atoms are not treated in an equivalent manner in these simulations. As a result, projections of the probability amplitudes will be divided into the pieces that depend on coordinates that only involve the atoms in the CH\textsubscript{3}+.
Figure 6.1: Jacobi vectors that define CH$_3^+$. The hydrogen atoms in the CH$_3^+$ subunit are represented by the blue circles, those in the H$_2$ subunit are red and the carbon atom is represented by the black circle. The Euler angles that are used to define the geometries of the complex as it combines are defined as the angle between $\vec{R}$ and $\vec{r}_{CH_3^+}$ ($\theta_{CH_3^+}$) and the angle between $\vec{R}$ and $\vec{r}_{H_2}$ ($\theta_{H_2}$). The angle $\phi_{H_2}$ is defined as the torsion angle involving $\vec{r}_{H_2}$, $\vec{R}$ and one of the blue dashed lines, which connects one of the hydrogen atoms in the CH$_3^+$ subunit to the center of mass of the carbon atom and the other two hydrogen atoms.

In this Chapter, the Diffusion Monte Carlo approach is used, as described by Anderson,[39, 40] to obtain the energies and wave functions of CH$_3^+$ as functions of $R$. The general approach, and our implementation of it, are described in detail in Chapter 3. This implementation of DMC requires that the kinetic energy operator be separable into $n$—contributions that each depend on one Cartesian component of the momentum, and that the coefficients be independent of the coordinates of the atoms, e.g.
\[ T = \sum_{j=1}^{n} \frac{p_j^2}{2m_j} \tag{6.1} \]

In developing a formalism for separating out a reaction coordinate and evaluating the zero-point energy and anharmonic wave function as a function of this coordinate, I wish to retain the above structure for the kinetic energy operator while introducing a parameter, \( R \), which can be varied to allow the molecule to form from its two constituent fragments.

A set of coordinates that provides such a structure for the kinetic energy operator is the Jacobi coordinates. In general, \( N \) vectors are needed to describe a \( N \)-atomic system. One provides the location of the center of mass of the system. As the kinetic energy of the center of mass commutes with the Hamiltonian, the components of this vector can be ignored. A second vector can be defined to connect the centers of mass of the fragments, and is denoted as \( R \) in Figure 6.1. The remaining \( N - 2 \) vectors provide information about the structure and orientation of the two fragments. They are set up either by connecting atoms to the center of mass of previously connected fragments, or by connecting the centers of mass of two such fragments. As such, the mass associated with each vector is the reduced mass of the fragments that are connected by the vector.

The definition of the vectors that define the separate fragments is flexible. In the case of \( \text{CH}_5^+ \), \( \vec{r}_{\text{H}_2} \) is used, which is the vector that defines the relative positions of the two hydrogen atoms in the \( \text{H}_2 \) portion (shown in red in Figure 6.1). The \( \text{CH}_3^+ \) part is described by three vectors. In the analysis of the probability amplitudes, two sets of coordinates are employed. The first includes the vector between two of the hydrogen atoms, \( \vec{r}_{\text{CH}_3^+,1} \); the vector between the third hydrogen atom and the center of mass associated with \( \vec{r}_{\text{CH}_3^+,1} \), \( \vec{r}_{\text{CH}_3^+,2} \); and the vector that connects the carbon atom to the center of mass of the three hydrogen atoms, \( \vec{r}_{\text{CH}_3^+,3} \). These vectors are identified in Figure 6.1. A second set of vectors is used to define \( \phi_{\text{H}_2} \). This set includes \( \vec{r}_{\text{CH}_3^+,1} \), the vector that connects the carbon atom to the center of mass associated with \( \vec{r}_{\text{CH}_3^+,1} \); and the vector that connects the remaining
hydrogen atom to the center of mass of \( \vec{r}_{CH_3^+} \). The three choices for this last vector are depicted with blue dashed lines in Figure 6.1. Since I am interested in how the energy and the probability amplitudes depend on the center of mass separation of the fragments, \( R \), and not the orientation of this vector, \( \vec{R} = (0,0,R) \).

With the coordinates defined, DMC simulations are performed in the usual way,[39, 42] except that the value of \( R \) is fixed and only the components of the \( \vec{r}_{a,i} \) vectors are allowed to diffuse. While the \( R \) dependence of the energy could be mapped out in this manner, it rapidly becomes tedious. Instead, the adiabatic Diffusion Monte Carlo approach is employed, developed by Lee, Herbert and McCoy.[43] This approach allows one to determine how the lowest energy eigenvalue of the Hamiltonian depends on a parameter in the Hamiltonian, in this case, \( R \). More specifically, \( R \) is made to be a linear function of the diffusion time, \( \tau \), with a slope chosen so that the change in energy resulting from changing the value of \( R \) at each time step in the simulation is small compared to the statistical fluctuations of the energy resulting from the Monte Carlo sampling. In the present work, \( R \) is increased by 0.0002 Å at each 10 a.u. time step, and the potential of Jin et al. is used to evaluate the potential energy as a function of the Cartesian coordinates of the six atoms.[30].

6.2 Results

In Figure 6.2, the energies of the \( CH_3^+ + H_2 \), \( CH_3^+ + HD \) and \( CH_2D^+ + H_2 \) systems as functions of \( R \), for \( R < 6 \) Å are plotted. In all cases, the simulations have been run in both directions, going from small to large values of \( R \) and from large to small values. The dynamics represented by the curves in Figure 6.2 can be divided into four regions.

At the smallest distances, \( R < 0.5 \) Å, the energy decreases with increasing \( R \), and there is a finite maximum in the potential energy at \( R = 0 \) in the reactions of \( H_2 \), while the energy diverges at \( R = 0 \) for the \( CH_3^+ + HD \) system. The \( R = 0 \) configuration corresponds to the centers of mass of the two subunits occupying the same point in space. This can be
Figure 6.2: Anharmonic zero-point corrected energies for the (a) CH$_3^+$ + H$_2$ → CH$_5^+$, (b) CH$_3^+$ + HD → CH$_4$D$^+$ (black) and CH$_2$D$^+$ + H$_2$ → CH$_4$D$^+$ (red) collision complexes.

achieved by a $D_{3h}$ saddle point structure, which was found to have an energy that is 3843 cm$^{-1}$ above the global minimum on the potential of Jin et al.[30] Such a structure can be achieved for the CH$_3^+$ + H$_2$ and CH$_2$D$^+$ + H$_2$ systems. When H$_2$ is replaced by HD the center of mass is no longer at the midpoint of the bond. As a result, the system cannot sample the $D_{3h}$ saddle point and is forced to sample higher energy regions of the potential when $R = 0$.

The second region spans from 0.5 to 1.3 Å. It is characterized by a number of local minima in the energy curves. By symmetry, when $R$ is evaluated at the 120 minimum energy structures of CH$_5^+$, seven unique values are obtained. The local minima in the curves in Figure 6.2 have been correlated to these seven unique values of $R$. The fact that
all seven configurations are sampled indicates that the artificial partitioning of the hydrogen atoms into \( \text{CH}_3^+ \) and \( \text{H}_2 \) subunits does not put any constraints on the possible minima that can be sampled in these simulations. In the case of the singly deuterated complex, it is found that the \( \text{CH}_2\text{D}^+ + \text{H}_2 \) curve lies at lower in energy than the \( \text{CH}_3^+ + \text{HD} \) curve. This is consistent with the localization of the deuterium in the \( \text{CH}_2\text{D}^+ \) group in \( \text{CH}_4\text{D}^+ \).[10]

Next, large values of \( R (> 2 \text{ Å}) \) are considered. In this region, the system should be considered as separated \( \text{CH}_3^+ \) and \( \text{H}_2 \) molecules. The calculated energy at the longest distance is consistent with this assertion. In the case of the \( \text{CH}_3^+ + \text{H}_2 \) system, the calculated energies are in agreement with the energy reported by Jin et al.[30] For the \( \text{CH}_4\text{D}^+ \) systems, the \( \text{CH}_2\text{D}^+ + \text{H}_2 \) channel is lower in energy than the \( \text{CH}_3^+ + \text{HD} \) channel, as is anticipated by the zero point energies of the fragments.

The intermediate region is the most interesting of the four. It corresponds to \( 1.3 < R < 2 \text{ Å} \). In this region, the energy increases with increasing \( R \). For the singly deuterated systems, the energies of the black and red curves cross in this region, placing the \( \text{CH}_3^+ + \text{HD} \) system lower in energy when \( 1.8 < R < 2.2 \text{ Å} \). To understand the origins of this crossing and to determine the distance at which we should consider \( \text{CH}_5^+ \) as a molecule rather than a long range ion molecule complex, we turn to an investigation of the probability amplitudes.

