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Infrared photophysics of gas phase ions in a Fourier transform ion cyclotron resonance mass spectrometer

Uechi, Guy Takeo, Ph.D.
Case Western Reserve University, 1993
INFRARED PHOTOPHYSICS OF GAS PHASE IONS IN A FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETER

by

GUY TAKEO UECHI

Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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CASE WESTERN RESERVE UNIVERSITY
January, 1993
CASE WESTERN RESERVE UNIVERSITY

GRADUATE STUDIES

We hereby approve the thesis of

GUY TAKAO UECHI

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Date  July 29, 1992

*We also certify that written approval has been obtained for any proprietary material contained therein.
INFRARED PHOTOPHYSICS OF GAS PHASE IONS IN A FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETER

Abstract
by
GUY TAKEO UECHI

Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry provides low pressure conditions under which ions can be trapped for periods of seconds. This length of time enables one to study the photophysics involving the emission of an the infrared photon, which occurs on the timescale of milliseconds to seconds.

Infrared radiative cooling of vibrationally excited n-butylbenzene ions was studied in chapter III. This was done by a technique called ion thermometry, where the internal energy of the ions could be probed by the branching ratio of two competitive photoproducts. The infrared radiative cooling rate constant was observed to be 0.8 s\(^{-1}\) for ions with energies of only 0.3 eV above room temperature.

Confidence in the thermometric data depended on the reliability of the measured branching ratios. In the chapter IV a computer simulation was used to show that erroneous peak height ratios were produced by the Coulombic repulsion between ions during ion excitation, and reliable ratios could be obtained by working at low
excitation, and reliable ratios could be obtained by working at low ion densities and using a short excitation pulse.

Chapter V discussed our first attempt to describe infrared multiphoton dissociation (IRMPD) of trapped ions in a thermal framework. Using a computer simulation the laser intensity was associated with an internal ion temperature for ions undergoing continuous laser irradiation. An Arrhenius type plot was constructed, and the activation energy obtained from it seemed reasonable within the expectations from Tolman's theorem.

To pursue the feasibility of the thermal analysis of IRMPD kinetics, the thermometric technique was used in chapter VI to observe the CO$_2$ laser pumping process for n-butylbenzene ions. The data showed that the steady state distribution of the ion energies reached during laser pumping is very dependent on the rate of photon absorption and emission. The generalized thermal analysis which was done in chapter V was found to be unfeasible.

Ion thermometry was also used in chapter V to observe the rate of photon emission from n-butylbenzene ions heated by the cw-CO$_2$ laser. Although the ions contained 0.3 eV more energy than the ions studied in chapter 2, the observed rate of cooling was the same.

Chapter VII describes the association reactions between silicon ions and a series of aromatic molecules (benzene, naphthalene, and anthracene). These reactions are mediated by the emission of an infrared photon, thereby termed radiative association reactions. In all three cases the silicon ion inserted into the C-H bond of
the molecules as shown by the collision induced dissociation spectra of the association product ions.
ACKNOWLEDGEMENTS

My appreciation extends to Dr. Robert C. Dunbar for his grooming, guidance, and support, to the ICR group—especially Dr. James D. Faulk, to my family, and to the saints in Cleveland.

And He said to me, My grace is sufficient for you...

II Corinthians 12:9
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CHAPTER I

INTRODUCTION
INTRODUCTION

INFRARED PHOTOCHEMISTRY IN GAS PHASE IONS

Under the low pressure conditions in a typical ion cyclotron resonance (ICR) ion trap experiment long trapping periods on the order of seconds are easily obtained. This lends itself to the study of infrared photochemistry of gas-phase ions that occurs on this time scale.

The study of four types of photoprocesses is described in this thesis. First, the rate of radiative relaxation of vibrationally excited ions has been observed. The lifetime of vibrationally excited polyatomic ions near thermal equilibrium is on the order of a second. Infrared photon emission of such ions was indirectly observed by the thermometric method of watching the time evolution of the internal energy of the ion as it cools.