Specifically, we focus on how the distribution of the values of the angles between the \( \vec{R} \) and \( \vec{r}_{\text{H}_2} \) or \( \vec{r}_\text{CH}_{1,3} \) (6.1) depend on \( R \). In Figure 6.3, the projections of the probability amplitudes onto the angle \( \phi_{\text{H}_2} \) are also plotted. This angle is defined as the torsion angle involving \( \vec{r}_{\text{H}_2} \), \( \vec{R} \) and a vector that connects one of the hydrogen atoms in the \( \text{CH}_3^+ \) subunit to the center of mass of the carbon and other two hydrogen atoms. As described, there are three possible definitions for \( \phi_{\text{H}_2} \), and the distributions plotted in Figure 6.3 represent the sum of the distributions obtained from these definitions.

To start, I focus on the \( \text{CH}_3^+ + \text{H}_2 \) system, shown in the top row of Figure 6.3, where the projections of the probability distributions onto these three angles are plotted for
Figure 6.3: Projections of the probability amplitudes for the CH$_3^+$ + H$_2$ (top), CH$_2$D$^+$ + H$_2$ (middle) and CH$_3^+$ + HD (bottom) systems onto the three Euler angles defined in the text for values of $R$ ranging from 0.64 to 5.0 Å.
0.64 < R < 5.0 Å. Arrows indicate the shift in the distributions with R. The longest (5 Å, shown in violet) and shortest (0.64 Å, shown in black) distances provide an indication of the asymptotic behavior. At the longest distances, the three angular distributions are isotropic once one notes that the distributions in $\theta_\alpha$ ($\alpha = H_2$ or CH$_3^+$) include sin $\theta_\alpha$ volume elements. At the shortest distances, the distributions are strongly peaked. The distributions in the two zenith angles are peaked at values of $\theta_\alpha$ that correlate to $\vec{R}$ and $\vec{r}_{\text{CH}_3,3}$ being collinear with $\vec{r}_{H_2}$ perpendicular to these vectors. Likewise the distribution in $\phi_{H_2}$ is strongly anisotropic for $R < 1.1$ Å. These distributions are consistent with the minimum energy structure of CH$_3^+$.[15] At intermediate values of $R$, the values of $\theta_{H_2}$ and $\phi_{H_2}$ change smoothly between the two limits. The behavior of $\theta_{\text{CH}_3}$ is more complicated.

Based on these plots alone it remains challenging to discern a particular value of $R$ at which the system makes the transition from two separate interacting molecules to a complex.

To address this question, I focus on how the projections of the probability amplitude onto the CH and HH distances evolve as $R$ is increased. It is found that a value of $R = 1.3$ Å corresponds to the transition from distributions that more closely resemble CH$_3^+$ to ones that can be described as CH$_3^+$ + H$_2$. These projections are plotted in Figure 6.5 for $R = 1.3$ Å, and the corresponding distributions for $R = 1.2$ and 1.4 Å are plotted in Figures 6.4 and 6.6. The distributions are divided into three contributions. Specifically those involving only the hydrogen atoms in the CH$_3^+$ subunit are plotted with blue dashed lines, those that involve only the hydrogen atoms in the H$_2$ subunit are plotted with red dotted lines, and those that involve one hydrogen atom from each subunit are plotted in purple dot-dot-dashed lines. Darker shades indicate that the distances involve one deuterium atom, while the lighter shades are for distances that only involve hydrogen and carbon atoms. The sums of the distributions are plotted in black. When $R \geq 1.3$ Å, the summed CH distance distribution is bimodal. Likewise, at these distances, the HH distance distribution can be described as the sum of two non-overlapping distributions. One involves the distance
between the hydrogen atoms that are connected by $\vec{r}_{\text{H}_2}$, and the other involves the other nine hydrogen-hydrogen distances. At shorter distances, the two distributions coalesce.

Next, the two CH$_4$D$^+$ systems are considered, plotted in the middle (CH$_2$D$^+$ + H$_2$) and bottom (CH$_3^+$ + HD) panels of Figures 6.3 and 6.5. In the case of the CH$_2$D$^+$ + H$_2$, the distributions are similar to those for CH$_3^+$ + H$_2$. There are small differences. For example, the $\theta_{\text{CH}_3^+}$ distribution is shifted to larger values of the angle, while the $\phi_{\text{H}_2}$ distribution contains both solid and dashed lines. These differentiate between the situations when a hydrogen (solid) or a deuterium atom (dashed) in CH$_2$D$^+$ is used to define $\phi_{\text{H}_2}$. In the case of CH$_3^+$ + HD, the distributions show larger deviations from the other two sets. The changes in the $\theta_{\text{CH}_3^+}$ distribution can be understood by recognizing that the center of mass of HD is shifted from the center of the HD bond to a position that is closer to the deuterium atom. The changes in the $\theta_{\text{H}_2}$ distribution reflect a more fundamental change in the physics. This is also seen in the plots in Figure 6.5 and 6.7. In this case, the partial deuteration leads to an energy difference between the configurations in which the hydrogen in the HD is closer to the CH$_3^+$ subunit is lower in energy than the configurations in which the deuterium atom is closer. This effect is only seen when the zero-point energy is included and is strictly quantum mechanical in nature.

There are several consequences of this behavior in the CH$_3^+$ + HD system. First, because the center of mass of HD is closer to the deuterium atom, the distance between the center of the HD bond and the center of mass of the CH$_3^+$ subunit is smaller than $R$. This difference is responsible for the crossing of the black and red curves in Figure 6.2. The hydrogen atom end of HD also appears to interact first with the CH$_3^+$ molecular ion. This is not a favored configurations for HD exchange reactions, and it is expected that direct collisions are likely to be relatively inefficient for hydrogen/deuterium exchange reactions in equation 1.2. This effect is however solely due to the location of the center of mass. When the CH$_3^+$ + HD
Figure 6.4: Projections of the probability amplitudes for the CH$_3^+$ + H$_2$ (top), CH$_2$D$^+$ + H$_2$ (middle) and CH$_3$ + HD (bottom) systems onto the CH (left column) and HH distances for $R = 1.2$ Å. The colors indicate the locations of the hydrogen (lighter shades) and deuterium (darker shades). As mentioned in the text, the hydrogen atoms are not treated equivalently and distances involving only the hydrogen atoms in the H$_2$ subunit are plotted in red with dotted lines; those that involve only hydrogen atoms in the CH$_3^+$ subunit are plotted with dashed lines in blue, while HH distances that involve hydrogen atoms in the two subunits are plotted in with dot-dot-dashed lines shades of purple. The sums of the distributions are represented by the black solid lines.
Figure 6.5: Projections of the probability amplitudes for the CH$_3^+$ $+$ H$_2$ (top), CH$_2$D$^+$ $+$ H$_2$ (middle) and CH$_3^+$ $+$ HD (bottom) systems onto the CH (left column) and HH distances for $R = 1.3$ Å. The colors indicate the locations of the hydrogen (lighter shades) and deuterium (darker shades). As mentioned in the text, the hydrogen atoms are not treated equivalently and distances involving only the hydrogen atoms in the H$_2$ subunit are plotted in red with dotted lines; those that involve only hydrogen atoms in the CH$_3^+$ subunit are plotted with dashed lines in blue, while HH distances that involve hydrogen atoms in the two subunits are plotted in with dot-dot-dashed lines shades of purple. The sums of the distributions are represented by the black solid lines.
Figure 6.6: Projections of the probability amplitudes for the CH$_3^+$ + H$_2$ (top), CH$_2$D$^+$ + H$_2$ (middle) and CH$_3^+$ + HD (bottom) systems onto the CH (left column) and HH distances for $R = 1.4$ Å. The colors indicate the locations of the hydrogen (lighter shades) and deuterium (darker shades). As mentioned in the text, the hydrogen atoms are not treated equivalently and distances involving only the hydrogen atoms in the H$_2$ subunit are plotted in red with dotted lines; those that involve only hydrogen atoms in the CH$_3^+$ subunit are plotted with dashed lines in blue, while HH distances that involve hydrogen atoms in the two subunits are plotted in with dot-dot-dashed lines shades of purple. The sums of the distributions are represented by the black solid lines.
Figure 6.7: Projections of the probability amplitudes onto the HH distances between CH$_3^+$ and H$_2$ subunits for the CH$_2$D$^+$ + H$_2$ (solid lines) and CH$_3^+$ + HD (dashed lines) systems onto the HH $R = 1.3$ Å (left) and 2.0 Å (right). For consistency with 6.4 and 6.6, the HH distances are plotted with dark purple, and the HD distances are plotted in light purple.

calculations are performed on the CH$_3^+$ + H$_2$ potential surface, the deuterium atom in HD interacts with the CH$_3^+$ molecular ion first.