Second, the irradiation of ions by a low-powered continuous-wave (cw) CO₂ laser results in dissociation by infrared multiphoton absorption. We measured the rate of this process for a model system (n-butylbenzene ions), and tried to analyze the kinetics of dissociation with a full master equation which takes into account the rate of photon absorption, photon emission, and dissociation. We wished to determine whether the distribution of internal energies of the ion population produced by the steady state condition between laser pumping and IR photon emission is near to being a Boltzmann distribution. If this is the case then a thermal
analysis of the kinetic data may prove fruitful.

Third, to investigate further the possibility of a thermal analysis of the infrared multiphoton absorption dissociation kinetics, the laser pumping of n-butylbenzene ions was observed by the thermometric technique. Ion thermometry provided a means to monitor the progress of the ion population's average energy during irradiation by the cw-CO$_2$ laser. It will be seen below that the photophysics of infrared multiphoton absorption is beautifully observed using this technique.

Fourth, radiative association reactions are governed by the rate of infrared photon emission by a gas phase ion-neutral collision complex. This is another class of reactions which occur on a timescale that requires collisionless conditions for periods of seconds. These reactions are of interest to the astrochemists who try to understand the formation of complex molecules detected spectroscopically in interstellar clouds. The molecular densities in these clouds are very low, so that association reactions mediated by collisional stabilization are very unlikely. Silicon ions are of particular interest, and several radiative association reactions of Si$^+$ were studied in this work.

ION THERMOMETRY

The absorption and emission of infrared photons will not be detected directly. All photoprocesses will be studied by the technique of ion thermometry where the internal energy or internal
temperature will be observed. Ion thermometry is the technique of being able to probe at any given time the internal energy of an ion. The method that will be used in chapters III and VI is competitive dissociation. If two dissociation channels exist the branching ratio of the two product ions will be dependent on the energy of the activated ion. By characterizing the branching ratio over a well defined energy range one has the means to probe the internal energy of an ion by observing the branching ratio.

Confidence in the thermometric technique of competitive dissociation is dependent on the accuracy of the branching ratios. Fourier transform ion cyclotron resonance mass spectrometry has been known to produce erroneous peak heights due to inherent problems of the technique. Chapter IV investigates the effect of Coulombic repulsion between ions on the detected peak heights. Experimental conditions are given under which reliable branching ratios can be determined.

INTERNAL ION TEMPERATURE

The assignment of an internal temperature to an individual ion at a given internal energy enables us to discuss quantitatively the rate of infrared photon emission and to compare the rates for different ions. By necessity, the usual definition of the temperature of any substance requires a distribution of energies in a macroscopic population. However a useful definition of a single ion's internal temperature can be made according to the average internal energy of the ion when it is in thermal equilibrium with a
thermal heat bath. If the ion is taken as an assembly of harmonic oscillators the internal energy of the ion will be the sum of the enthalpy contributions from each oscillator given by the Boltzmann factor at the temperature of the heat bath. Using this criterion, an ion having a given internal energy will be associated to the temperature of the heat bath that produces this energy.

One can see that if two molecules are in contact with the same heat bath (i.e., both ions are at the same temperature) the larger molecule will have a higher internal energy at that temperature than the smaller molecule since more degrees of freedom contribute to the energy of the molecule. It will be shown in chapter III that for different polyatomic ions containing different internal energies, if their internal temperatures are similar they will radiate infrared photons at comparable rates. The rate of photon emission in radiative association reactions in chapter VII can also be understood by noting the internal temperature of the collision complex.