### 6.3 Conclusions

In this Chapter I present a general approach for investigating reaction paths for highly quantum mechanical systems. The approach was applied to a study of the CH$_3^+$ + H$_2$ system and its single deuterated analogues. The plots of energy as a function of the dissociation coordinate show structure at short distances, which is indicative of the multiple minima on the potential surface. By using DMC in this study, I have also investigated how the wave functions change as the system evolves from reactants to complex formation. Analysis of these wave functions allows one to determine the separation at which the transition from two separated reacting species evolves into a complex in which the hydrogen atoms exchange freely. This provides a way to determine the center of mass separation at which statistical models, that are based on long-lived complex formation, are expected to become
applicable. The situation becomes more interesting when a single deuterium atom is introduced. Here quantum mechanical zero-point effects lead to the non-statistical entrance channel geometries, with the hydrogen end of HD approaching the CH$_3^+$ with greater probability. At low collision energies this has interesting implications for the hydrogen/deuterium exchange reactions.

Since the full quantum dynamics of CH$_3^+$ are beyond our current capabilities, insights on this and other similar reactions, like HD + H$_3^+$ obtained from the reaction path DMC approach described here will be helpful in directing future classical, semiclassical and statistical treatments of these important reactions.
CHAPTER 7

Isotopic effects on the Minimized Energy paths of the reaction

\[ \text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ \rightarrow \text{CH}_3^+ + \text{H}_2 \]

In Chapter 6 I focused on the effects singly deuterating \( \text{CH}_5^+ \). In studying the minimized energy paths it was noted that there is structure at the bottom of the potential well, indicative of a reorganization of the hydrogen atoms within \( \text{CH}_5^+ \). This reorganization occurs because of the extremely flat potential surface that allows for easy reorganization of any pair of the hydrogen/deuterium atoms between multiple equivalent minima. Wave functions for stationary points of \( R \) are also calculated from this data and used determine when there was free exchange of hydrogen atoms and no interaction between the \( \text{H}_2 \) and \( \text{CH}_3^+ \) subunits. The wave function data also shows that in the reaction of \( \text{CH}_3^+ + \text{HD} \) the hydrogen atom approaches the \( \text{CH}_3^+ \) group first rather than the deuterium atom. Here these studies are expanded for all deuterated isotopologues of \( \text{CH}_5^+ \) and for those with up to two tritium atoms.

7.1 Theory

7.1.1 Diffusion Monte Carlo

All minimized energy path calculations are performed for 30 000 time steps with a time step of \( \Delta \tau = 10 \text{ a.u.}, \alpha = 0.1 \text{ Hartree} \). In most cases, the calculations are performed from
Figure 7.1: The $C_2v(I)$ equilibrium structure of $\text{CH}_5^+$ with the $\text{H}_2$ (circled in red) and $\text{CH}_3^+$ (circled in blue) groups highlighted (a). Panel (b) shows how the Jacobi vectors connect to form $R$, with $R$ in purple and the Jacobi vectors for the $\text{CH}_3^+$ group shown in blue and the Jacobi vector for the $\text{H}_2$ group shown in red.

6.0 to 0.0 Å and from 0.0 to 6.0 Å, with a step size of $\Delta R = 0.0002$ Å. In instances where the $\text{H}_2$ group is comprised of a hydrogen and a tritium atom, the second calculation is run from 0.2 to 6.0 Å, also for 30 000 time steps. Minimized energy path and minimized energy structures are also calculated by numerically minimizing the energy of the complex as a function of $R$ and compared to the results obtained from the DMC simulations. Figure 7.1(b) shows a pictorial representation of $R$.

7.1.2 Probability Amplitudes

To calculate the energy of the system, at fixed values of $R$, reduced dimensional Diffusion Monte Carlo calculations, are employed. Descendent weighting is employed to generate the probability amplitudes from the wave functions.[42, 45] In particular the probability amplitude is projected onto the $r_{\text{CH}}$ and $r_{\text{HH}}$ coordinates.[31] The $\phi_{\text{H}_2}$, $\theta_{\text{H}_2}$, and $\theta_{\text{CH}_3^+}$ projections of the probability amplitude are also calculated. These are the same projections of the probability that were employed in chapter 6. The projection of the probability amplitude onto the distance between the carbon and the hydrogen atoms is $r_{\text{CH}}$, the projection of the
probability amplitude onto the distance between two of the hydrogen atoms is \( r_{HH} \). The projections of the probability amplitude onto \( r_{CH} \) and \( r_{HH} \) must be divided into multiple pieces representing the atoms in the \( \text{H}_2 \) group and the \( \text{CH}_3^+ \) group. The hydrogen atoms in the \( \text{CH}_3^+ \) and \( \text{H}_2 \) groups have different properties and except at the shortest distances they do not freely exchange. These two portions of the probability amplitude must be treated separately. The averages and standard deviations of the \( r_{CH} \) and \( r_{HH} \) distances have also been calculated. While we tend to think of \( R \) as connecting together the two atoms in the \( \text{H}_2 \) group to the atoms in the \( \text{CH}_3^+ \) group, this is not necessarily what happens in the calculations. When a simulation is performed, the center of mass between two hydrogen atoms is calculated as well as a center of mass for the carbon atom and the three remaining hydrogen atoms, where \( R \) is the vector between these two groups. There is no assigned parameter that forces the two hydrogen atoms that the center of mass of the \( \text{H}_2 \) group is calculated for to actually make up the \( \text{H}_2 \) group, nor do the hydrogen atoms that are employed in the calculation of the center of mass of the \( \text{CH}_3^+ \) group actually have to be within the \( \text{CH}_3^+ \) group.

The \( \phi_{\text{H}_2} \), \( \theta_{\text{H}_2} \), and \( \theta_{\text{CH}_3^+} \) probability distributions are projections of the probability amplitude based on angles between the two fragments. The \( \phi_{\text{H}_2} \) angle is defined as a torsional angle comprised of \( r_{\text{H}_2} \), \( R \), and a vector that connects one of the hydrogen atoms in \( \text{CH}_3^+ \) to the center of mass of the carbon atom and the other two hydrogen atoms. With three hydrogen atoms in \( \text{CH}_3^+ \), there are six possible definitions of \( \phi_{\text{H}_2} \) due to the two hydrogen atoms in the \( \text{H}_2 \) group. When the \( \text{H}_2 \) group is comprised of a hydrogen and a deuterium atom there are three \( \phi_{\text{H}_2} \) projections for the hydrogen atom and three for the deuterium atom. The plots are a sum of three of these distributions in the case of \( \text{CH}_3^+ \) or \( \text{CD}_3^+ \) as the \( z \)-axis is tied to one of the hydrogen atoms within the \( \text{H}_2 \) group in the plots. When the \( \text{CH}_3^+ \) group is comprised of both hydrogen and deuterium or tritium atoms, the distributions for the hydrogen atoms in the \( \text{CH}_3^+ \) group are summed together, and the
distributions for the deuterium or tritium atoms in the \( \text{CH}_3^+ \) group are summed together. The \( \theta_{\text{H}_2} \) angle is the angle between the Jacobi vector of \( r_{\text{H}_2} \) and \( R \) and the \( \theta_{\text{CH}_5^+} \) angle is the angle connecting the center of mass of \( \text{H}_2 \) to the center of mass of the \( \text{CH}_3^+ \) group, to the center of mass of the three hydrogen atoms in \( \text{H}_3^+ \).

7.2 Results

7.2.1 Minimized Energy Paths

Minimized energy paths from 6.0 to 0.0 Å and from 0.0 to 6.0 Å for \( \text{CH}_5^+ \) and its deuterated and partially tritiated isotopologues have been calculated. Figure 7.2 shows the minimized energy paths for \( \text{CH}_5^+ \) (a), \( \text{CH}_4^+ \)D\(^+\) (b), and \( \text{CH}_3^+ \)D\(^2\) (c). Minimized energy paths for \( \text{CH}_2^+ \)D\(^3\) (a), \( \text{CHD}_4^+ \) (b) and \( \text{CD}_5^+ \) (c) are shown in Figure 7.3 and minimized energy paths for \( \text{CH}_4^+ \)T\(^+\) (a) and \( \text{CH}_3^+ \)T\(^2\) (a) are shown in Figure 7.4. All of these minimum energy paths display the same basic trends. For all systems it is found that at distances between 6 and 3 Å all of the minimized energy paths are gently sloping downwards in energy as they approach 3 Å. At distances shorter than approximately 3 Å, the energy of the system decreases rapidly as \( R \) goes from 3.0 to 1.3 Å. Consequently the interaction between the two fragments increases throughout this region until at approximately 1.3 Å where the energy reaches a local minimum. At distances of less than approximately 1.3 Å, \( \text{CH}_5^+ \) has formed and the energy of the minimized energy path is nearly constant. At distances shorter than approximately 0.5 Å, the energy increases. For a given arrangement of hydrogen or deuterium atoms within the system, the minimized energy paths should be identical regardless of the direction the minimized energy path is scanned (6.0 to 0.0 Å or 0.0 to 6.0 Å). However at values of \( R < 0.7 \) Å differences between the two paths based on the direction of scanning are observed. These differences come from a scan becoming
captured in a certain configuration of the CH$_3^+$ and H$_2$ groups that is not necessarily the minimized energy structure for that value of $R$. 

Figure 7.2: Minimized energy paths for the CH$_3^+$ (a), CH$_4^+$ (b) and CH$_3$D$_2^+$ (c) reactions from 0.0 to 6.0 Å. In panel (a), the CH$_3^+$ + H$_2$ minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. In panel (b), the CH$_3^+$ + HD minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CH$_2$D$_2^+$ + H$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan. In panel (c), the CH$_3^+$ + D$_2$ minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CH$_2$D$_2^+$ + HD minimized energy path is shown in yellow for the 6.0 to 0.0 Å scan and green for the 0.0 to 6.0 Å scan. The CHD$_2^+$ + H$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan. Panel (a) also shows the D$_{3h}$ geometry observed at 0.0 Å.
Figure 7.3: Minimized energy paths for the CD$_5^+$ (a), CHD$_4^+$ (b) and CH$_2$D$_3^+$ (c) reactions from 0.0 to 6.0 Å. In panel (a), the CD$_5^+$ + D$_2$ minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. In panel (b), the CD$_5^+$ + HD minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CHD$_2^+$ + D$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan. In panel (c), the CD$_5^+$ + H$_2$ minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CHD$_2^+$ + HD minimized energy path is shown in yellow for the 6.0 to 0.0 Å scan and green for the 0.0 to 6.0 Å scan. The CH$_2$D$_2^+$ + D$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan.
Figure 7.4: Minimized energy paths for the CH$_4$T$^+$ (a) and CH$_3$T$^+_2$ (b) reactions from 0.0 to 6.0 Å. In panel (a), the CH$_4$T$^+$ + HT minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CH$_2$T$^+$ + H$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan. In panel (b), the CH$_3$T$^+$ + T$_2$ minimized energy path is shown in black for the 6.0 to 0.0 Å scan and red for the 0.0 to 6.0 Å scan. The CH$_2$T$^+$ + HT minimized energy path is shown in yellow for the 6.0 to 0.0 Å scan and green for the 0.0 to 6.0 Å scan. The CHT$^+_2$ + H$_2$ minimized energy path is shown in gray for the 6.0 to 0.0 Å scan and blue for the 0.0 to 6.0 Å scan.

In cases where the minimized energy path of a mixed isotopologue is calculated, there are multiple minimized energy paths that can be calculated because the properties of the system will be different depending on the location of the hydrogen/deuterium/tritium atoms within the CH$_3$$^+$ and H$_2$ groups. This will also affect the energies of the minimized energy path at short distances. These minimized energy paths fall into two distinct categories, which depend on whether or not the two atoms in the H$_2$ group have the same mass. In cases where the H$_2$ group is comprised of two identical atoms, the location of the center of mass of
the H$_2$ group is at the location of the center of bond, and the energy increases as $R \to 0$. At 0 Å the D$_{3h}$ (trigonal bipyramidal) transition state structure is formed. This corresponds to the hydrogen atoms within CH$_5^+$ arranging themselves to form the D$_{3h}$ structure of CH$_5^+$. This structure is shown in Figure 7.2 (a). When the H$_2$ group is comprised of two different isotopes of hydrogen, the center of mass of the H$_2$ group is no longer equivalent to the center of bond, and the energy increases steeply as $R \to 0$. When the center of mass of the H$_2$ group is no longer equal to the center of bond, the heavier isotope is found to be nearer to the CH$_3^+$ group. A strong repulsion of the H$_2$ group from the CH$_3^+$ group as $R \to 0$ is observed. Interestingly, breaking the symmetry of the CH$_3^+$ group does not result in a significant enough change in the symmetry of the molecule to cause a change in the minimized energy path from what is observed for non-isotopically mixed H$_2$ as $R \to 0$. This is because the change in the center of mass compared to the location of the center of bond is small compared to that of the H$_2$ group.

### 7.2.2 Probability Distributions

To get a full picture of the quantum mechanical behavior of CH$_5^+$ and its deuterated and partially tritiated isotopologues the probability distributions obtained from projections of the probability amplitude at fixed values of $R$ can also be calculated. Projections of the probability distributions onto the $r_{\text{CH}}$ and $r_{\text{HH}}$ distances as well as onto the angles, $\phi_{\text{H}_2}$, $\theta_{\text{H}_2}$, and $\theta_{\text{CH}_3^+}$ have been generated. The center and width of the $r_{\text{CH}}$ and $r_{\text{HH}}$ distributions have been obtained as a function of $R$.

One of the ways that probability amplitude data has been previously analyzed in the McCoy group[9, 16, 31] is by projecting the probability amplitude onto $r_{\text{CH}}$ and $r_{\text{HH}}$. These distributions have been calculated for $R$ varying from 1.0 to 1.8 Å in increments of 0.1 Å as shown for CH$_3^+ + \text{HD}$ in Figures 7.5, 7.6 and 7.7. Figures 7.8, 7.9, and 7.10, show these distributions for CH$_3^+ + \text{H}_2$ and for CH$_2\text{D}^+ + \text{H}_2$, Figures 7.11, 7.12, and 7.13. These plots
are divided up from 1.0 to 1.2 Å, 1.3 to 1.5 Å and 1.6 to 1.8 Å to show when the two hydrogen atoms in the H₂ portion of the system clearly form a molecule that is separating from CH₃⁺ as R increases. The vertical lines in Figures 7.5, 7.6, 7.7, 7.8, 7.9, 7.10, 7.11, 7.12, and 7.13, represent the positions of the hydrogen and deuterium atoms in numerically minimized structures.
Figure 7.5: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_3^+$ + HD for 1.0 (a), (b), 1.1 (c), (d) and 1.2 (e), (f) Å.
Figure 7.6: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_3^+$ + HD for 1.3 (a), (b), 1.4 (c), (d) and 1.5 (e), (f) Å.
Figure 7.7: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for CH$_3^+$ + HD for 1.6 (a), (b), 1.7 (c), (d) and 1.8 (e), (f) Å.
Figure 7.8: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_3^+ + \text{H}_2$ from 1.0 (a), (b), 1.1 (c), (d) and 1.2 (e), (f) Å. The red curves represent the $r_{\text{CH}}$ and $r_{\text{HH}}$ probability distributions while the green lines describe the numerically minimized energy structures.
Figure 7.9: Comparison of $r_{CH}$ (a), (c), (e), and $r_{HH}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_3^- + \text{H}_2$ from 1.3 (a), (b), 1.4 (c), (d) and 1.5 (e), (f) Å. The red curves represent the $r_{CH}$ and $r_{HH}$ probability distributions while the green lines describe the numerically minimized energy structures.
Figure 7.10: Comparison of $r_{CH}$ (a), (c), (e), and $r_{HH}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_3^+ + \text{H}_2$ from 1.6 (a), (b), 1.7 (c), (d) and 1.8 (e), (f) Å. The red curves represent the $r_{CH}$ and $r_{HH}$ probability distributions while the green lines describe the numerically minimized energy structures.
Figure 7.11: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_2\text{D}^+ + \text{H}_2$ for 1.0 (a), (b), 1.1 (c), (d) and 1.2 (e), (f) Å.
Figure 7.12: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b),(d),(f), probability distributions with the numerically minimized energy structures for CH$_2$D$^+$ + H$_2$ for 1.3 (a), (b), 1.4 (c), (d) and 1.5 (e), (f) Å.
In Figures 7.5, 7.6 and 7.7, the $r_{CH}$ distributions, the red solid ($CH_3^+$) and dashed ($H_2$) vertical lines represent the CH bond distances and the blue lines represent CD bond distances. In the $r_{HH}$ distributions, the red solid ($H_2$), dashed ($CH_3^+$), and dash-dot-dot (one hydrogen atom in the $H_2$ group and one in the $CH_3^+$ group) vertical lines represent distances between two hydrogen atoms, and the purple lines represent distances between a hydrogen and a deuterium atom. The quantum mechanical distributions are represented by the curves. In Figures 7.8, 7.9 and 7.10 the green solid ($CH_3^+$) and dashed ($H_2$) vertical lines represent the CH bond distances. In the $r_{HH}$ distributions, the green solid ($H_2$), dashed ($CH_3^+$), and dash-dot-dot (one hydrogen atom in the $H_2$ group and one in the $CH_3^+$ group) vertical lines represent distances between two hydrogen atoms. The quantum mechanical distributions are represented by the curves. Curves with a dash-dot-dot line correspond to interactions with one hydrogen in the $H_2$ group and one in the $CH_3^+$ group. In Figures 7.11, 7.12, and 7.13, the $r_{CH}$ distributions, the red solid ($H_2$) and dashed ($CH_3^+$) vertical lines represent the CH bond distances and the blue lines represent CD bond distances. In the $r_{HH}$ distributions, the red solid ($H_2$), dashed ($CH_3^+$), and dash-dot-dot (one hydrogen atom in the $H_2$ group and one in the $CH_3^+$ group) vertical lines represent distances between two hydrogen atoms, and the purple lines represent distances between a hydrogen and a deuterium atom. The quantum mechanical distributions are represented by the curves.