**FOURIER-TRANSFORM ION CYCLOTRON RESONANCE (FT-ICR) SPECTROMETRY**

ICR spectrometry is based on the motion of ions under the constraint of the forces in the Lorentz equation:

\[ F = qE + qv \times B \]

An ion with an initial velocity travels in a cyclotron orbit perpendicular to the axis of the magnetic field. Without the presence of an external electric field the ion will ideally remain
in its orbiting path. The frequency is determined by the equation:

\[ \text{freq (Hz)} = \frac{qB}{2\pi m} \]

where \( q \) is the charge of the ion, \( B \) is the magnetic field strength in Tesla, and \( m \) is the mass in kg. Since the cyclotron frequency remains constant for all ion velocities the radius at which the ion orbits must increase at higher kinetic energies. Ions can be accelerated to higher kinetic energies and larger cyclotron orbital radii by applying an external oscillating electric field at the resonant frequency of the ion.

The typical geometry for an ICR cell is a cubical cell. Two plates along the axis of the magnetic field (normally designated the z-axis) are held at equal positive potentials to trap positive ions, and negative potentials for negative ions. The cyclotron motion is in the x-y plane and ions can be trapped for periods of seconds with great ease. Two plates are used as transmitters to apply the electric field to excite the ions from low to high kinetic energies resulting in larger cyclotron orbiting radii. The final two plates of the cubical cell serve as receivers to detect the signal induced by the orbiting ions\(^1\).

Ideally all the ions are travelling with the same cyclotron orbiting radius each at the cyclotron frequency specific to the mass of the ion. The signal is produced by the electric charge the ion induces as it travels near the receiver plates. A single ion will produce a sinusoidal waveform at the frequency of the ion's cyclotron frequency. A coherently orbiting packet of ions at the same mass will produce a waveform at the same frequency, but the
amplitude will be directly proportional to the total number of ions. The signal from ions of different masses will produce a waveform which is the sum of the sinusoidal waveforms at the specific frequencies corresponding to each ion. Fourier transform ICR excites, and then detects, all the ions simultaneously. The amplitude and the frequency of each waveform produced by each ion can be obtained by taking the Fourier transform of the signal detected from the receiver plates².
REFERENCES


CHAPTER II

EXPERIMENTAL SECTION
EXPERIMENTAL SECTION

Fourier transform ion cyclotron resonance mass spectrometry

All experiments were done using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Experiments described in chapters III, IV, and V were done on a homebuilt ICR controlled by an IonSpec data system. The instrument contains a one inch cubic cell located in a high vacuum chamber in the gap of a 1.4 T electromagnet. Vacuum is obtained by a Balzers turbomolecular pump and an ion pump. The pressure is normally monitored by the current of the ion pump, but calibrated by measuring a known charge transfer or proton transfer reaction.

Samples are introduced through a manifold system held at approximately 1x10^{-4} Torr by a mechanical pump. All samples are purified by repeated freeze-thaw cycles under the manifold's vacuum to degas any air or other volatile substances. The flow of sample gas is controlled by a Varian variable leak valve which maintains pressures of the order of 1x10^{-8} Torr on the high vacuum side with 1x10^{-4} Torr on the low pressure side. By necessity, all samples need to be reasonably volatile in the manifold system in order to produce a vapor pressure in the high vacuum chamber of the ICR spectrometer.

Ion manipulation is controlled by the hardware of the IonSpec data system. Ions are produced by electron impact. Electrons from a rhenium filament at nominal energies of typically 12 eV are pulsed through the center of the cell parallel to the magnetic
field. The trapping plates are held at potentials of 1 to 2 volts to trap positive ions. At low pressures like $1 \times 10^{-8}$ Torr, the ions can be trapped for periods of seconds.

Excitation of the ions was done by two methods. Chirp excitation applied an r.f. waveform to the transmitter plates which swept through the frequency of the desired ions. Impulse excitation applied to the transmitter plates a short (~1 μs) pulse of high amplitude. Effects on the observed spectra due the nature of the excitation will be discussed in a later chapter. In both excitation schemes all ions are accelerated to a large cyclotron orbiting radius. An image current is induced by the ions on the receiver plates. The image current is detected and converted into a voltage signal which is amplified. The resulting stored signal transient is converted into the frequency-domain spectrum by fast Fourier transform processing, from which masses and ion abundances are obtained.

The vacuum chamber of the instrument contains three windows to permit the irradiation of the trapped ions by laser light. The first window is equipped with a NaCl plate which allows IR photons as well as visible light to be transmitted. This window is located along an axis perpendicular to the magnetic field. The other two windows, both along the same axis, are sapphire through which visible light can be directed.

Among the light sources used on this instrument the first was a continuous wave (cw) Coherent Radiation CR-12 argon ion laser. A
series of visible wavelengths are produced. The photons from the line at 458 nm were used in the first thermometry study of n-butylbenzene. Typical power for this line was around 1.0 to 1.5 W. Second, infrared photons were produced by a homebuilt cw-CO₂ laser. The wavelength of the photons was 940 cm⁻¹. Third, short 10 ns visible light pulses were produced by a Lumenics Nd-YAG pulsed laser pumping a dye laser. Using Coumarin 440 dye in the dye laser pumped by the 355 nm light of the Nd-YAG laser, up to 8 mJ of energy was produced at 440 nm. The 355 nm light of the Nd-YAG is the output of tripling the fundamental 1065 nm wavelength.

The light pulses obtained by shuttering the cw-argon ion laser were 20 to 50 ms in duration. The 10 ns pulses from the pulsed dye laser enabled better resolution of the photophysical processes of radiative relaxation and infrared multiphoton absorption.

**Extral FT/MS 2000.** The instrument used in the work described in Chapter 6 is an Extral FT/MS 2000, a commercially available FT-ICR mass spectrometer designed for analytical use. The basic operation of the instrument is similar to the TCR described above with a few differences in the structural design. It contains a dual cell configuration which consists of two adjacent two-inch cubical cells connected by a pinhole. Each cell is differentially pumped by its own diffusion pump. This allows one cell to be kept a very low pressure (analyzer region) while the other cell can be at a higher pressure (source region) for the production of ions. Having produced ions in the source region ions can be transferred to the
analyzer region and detected at higher resolution and sensitivity. For the experiments done in Chapter 6, all ion formation, trapping, and detecting were done in the source region of the cell.

The vacuum chamber of the Extrel FT/MS 2000 is held in the six inch bore of a 3 T superconducting magnet. A few options are available for sample introduction. First, volatile substances can be introduced through the manifold system by a batch inlet. There are no leak valves to slowly flow a constant stream of sample gas. But a bulb can be filled to a pressure of millitorr from which the gas is leaked into the high pressure vacuum chamber through a pinhole leak. One problem with this method is maintaining a constant pressure of sample gas in the vacuum chamber. As the bulb in the batch inlet becomes depleted the pressure in the vacuum chamber also drops so the bulb must constantly be replenished during the course of the experiment.

Second, sample vapor in the bulb of the batch inlet system may also be introduced into the vacuum chamber by means of a pulsed valve. Rather than a constant flow of reagent gas, one can give a burst of gas into the chamber. A sudden increase in pressure is produced which is pumped away by the diffusion pumps after a few hundred milliseconds. This was used to introduce argon as a collision gas in the collision induced dissociation experiments. Another use for the pulsed valve is to introduce a reagent gas to investigate the reaction of product ions already produced in the cell.
Third, samples can be directly placed into the vacuum chamber by placing them on the tip of the sample autoprobe found on the Extrel FT/MS spectrometer. The autoprobe is a rod located in a chamber called the sample lock where samples can be placed at atmospheric pressure. The chamber is then sealed and pumped down by a mechanical pump to approximately $10^{-3}$ Torr. A motor drives the rod into the high vacuum chamber through a valve and a teflon seal to maintain the high vacuum. Less volatile substances which normally could not be introduced into the chamber by the batch inlet system can sublime if their vapor pressure is high enough.