From Figure 7.5 it is noted that when $CH_5^+$ is formed all of the $r_{CH}$ distributions overlap and that while the sum of the $r_{HH}$ distributions is bimodal, the two peaks that come from the CH distances within the $CH_3^+$ unit and from the CH distances involving the $H_2$ group overlap. As is shown in Table 7.1, at approximately 1.3 Å the complex shifts from being $CH_5^+$ to a situation that can better be described by interacting $CH_3^+$ and $H_2$ fragments.
Figure 7.13: Comparison of $r_{\text{CH}}$ (a), (c), (e), and $r_{\text{HH}}$ (b), (d), (f), probability distributions with the numerically minimized energy structures for $\text{CH}_2\text{D}^+ + \text{H}_2$ for 1.6 (a), (b), 1.7 (c), (d) and 1.8 (e), (f) Å.
The $r_{\text{CH}}$ and $r_{\text{HH}}$ distributions are summarized in Figure 7.14(b) and (e). As the value of $R$ increases, the distance between the CH$_3^+$ and H$_2$ groups increases. Similar behavior is observed in all isotopologues.

Table 7.1: Interaction Regions based on value of $R$ for CH$_3^+$ and its deuterated and partially tritiated isotopologues.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Short Range Repulsion Å</th>
<th>Complex Å</th>
<th>Short Range Fragment Interaction Å</th>
<th>Long-range Fragment Interaction Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3^+$ + H$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_3^+$ + HD</td>
<td>&lt;0.6</td>
<td>0.6-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_2$D$^+$ + H$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_3^+$ + D$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_2$D$^+$ + HD</td>
<td>&lt;0.6</td>
<td>0.6-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CHD$_2^+$ + H$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_2$D$^+$ + D$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CHD$_2^+$ + HD</td>
<td>&lt;0.6</td>
<td>0.6-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CD$_3^+$ + H$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CD$_2^+$ + D$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CD$_2^+$ + HD</td>
<td>&lt;0.6</td>
<td>0.6-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_3^+$ + HT</td>
<td>&lt;0.7</td>
<td>0.7-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_2$T$^+$ + H$_2$</td>
<td>&lt;0.4</td>
<td>0.4-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_3^+$ + T$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.3</td>
<td>1.3-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CH$_2$T$^+$ + HT</td>
<td>&lt;0.7</td>
<td>0.7-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>CHT$_2^+$ + H$_2$</td>
<td>&lt;0.5</td>
<td>0.5-1.4</td>
<td>1.4-2.5</td>
<td>&gt;2.5</td>
</tr>
</tbody>
</table>

The center and width of the distributions are plotted as a function of $R$ for all of the isotopologues of CH$_3^+$ show similar trends. The plots for CH$_3^+$ + H$_2$ (a) (d), CH$_3^+$ + HD (b) (e), and CH$_2$D$^+$ + H$_2$ (c) (f) are shown in Figure 7.14. The plots for CH$_3^+$ + D$_2$ (a) (d), CH$_2$D$^+$ + HD (b) (e), and CHD$_2^+$ + H$_2$ (c) (f) are shown in Figure 7.15. The plots for CH$_2$D$^+$ + D$_2$ (a) (d), CHD$_2^+$ + HD (b) (e), and CD$_2^+$ + H$_2$ (c) (f) are shown in Figure 7.16. The plots for CH$_3^+$ + HT (a) (c), and CH$_2$T$^+$ + H$_2$ (b) (d) are shown in Figure 7.19. The plots for CH$_3^+$ + T$_2$ (a) (d), CH$_2$T$^+$ + HT (b) (e), and CHT$_2^+$ + H$_2$ (c) (f) are shown in Figure 7.20. The circle, square, or triangle is the center of the distribution and the
error bars represent the width. In Figure 7.14 (a) the circles represent the center of the
distribution for the $H_2$ group, and the triangles represent the $CH_3^+$ group for the CH bond
length distribution. In Figure 7.14 (d), the filled circle corresponds to the center of the
distribution in the $H_2$ group, the filled triangle the $CH_3^+$ group, and the square represents
the center of the distribution when one hydrogen atom is in the $H_2$ group and one is in
the $CH_3^+$ group for the HH distance distribution. In Figure 7.14 (b) the circles represent
the center of the distribution for the $H_2$ group where the red circles represent the CH bond
length and the dark red circles the CD bond length, and the triangles represent the $CH_3^+$
group CH bond lengths. In Figure 7.14 (d), the filled circle corresponds to the center of
the distribution of the HD group, the filled triangle the $CH_3^+$ group, and the red square
represents the center of the distribution when one hydrogen atom is in the HD group and
one is in the $CH_3^+$ group, the purple square when the deuterium atom and one of the
hydrogen atoms in the $CH_3^+$ group are interacting. In Figure 7.14 (c) the circles represent
the center of the distribution for the $H_2$ group, and the blue triangles represent the $CH_2D^+$
group CH bond lengths, the teal triangles the $CH_2D^+$ CD bond length. In Figure 7.14 (d),
the filled circle corresponds to the center of the distribution of the $H_2$ group, the filled red
triangle the $CH_2D^+$ group HH distance, the purple triangle the $CH_2D^+$ group HD distances,
and the red square represents the center of the distribution when one hydrogen atom is in
the $H_2$ group and one is in the $CH_3^+$ group, the purple square when the deuterium atom
and one of the hydrogen atoms in the $H_2$ group are interacting.

As these plots are easier to interpret, I will focus the remainder of my discussion of $r_{\text{CH}}$
and $r_{\text{HH}}$ distributions on these plots. While all of the complexes show similar patterns in
dissociation and bonding, there are some things worth noting. Once $CH_5^+$ is formed, as
the value of $R$ is further decreased, the atoms that make up the $CH_3^+$ and $H_2$ can change.
While the hydrogen atoms in the $CH_3^+$ and in the $H_2$ group localize into specific positions,
these positions can change at different values of $R$. 

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Figure 7.14: The center and width of the $r_{CH}$ and $r_{HH}$ probability distributions for the CH$_3^+$+H$_2$ (a), (d), CH$_3^+$+HD (b), (e), and CH$_3$D$^+$+H$_2$ (c), (f) minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å. The complex is present when the width of the $r_{CH}$ distributions for the H$_2$ and CH$_3^+$ groups overlap. In frames (d), (e), and (f), the phrase “mix” represents a distribution with one hydrogen/deuterium atom in the H$_2$ group and one in the CH$_3^+$ group.
Figure 7.15: The center and width of the $r_{\text{CH}}$ and $r_{\text{HH}}$ probability distributions for $\text{CH}_3^+ + \text{D}_2$ (a) (d), $\text{CH}_2\text{D}^+ + \text{HD}$ (b) (e), and $\text{CHD}_2^+ + \text{H}_2$ (c) (f), minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.
Figure 7.16: The center and width of the $r_{CH}$ and $r_{HH}$ probability distributions for CH$_3$D$^+$ + D$_2$ (a) (d), CHD$_2^+$ + HD (b) (e), and CD$_3^+$ + H$_2$ (c) (f), minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.
Figure 7.17: The center and width of the $r_{\text{CH}}$ and $r_{\text{HH}}$ probability distributions for CHD$_2^+ + D_2$ (a) (c), CD$_2^+ + HD$ (b) (d), minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.
Figure 7.18: The center and width of the $r_{CH}$ and $r_{HH}$ probability distributions for CD$_3^+$ + D$_2$ (a) (b) minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.
Figure 7.19: The center and width of the $r_{CH}$ and $r_{HH}$ probability distributions for CH$_3^+$ + HT (a) (c), CH$_2$T$^+$ + H$_2$ (b) (d), minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.
Figure 7.20: The center and width of the $r_{\text{CH}}$ and $r_{\text{HH}}$ probability distributions for CH$_3^+$ + T$_2$ (a) (d), CH$_2^+ + $ HT (b) (e), and CHT$_2^+ + $ H$_2$ (c) (f), minimized energy paths at 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.5, 3.0, 4.0, and 5.0 Å.