Silicon ions were produced by placing a silicon wafer on the tip of the sample autoprobe onto which a focussed pulsed CO$_2$ laser was fired. By the process of laser desorption silicon atoms are produced in the gas phase and are also ionized into monatomic ions. By setting the trapping plates to a positive potential, cations are trapped in the ICR ion trap.
CHAPTER III

RADIATIVE RELAXATION RATE DETERMINATION BY COMPETITIVE PHOTODISSOCIATION OF N-BUTYL BENZENE IONS
INTRODUCTION

The study of radiative association reactions in interstellar clouds has created an interest in the study of infrared photon emission by gas phase ions. Studies in our group have observed the decay of the internal energy of ions under collisionless conditions. This cooling process has been attributed to the emission of infrared photons in vibrationally excited ions.

Various previous studies have measured the radiative relaxation rates of polyatomic ions. Many rates found in our group have been in an internal energy regime of approximately 2-3 eV above thermal energy. Recent experiments have obtained the radiative rates for ions having only a few tenths of an electron volt of internal energy above thermal. Cooling rates in the lower energy regime are predicted and observed to be substantially slower than the higher energy regime.

A convenient approach to the determination of ion internal energy is the branching ratio between two competitive dissociation reactions. This thermometric technique has been successfully applied to 1,4-dioxane. The n-butylbenzene ion, whose fragmentation pattern as a function of internal energy has been extensively studied, was used in the present work. The competitive fragmentation of interest here forms ions at m/z 92 and m/z 91. The ratio of m/z 91 to 92 as a function of internal energy has been well characterized by photodissociation, dissociative charge transfer, and photoelectron photoionization coincidence.
From this information the branching ratio as a function of internal energy (or temperature) can be calibrated, making the branching ratio a powerful and convenient thermometric tool. Using this tool one can probe the internal energy of the ion at any point in time and observe a dynamic process like radiative cooling of vibrationally excited ions.
EXPERIMENTAL SECTION

All experiments were done in a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer using an IonSpec data system. The trapping plates of the one inch cubic cell were set at 0.8 volts. The d.c. potentials of all other plates were set at zero. The electron beam pulse length ranged from 2 to 50 ms, keeping the number of ions at all pressures relatively constant. The filament current was set between 2.4 and 2.6 A at a nominal electron energy of 12.5 eV.

Figure 1 shows the sequence of pulses for the experiment. Fragment ions produced by electron impact were ejected from the cell by an r.f. chirp ejection pulse. After a delay period, T, the ions were irradiated with 458 nm light from a Coherent Radiation CR-12 argon ion laser. Laser pulse length ranged from 20 to 50 ms. The total power ranged between 1.0 and 1.5 W. The laser beam was expanded by a telescope to approximately one centimeter in diameter to assure a uniform irradiation of the whole ion cloud. Ions between m/z 88 and m/z 95 were detected by a chirp excite pulse of length 100 microseconds, with transient lengths of 4 ms being acquired.

The energy of one photon dissociates the parent ion into fragments m/z 92 and m/z 91. The ratio of photofragment abundances is quite well known as a function of internal energy of the dissociating parent ion (ratio-energy curve). However a complication arises when ion m/z 92 absorbs a photon and
FIG. 1. Pulse sequence used for competitive photodissociation.

Laser delay varied from 100 ms to 5 s.
PULSE SEQUENCE

2.50ms  2.5ms  20-50ms
ELECTRON  EJECTION  LASER 458 nm  DETECT  QUENCH
BEAM    m/z 88 - 95

T - LASER DELAY

TIME
dissociates to m/z 91. The ratio-energy calibration curve is appropriate for ions produced solely from the primary photodissociation of parent ions. This problem was overcome by reducing the light intensity until the m/z 91 fragment production was linearly dependent on the light intensity. Ten percent total dissociation was an empirically found level where the interference from secondary photodissociation was negligible.

Confidence in the peak ratios of the fragment ions was critical to the experiment. Obtaining accurate peak heights in FT-ICR is known to be a problem⁷. The most severe problem we encountered was the high sensitivity of the peak heights to the r.f. excitation level. This was especially dramatic for ions close in mass. Empirically found conditions that reduced the sensitivity to excitation were low number of ions, low trapping potentials (0.8v), short excite pulses (100 microseconds), high r.f. excitation amplitudes, and excitation of fragment ions only (m/z 88 - m/z 95) for detection. Many of these conditions will be accounted for in the next chapter where computer modelling has attributed the mass discrimination to Coulomb repulsion between the ions.

The pressure was measured from the ion pump current, which was calibrated by observing the loss of m/z 78 ions produced by electron impact of n-butylbenzene. This ion is known to be highly reactive and was assumed to react at the ion-molecule collision rate³⁷.
RESULTS AND DISCUSSION

The experiment is depicted in the series of spectra in Figures 2a, b, and c. Parent n-butylbenzene ions were produced by electron impact and all fragment ions were ejected from the cell, Figure 2a. Fragment ions, m/z 91 and 92, were produced by laser irradiation as seen in Figure 2b. Total dissociation of the parent ion is less than 10%, for reasons mentioned earlier. The actual determination of the ratio of m/z 91 and 92 was obtained using excitation of only the fragment ions, as seen in Figure 2c. Figure 3 shows the 91/92 ratio as a function of the time delay between ion production and laser irradiation. The ratio decreases with time indicating a decrease in internal energy.

Ratio-Energy Calibration Curve. The use of competitive photodissociation as a thermometric tool is completely dependent on the reliability of the branching ratio-internal energy calibration curve. This was assembled for the present purpose from literature values from three different techniques4-6. Table I lists the branching ratios of n-butylbenzene ions at 3.04 eV internal energy found in four studies. The values for the two studies of references 4 and 5 did not take ion thermal energies into account, and appropriate corrections have been applied to give corrected values listed in Table I.

Ions produced in the PEPICO experiment have the least doubt about their internal energy. Since ions in this technique are formed from totally thermal neutral molecules, and are specifically
FIG. 2. Magnitude mode frequency spectrum of n-butylbenzene.
(a) Light off; (b) light on; (c) excitation and detection of fragment ions only.
FIG. 3. Branching ratio of fragment ions m/z 91 and 92 as a function of laser delay time.
Table I. Branching ratio at 3.04 eV internal energy.

<table>
<thead>
<tr>
<th></th>
<th>91</th>
<th>92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baera</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Chen</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Harrison</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>this work</td>
<td>0.27</td>
<td></td>
</tr>
</tbody>
</table>

a) reference 6  PEPICO study  
b) reference 2  photodissociation in ICR  
c) reference 5  charge transfer reaction
selected according to their internal energy, the absolute
calibration of energies from the PEPICO study should be highly
reliable, and these values have been chosen to provide the absolute
calibration of the ratio-energy curve used in the present work.
The charge-transfer results of Harrison and Lin\textsuperscript{5} and the result
from the present study are in satisfactory agreement with the
PEPICO result\textsuperscript{6}, giving confidence to the absolute calibration of
the curve. The somewhat lower value obtained in the previous ICR
study of Chen et al.\textsuperscript{4} can probably be attributed to a lack of
experience and care in this earlier work in measuring the ratios of
the very small ICR signals involved. All of these different
studies give the same slope for the ratio-versus-energy dependence.