When the value of $R$ is restricted, instead of CH$_5^+$ automatically going to its lowest energy configuration when the complex is formed, and the potential being flat from approximately 1.3 to 0.5 Å, bumps and wiggles are observed in this area of the minimized energy path as is seen in Figure 7.2. In Figure 7.5 panels (b) and (d) show this reorganization of the atoms within CH$_5^+$. Different pairs of atoms are making up the H$_2$ group (have the shortest $r_{\text{HH}}$ distance), not just the atoms defined to be the “H$_2$ group” by the Jacobi vectors. In panel (b), two hydrogen atoms within the CH$_5^+$ group as defined by the Jacobi vectors, make up the H$_2$ group of the C$_s$(I) structure shown in Figure 7.1 (a), while in panel (d), a hydrogen and deuterium atom make up the H$_2$ group of the C$_s$(I) structure shown in Figure 7.1 (a). For cases where there is a mixed isotopologue in the H$_2$ group, the $r_{\text{CH}}$ distributions for the hydrogen and deuterium or tritium atom in the H$_2$ group no longer are the same within the short range interaction region as is observed in Figure 7.14.
The hydrogen atom in the HD/T group is observed to approach the CH$_3^+$ molecular ion first.\[73\] In Asvany’s study of the reaction of CH$_3^+$ with HD, the deuterium was observed to approach the CH$_3^+$ molecular ion first.\[3\] For the hydrogen/deuterium exchange reaction to occur between CH$_3^+$ and HD to occur through a direct mechanism, the hydrogen atom would need to approach first. The opposite is being observed. When the CH$_3^+$ + HD minimized energy path is calculated with the HD center of bond instead of the HD center of mass, the deuterium atom is observed to be closer to the CH$_3^+$ group. Since the center of mass of HD is closer to the deuterium atom, this likely means that since Diffusion Monte Carlo always goes to the lowest energy solution, that it is lower in energy for the minimized energy path to lengthen $R$ by pointing the deuterium away from the CH$_3^+$ group. It has been observed that when the length of $R$ is calculated from the angle of the HH bond in H$_2$ with $R$ and the location of the center of mass, that the calculated value of $R$ is in fact shorter for HD than for H$_2$. When the center of mass is forced to be in the same location as the center of bond, it is lower in energy for the deuterium atom to be closer to the CH$_3^+$ group. Having the deuterium atom closer to CH$_3^+$ would mean that an exchange reaction of a hydrogen atom on CH$_3^+$ and the deuterium atom could occur through a direct mechanism.

At the longest distances ($R > 2.5\text{Å}$), when there is very little interaction between the CH$_3^+$ and H$_2$ groups, the widths of the H$_2$ $r_{CH}$ and $r_{CD}$ distributions again overlap as is observed in Figure 7.14 (b). When a deuterium or tritium atom is placed in the CH$_3^+$ group, the width of the $r_{CH}/r_{CD}$ always overlap as can be seen in Figure 7.14 (c). As $R$ increases, the HH distance in the H$_2$ group quickly decreases to a value approximately equal to the distance between a non-perturbed H$_2$ molecule.

While the CH and HH distance distributions and standard deviations give a big picture of the H$_2$ and CH$_3^+$ fragment interaction for 1.0 to 5.0 Å, more can be determined about the interaction between the CH$_3^+$ and H$_2$ groups by studying projections of the $\phi_{H_2}$, $\theta_{H_2}$, and
$\theta_{\text{CH}_3^+}$ distributions of the probability amplitude. These distributions show how placement of hydrogen and deuterium atoms within the CH$_3^+$ and H$_2$ groups affect the interaction between the two fragments. If these distributions were completely isotropic no changes in the distributions would be observed based on the number or location of the hydrogen or deuterium atoms. The level of interaction differs depending on which projection of the probability distribution is plotted.

Figure 7.21 shows the $\phi_{\text{H}_2}$ distribution for CH$_5^+$ (a), and CH$_4^+$D$^+$ (b), (c) along with an illustration of the $\phi_{\text{H}_2}$ motion. At 1.0 Å the complex is bound and the distribution is represented by the black curve, in this distribution it is observed that there is a larger probability of $\phi_{\text{H}_2}$ being at 0, 90, and 180°, indicating a barrier in the rotation of the H$_2$ group. At 1.5 Å, the distribution is represented by the red curve, the distribution is flatter, with a very small increase in probability at 90°, indicating a small barrier for rotation of the H$_2$ group at this distance compared to the barrier felt at 1.0 Å. By 2.0 Å, the green curve indicates completely free rotation of the H$_2$ group and is shown by a completely flat distribution.[73] The $\phi_{\text{H}_2}$ motion shows interaction between the CH$_3^+$ group and the H$_2$ group at only values of $R$, where $R$ is in the CH$_5^+$ complex or the two fragments are at the smallest distances ($R \leq 1.5$ Å) of short range interaction. Similar behavior is observed for all isotopologues.

The $\theta_{\text{H}_2}$ projection of the probability amplitude shows interaction between the CH$_3^+$ and H$_2$ groups that extends to larger values of $R$. These distributions are shown in Figure 7.22. While only the distributions for CH$_5^+$ and CH$_4^+$D$^+$ are plotted, the corresponding distributions for all of the other isotopologues display similar trends to those shown here. The precise details of the distribution depend on whether or not the H$_2$ group contains two identical atoms. In cases where the H$_2$ group is comprised of two identical atoms, rotation of the H$_2$ group is hindered as is shown by the peaked distribution centered at 90° for values of $R < 2.0$ Å shown by the black (1.0 Å) and red (1.5 Å) curves. For values of $R \geq 2.0$ Å
green (2.0 Å), blue (2.5 Å), and pink (3.0 Å), the distributions look identical to each other. The projections of the probability amplitude are not flat for the free rotation of the $\theta_{H_2}$ projection of the probability amplitude. This distribution has a $\sin(\theta_{H_2})$ volume element. In the isotropic limit the projection of the $\theta_{H_2}$ probability amplitude in the isotropic limit is a sine function. However, when the H$_2$ group is comprised of two different isotopes of hydrogen, the probability amplitude is not described by a simple sine function as would be expected for an isotropic distribution and interaction is observed to longer distances. This is because the effective value of $R$ is in the shortest possible configuration that will be lowest in energy due to the center of mass being not equal to the center of bond.\[73\] Breaking of the symmetry of the CH$_3^+$ group does not appear to impact the overall $\theta_{H_2}$ probability...
Figure 7.22: Probability distributions for the $\theta_{H_2}$ interaction angle for the reactions CH$_3^+$ + H$_2$ (a), CH$_3^+$ + HD (b), CH$_2$D$^+$ + H$_2$ (c) from 1.0 to 3.0 Å. For clarification an illustration of the $\theta_{H_2}$ motion is also shown.

distributions likely because the overall change in the center of mass when compared to the center of bond is very small.

Projections of the probability amplitude onto $\theta_{CH_2^+}$ are found to be anisotropic out to values of $R < 3.0$ Å. Figure 7.23 shows these distributions for CH$_3^+$ and CH$_4$D$^+$ along with an illustration of the motion in $\theta_{CH_3^+}$. These probability distributions are dependent upon the symmetry of the center of mass of the H$_2$ and CH$_3^+$ groups. These distributions reach the isotropic limit at 3.0 Å in (a) and (b) (in pink). Figure 7.23 (c) has a narrowed distribution when compared to (a) and (b). In this case the deuterium is placed in the CH$_3^+$ group. Interaction between the two fragments is again observed out to 2.5 Å by the distributions approaching the geometry of the distribution at 3.0 Å. At 1.0 (black) and 1.5
(red) Å, the distributions are narrowed compared to the other distributions in panels (a), (b), and (c) indicating a small range of motion for the H$_2$ group at these distances.
Figure 7.23: Probability distributions for the $\theta_{CH_3}$ interaction angle for the reactions $CH_3^+ + H_2$ (a), $CH_3^+ + HD$ (b), $CH_2D^+ + H_2$ (c) from 1.0 to 1.3 Å. For clarification an illustration of the $\theta_{H_2}$ motion is also shown.