\textbf{Ion Cooling Curves.} Using the calibration curve of Figure 4, data
like that of Figure 3 can now be converted quantitatively into
plots of ion internal energy versus time. Figures 5a, b and c
display the three data sets obtained in this work. The ratio
resulting from competitive photodissociation corresponds to the
energy of the absorbed photon plus the internal energy of the
excited ion just prior to photon absorption. In assigning the
internal energy axis for the plots in Figures 5a-c, the photon
energy (458 nm, or 2.71 eV) has been subtracted from the internal
energy, so that the energy plotted in these figures is the ion
energy \textit{just prior} to photon absorption. These curves display the
cooling of vibrationally hot ions as a function of time.
FIG. 4. Branching ratio-internal energy calibration curve. This curve was chosen such that the branching ratio for thermal ions (375 K) was 0.27.
FIG. 5. Cooling curves fitted to an exponential decay rate constant at pressures (a) $1 \times 10^{-8}$ Torr; (b) $3 \times 10^{-8}$ Torr; (c) $2 \times 10^{-7}$ Torr.
The value of the initial excess internal energy (in excess of the asymptotic, thermal energy) derived from the extrapolation to zero time is consistently 0.3 eV in all three cooling curves. This is a reasonable value to be deposited by electron impact. The parent n-butylbenzene ions cannot contain more than 1.0 eV of internal energy without dissociating to m/z 92 ions, so that an unbiased internal energy distribution would be expected to give an average of 0.5 eV. Energy deposition by electron impact is known to be biased toward lower amounts of excitation energy, which rationalizes the observed average of about 0.3 eV.

An interesting approach to interpreting the energetics of the vibrational cooling is by defining an internal temperature for the ions. An internal temperature will enable one to discuss the rate of infrared emission. The temperature is defined by assuming a Boltzmann distribution of energies among the normal mode harmonic oscillators of the ions. The harmonic oscillator assumption is reasonable since the internal energy of the ion is near thermal equilibrium with the walls of the ion trap (373 - 500 K). Each normal mode is in its lowest energy state or contains only a few quanta of energy where anharmonic contributions to the vibrational modes are not significant. Due to the large number of internal degrees of freedom, the energy distribution within the molecule is well described by a Boltzmann distribution.

The right axes of figures 5a, b, and c express the internal energy of the ions as an internal temperature. The initial internal temperature of the n-butylbenzene ions was only 490 K,
which was not far above the temperature of the cell, 373 K. This internal temperature corresponds to an internal energy of 0.33 eV. The sensitivity of the branching ratio thermometric technique resolved these moderate temperature changes well.

Figures 5a, b, and c show that ions obtained by electron impact are vibrationally excited, and subsequently cool until thermal equilibrium is reached with the walls of the ICR ion trap cell. One can see that the internal temperature regime of these ions before photon absorption is not far above thermal and the decrease in internal temperature of the ion is around 100 degrees during the course of the cooling process.

Figure 5a appears to be shifted up in energy by 0.1 eV compared to the cooling curves taken at the two higher pressures. The source of this shift is unclear. However, it should not affect the determination of the radiative relaxation rate constant which, being obtained by observing the change in internal energy with time, is quite insensitive to a shift in effective cell temperature.

**Relaxation Rate Constants**

The relaxation rate constant was obtained from the data by assuming that the rate of energy loss is proportional to the ion’s internal energy. This is described by a simple exponential decay curve,

\[ E = E_{th} + E_0 e^{-kt} \]

where \( E \) is the internal energy of the ion at a given point in time,
$E_{th}$ is the internal energy of the ion at thermal equilibrium, $E_0$ is the initial amount of energy in excess of $E_{th}$, and $k$ is the relaxation rate constant. The superthermal energy dissipates until it reaches an asymptotic level at thermal equilibrium. Energy relaxation rate constants found in this study are listed in Table II.

Under collisionless conditions the only means of internal energy relaxation is infrared emission. At higher pressures, the number of ion-neutral collisions become substantial and their rate of cooling increases since both radiative cooling and collisional cooling occur. The cooling rate constant is expressed as

$$k = k_r + k_c C$$

where $k_r$ is the radiative cooling rate constant ($s^{-1}$), $k_c$ is the collisional cooling rate constant ($cm^3$ molecule$^{-1}$ s$^{-1}$), and $C$ is the concentration of neutral molecules (molecules cm$^{-3}$). The collision rate as a function of pressure can be taken to be the ion-molecule orbiting collision rate, $1.4 \times 10^{-9}$ cc molecule$^{-1}$ s$^{-1}$. The collisional and radiative cooling rate constants can be extracted as the slope and intercept of a plot of $k$ versus $C$, as shown in Fig. 6. The radiative rate constant, $k_r$, and collisional rate constant, $k_c$, are found to be 0.8 s$^{-1}$ and $5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ respectively.