The probability distributions hint at a complicated picture for the values of $R$ that correspond to long-range fragment interactions of the $CH_3^+$ and $H_2$ fragments. Smaller amplitude motions like the $\phi_{H_2}$ projection of the probability amplitude only show perturbation of the probability amplitude when $CH_3^+$ has formed or when $R \leq 1.5$ Å. This would indicate that the larger the motion necessary to perturb the system, the further out the interaction between the two fragments are observed. The widths of the $r_{CH}$ and $r_{HH}$ distance distributions do not overlap after the complex breaks apart into $CH_3^+$ and $H_2$, but the $\phi_{H_2}$, $\theta_{H_2}$, and $\theta_{CH_3}$ projections of the probability amplitude still indicate interaction between the two fragments. By studying the numerically minimized energy structures I aim to better understand the interactions between the two fragments.
7.2.3 Comparison of Numerically Minimized Energy Structures to the Quantum Mechanics Calculations

In order to better understand the interactions between the CH$_3^+$ and H$_2$ groups and the effect of deuteriation on the system, the numerically minimized energy paths and values of the $r_{CH}$ and $r_{HH}$ distances from 1.0 to 1.8 Å have been calculated. The numerically minimized energy paths for CH$_5^+$ and CH$_4$D$^+$ are shown in Figure 7.24 along with the quantum mechanical plots for comparison. The minimized energy paths are in good agreement with the quantum mechanical calculations except in the region where the CH$_5^+$ complex has formed. In this region, the numerically minimized energy path calculation immediately falls to its lowest possible energy. However, four small increases in energy are observed as the hydrogen atoms reorient themselves. These first (and largest) increase in energy is close to that of the $C_{2v}$ saddle point energy (approximately 340 cm$^{-1}$) and the other three increases in energy are close to that of the $C_s$(II) saddle point energy (approximately 30 cm$^{-1}$). The increases in energy in the numerically minimized energy path plots are most easily observed in Figure 7.24(c) The numerically minimized energy paths follow the quantum mechanical path regardless of the isotopologue of CH$_5^+$ that they are calculated for. To align the two plots the dissociation energy of the CH$_3^+$ and H$_2$ fragments, as calculated by Jin and co-workers,[30] has been subtracted from the minimized energy path calculations.
Figure 7.24: Minimized energy paths (red, black) with numerically minimized energy structures (blue) for the CH$_3^+$ + H$_2$ (a), CH$_3^+$ + HD (b), CH$_2$D$^+$ + H$_2$ (c) reactions.
The CH and HH distances associated with the numerically minimized energy structures have been evaluated and are shown plotted along with the quantum mechanical probability distributions for CH$_3^+$ + HD in Figures 7.5, 7.6, and 7.7. The lines representing the numerically minimized energy CH and HH fixed values are at the center of the distribution of the corresponding projection of the probability amplitude. This, however, is not necessarily surprising given that $R$ is defined as the vector connecting the center of mass of the CH$_3^+$ group with the center of mass of the H$_2$ group. Given that these positions are mass dependent, one would expect one atom to be closer to the CH$_3^+$ than the other, generating results that would show a repulsive wall and mirror those of the quantum mechanical study.

In the numerically minimized energy structures the fixed values the of CH bond lengths in the H$_2$ group are very similar in length to each other for values of $R$ less than approximately 1.5 Å. When the two atoms in the H$_2$ group both have the same mass, this trend continues out into the short range interaction region. However, at distances $\geq$ 1.5 Å a small rotation of the H$_2$ group, shown by one hydrogen atom being slightly further away from the carbon atom than the other, is observed as a broadening of the quantum mechanical distribution, and the two CH distances that comprise the H$_2$ group no longer having the same CH bond length as is shown in the $r_{CH}$ distribution by two visible lines. When the H$_2$ group is comprised of hydrogen atoms with different masses, and the center of mass is no longer at the center of bond, this effect is amplified. The hydrogen atom in the H$_2$ group is observed to be nearer to the CH$_3^+$ group. When the CH$_3^+$ group is bound to the H$_2$ group, two of the CH bond lengths in the CH$_3^+$ group are the same and one is slightly longer. When the CH$_3^+$ complex is no longer formed, all of the CH bond lengths in the CH$_3^+$ group are observed to be of similar length. This is observed regardless of the isotope or hydrogen/deuterium atom ordering. This trend is observed for the quantum mechanical system as well, however the fragments must be further apart than what is observed in
the numerically minimized energy calculations such that the two fragments are no longer quantum mechanically interacting with each other.

### 7.2.4 Interaction Regions

The minimized energy paths hint at the possibility to discuss the interaction between the H₂ and CH₃⁺ units in terms of several different interaction types, which depend on the value of \( R \). These regions can be defined as a region of short range repulsion, the “CH₅⁺” complex, short range fragment interaction between the CH₃⁺ and H₂ groups, and long-range fragment interaction between the CH₃⁺ and H₂ groups. These ranges of \( R \) values that correspond to each of these regions are reported in table 7.1. The short range repulsion is defined as going from \( R = 0.0 \) Å to the location of the minima closest to \( R = 0.0 \) Å on the minimized energy path. While the values of \( R \) vary slightly for CH₅⁺ and its isotopologues, the differences in these values are found to be within the reported accuracy. For the partially tritiated systems, the difference between the center of mass and the center of bond is more pronounced when there is a tritium atom in the H₂ group.

The region after short range repulsion is the “CH₅⁺” complex, which is defined as being the distance from the local minima along the minimized energy path closest to \( R = 0 \) Å to the distance at which the widths of the \( r_{CH} \) distributions of the H₂ and CH₃⁺ groups no longer overlap. The third region, short range interaction between the H₂ and CH₃⁺ fragments, is defined as the range of \( R \) from which the widths of the \( r_{CH} \) distances of the H₂ and CH₃⁺ groups no longer overlap to the values where the \( \phi_{H_2} \), \( \theta_{H_2} \), and \( \theta_{CH_3^+} \) angles of interaction are isotropic. The values of \( R \) in these these regions are also independent of the location or number of the the hydrogen, deuterium or tritium atoms. The long-range fragment interaction region is defined as the region where no significant interaction between the H₂ and CH₃⁺ groups as judged by the projection of the \( \phi_{H_2} \), \( \theta_{H_2} \), and \( \theta_{CH_3^+} \) probability
amplitudes. This indicates that the location or number of hydrogen, deuterium or tritium atoms does not impact the distance at which a change in molecular interaction is observed.

The energies at fixed values of $R$ can also be calculated. The energies for the isotopologues for $R = 1.0$ Å, a value at which CH$_3^+$ is best described as a molecular ion bound by covalent bonding is observed, and $R = 5.0$ Å, where only very weak interactions between the CH$_3^+$ and H$_2$ fragments are observed, have been calculated. Due to a variance in bond length caused by the center of mass no longer being equal to the center of bond for the reaction paths where the is an HT or an HD group in place of the H$_2$ group, energies have not been calculated for the fragment interaction region. These energies are reported in table 7.2. Within a given isotopologue, the energies decrease when more of the deuterium or tritium atoms are placed in the CH$_3^+$ group, i.e. $E_{\text{CHD}_{2}^+ + \text{H}_2} < E_{\text{CH}_3\text{D}^+ + \text{HD}} < E_{\text{CH}_3^+ + \text{D}_2}$.

Based on Chapter 6 and the work of Gerlich and co-workers,[3] that showed that it is kinetically favorable for the deuterium atoms to be within the CH$_3^+$ group shown in Figure 7.1 (a), the reduction of energy as the deuterium atoms are placed in the CH$_3^+$ group instead of the H$_2$ moiety, fits within this kinetic picture. This effect increases for tritium and it is very energetically favorable to place the tritium atoms on the CH$_3^+$ group. In the long-range fragment interaction region, increasing the number of deuterium or tritium atoms lowers the energy of the overall system, regardless of if the deuterium, or tritium atoms are placed in the H$_2$ or CH$_3^+$ group. While this usually holds true in the region where there is CH$_5^+$, for the cases of CH$_3^+$ + D$_2$ and CH$_3^+$ + T$_2$, the energies are observed to be higher than some of the other isotopologues. In the case of CH$_3^+$ + D$_2$ the energy at 1.0 Å is higher than that of CH$_2$D$^+$ + H$_2$ at 1.0 Å and in the case of CH$_3^+$ + T$_2$ the energy at 1.0 Å is higher than that of CH$_2$T$^+$ + H$_2$ and CH$_2$D$^+$ + HD. Previous work of Marx[7, 74] and of the McCoy group[9, 10] has shown that there is a low probability of having both deuterium atoms in the H$_2$ group for CH$_3$D$_2^+$, which most likely explains this reversal in the energetic trend. If this were due to CH$_3^+$ + D$_2$ getting stuck in a local minima, one would think that the
calculation when run from 0 to 6 Å would have a different energy than the calculation run from 6 to 0 Å. This is not observed in Figure 7.3 or 7.4. The same increase in energy is not observed for CH₂D⁺ + D₂, which could be due to the deuterium atom in the CH₃⁺ group perhaps increasing the stability of the complex. Since there is already a deuterium atom in the CH₃⁺ group, the kinetic energy could be slightly stabilized in this arrangement.

Table 7.2: Energies in cm⁻¹ of the CH₃⁺ complex at R = 1.0 Å and the CH₃⁺ + H₂ fragments at R = 5.0 Å for CH₅⁺ and its deuterated and partially tritiated isotopologues. Where possible, the energies are reported in order from highest to lowest. The energies are lower than those observed in previous studies for the ground state of CH₅⁺[10,41] because of the loss of degrees of freedom with the implementation of the Jacobi vectors.[73]

<table>
<thead>
<tr>
<th>Isotopologue</th>
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<th>R = 5.0 Å</th>
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<td>CH₃⁺ + H₂</td>
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<tr>
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<tr>
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</tr>
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<td>8589±1</td>
<td>24472±1</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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<td>22909±1</td>
</tr>
</tbody>
</table>

7.3 Conclusions

By employing DMC to calculate minimized energy paths and energies at fixed values of the length of the Jacobi vector, R, more has been learned about how the H₂ and CH₃⁺
fragments of CH$_3^+$ and its deuterated and partially tritiated isotopologues interact with each other. Adding more deuterium or tritium atoms is found to lower the overall energy of the non-bonded system, while for the CH$_3^+$ + D$_2$ and CH$_3^+$ + T$_2$ systems, the addition of the second deuterium or tritium atom is actually higher in energy than the CH$_2$D$^+$ + H$_2$ or CH$_2$T$^+$ + H$_2$ at $R = 1.0$ Å. There are four distinct regions of interaction of the CH$_3^+$ and H$_2$ groups: short range repulsion, “CH$_5^+$” complex, short range fragment interaction, and long-range fragment interaction. The values of $R$ at different regions of interaction show that regardless of whether the system is comprised of hydrogen, deuterium, or tritium atoms the values of $R$, where there are changes in the level of interaction, are the same to within statistics.

The projection of the probability amplitudes onto $r_{CH}$, $r_{HH}$, $\phi_{H_2}$, $\theta_{H_2}$, and $\theta_{CH_3^+}$ have been calculated, and the center and width of the $r_{CH}$ and $r_{HH}$ distributions at various values of $R$. These show that unless symmetry of the CH$_3^+$ or H$_2$ group is broken, the probability distributions do not change with respect to deuteration or tritiation. The changes to the projections of the probability amplitude when the symmetry of the CH$_3^+$ group is broken are much smaller than the changes in the projections of the probability amplitude when the symmetry of the H$_2$ group is broken. When the symmetry of the H$_2$ group is broken, it is found that of the two atoms comprising the H$_2$ group, the hydrogen atom is closer to the CH$_3^+$ group in the region of short range fragment interaction region interaction. This is because when a DMC calculation is performed, DMC always calculates the lowest energy path. When CH$_3^+$ + HD calculations are performed, with the center of mass being placed at the center of bond, the deuterium atom is found to be closer to the CH$_3^+$ group, which follows the results of Gerlich and co-workers.[3]

Numerically minimized energy paths and CH and HH fixed values have also been calculated. These show that some quantum mechanical effects are observed within the bonded region of the minimized energy path. In the bonded region of the minimized energy path,
the quantum mechanical path has bumps and wiggles in the bottom of the potential well before the minimized energy path enters the repulsive region of the potential. The numerically minimized energy path drops directly to the lowest energy and small energy increases are observed to reorder the hydrogen atoms within \( \text{CH}_5^+ \). Otherwise, the paths are in good agreement. The calculated numerically minimized energy CH and HH fixed values are in good agreement with the quantum mechanical distributions and align to the center of the peaks of the quantum mechanical probability distributions. In cases where the symmetry of the \( \text{H}_2 \) group is broken, it is found that the numerically minimized energy calculations also show that the hydrogen atom is closer to the \( \text{CH}_3^+ \) group in the region of interaction between the two fragments, again because of differences in the center of mass compared to the center of bond.
CHAPTER 8

Conclusions

I have investigated the excited state energies and wave functions for several vibrationally and ro-vibrationally excited states of CH$_5^+$ and its deuterated isotopologues. From these excited states, we have learned more about the excited states of CH$_5^+$ and its deuterated isotopologues and their wave functions. The states that emerged from the calculations reflect combination bands and should aid in the assignment of the spectra. In both cases, by employing projections of the probability amplitudes more is learned about the nature of these excited states. The participation ratios show that in the case of the vibrationally excited states, that while a mode can have the same symmetry operation according to the $G_{240}$ Complete Nuclear Permutation Inversion Group, its sampling of the 120 minima can be different from another excited state with the same symmetry. In the case of the ro-vibrational states, an inversion mode cannot be separated from the rotationally excited states due to the extremely high symmetry of CH$_5^+$. In both cases, the structure of the nodal surface hints at a the complicated nature of the isomerization coordinates. The consequences of this in the spectroscopy are not straightforward and reinforces the experimental observation that the rotation-vibration spectrum is complex. It is hoped that with the additional information learned about the excited states of CH$_5^+$ from these studies that an assignment of the high-resolution spectra can be made. Of particular interest may be the inversion excited state energy.
Minimized energy paths were also calculated for CH\textsubscript{5}\textsuperscript{+} and its deuterated and partially tritiated isotopologues. They also give more information about CH\textsubscript{5}\textsuperscript{+}, particularly about the interaction between the two fragments as the CH\textsubscript{3}\textsuperscript{+} and H\textsubscript{2} fragments associate and dissociate. There are four distinct regions of interaction between the two fragments. The change in the regions of interaction is found to be independent of isotopologue. These regions indicate a complex behavior of interaction between the two fragments and reorganization of the hydrogen atoms in the bound complex is observed. When changes in the center of mass, when the center of mass is no longer equal to the center of bond, are accounted for it is found that our results mirror those of Gerlich and co-workers\cite{3} and indicate that it is energetically favorable for deuterium atoms to localize on the CH\textsubscript{3}\textsuperscript{+} group. Results from both the minimized energy path studies and the vibrational and ro-vibrational excited state energy studies may help in the identification of CH\textsubscript{5}\textsuperscript{+} on interstellar grains and within the diffuse interstellar medium.

Despite the great leaps and bounds that have been made in understanding CH\textsubscript{5}\textsuperscript{+}, there are still many challenges that remain. Its high-resolution CH-stretching region spectra\cite{5, 8} are still unassigned, and the high fluxionality of CH\textsubscript{5}\textsuperscript{+} presents challenges for calculating excited state energies to aid in the assignment. Also, like H\textsubscript{3}\textsuperscript{+}, CH\textsubscript{5}\textsuperscript{+} has both ortho and para nuclear spin configurations. While research has been performed on these spin configurations for H\textsubscript{3}\textsuperscript{+}\cite{75, 76}, little has been done for CH\textsubscript{5}\textsuperscript{+}. By employing a combination of the minimized energy path technique and the fixed node rotationally excited state calculation, one could learn about the nature of the ortho and para spin configurations of CH\textsubscript{5}\textsuperscript{+} and potentially learn more about the zero-point and excited state energies and properties of these separate species. Answering these questions would aid in determining if CH\textsubscript{5}\textsuperscript{+} is a species within the interstellar medium.
BIBLIOGRAPHY


One can find paths from one minimum to another either by moving across the $C_{2v}$ saddle point followed by a $60^\circ$ rotation of the $\text{CH}_3^+$ group, repeated five times or by moving across the $C_{2v}$ saddle point followed by a $180^\circ$ rotation of the $\text{CH}_3^+$ group, repeated three times.