**Internal Temperatures**

A useful approach to interpreting the energetics of
<table>
<thead>
<tr>
<th>pressure (torr)</th>
<th>concentration of neutral molecules (cm$^3$ molecules$^{-1}$ s$^{-1}$)</th>
<th>relaxation rate constants (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-8}$</td>
<td>$3.5 \times 10^8$</td>
<td>0.95</td>
</tr>
<tr>
<td>$3 \times 10^{-8}$</td>
<td>$1.1 \times 10^9$</td>
<td>1.5</td>
</tr>
<tr>
<td>$2 \times 10^{-7}$</td>
<td>$7.0 \times 10^9$</td>
<td>4.5</td>
</tr>
</tbody>
</table>
FIG. 6. Graphical analysis of the cooling rate constants found from the data seen in Table II.
$k_{\text{cool}}$ VS. $C$

Cooling Rate Constant (s$^{-1}$) vs. Concentration ($10^8$ cm$^3$/molecules s)
vibrational cooling, often informative in making comparisons between different ions, is to define an internal temperature for the ions. The right axes of Figures 5a-c express the internal energy of the ions as an internal temperature. One can see that the total ion internal temperature range of these experiments only extended to approximately 100 degrees above the temperature of the cell. The sensitivity of the branching ratio as a thermometric technique was able to resolve these moderate temperature changes well.

**Infrared Radiative Cooling**

The work described here adds to the small body of observation of radiative cooling of polyatomic ions in the near-room temperature regime. It is of interest to put this result into the context of previous measurements of radiative cooling for various-sized ions and different temperature regimes.

We start with a consideration of diatomic molecules, which have a single vibrational mode whose quantum number ν corresponds precisely to the internal energy of the molecule. The rate of emission of IR photons is given by the Einstein spontaneous emission coefficient $A_{ν,ν-1}$, which depends on the vibrational transition dipole moment $μ$. For molecules of similar $μ$, the $A_{ν,ν-1}$ coefficient depends strongly on the mode frequency, rising as $ν^3$, and on the quantum number, increasing linearly with $ν$ (in the harmonic oscillator approximation). It is a property of the harmonic oscillator approximation for a diatomic molecule that the
radiative cooling rate constant $k_r$, as defined in Eq. (1) and (2), is independent of the quantum number $v$ (or, for a non-uniform population with a distribution of $v$'s, is independent of the distribution). In the language used below, the cooling rate constant is strictly temperature independent.

Table III shows observed and calculated radiative emission rates for three diatomic ions. $k_r$ is equal to the $v=1$ to $v=0$ radiative rate. For the two ions CH$^-$ and HCl$^+$ which are strongly radiatively allowed, it is seen that the radiative time constant is a few milliseconds. For NO$^+$ and HC$^-$ the radiative rate follows approximately the expected linear dependence on $v$. Thus diatomic ions have two characteristics which contrast strongly with the polyatomic case: Infrared radiative relaxation is fast (with a time scale of a few milliseconds) when the infrared transition is strong; and the cooling rate constant $k_r$ is independent of the internal energy of the ion (within the harmonic oscillator approximation).

The contrasting behavior of polyatomic molecules\(^9\) comes about because they contain many vibrational modes compared to the single mode of a diatomic molecule, and only a small fraction of these normal modes are infrared active. Most of the modes serve as energy reservoirs contributing to the heat capacity of the molecule, but not to its radiative cooling. This leads to the much slower radiative cooling of polyatomics in the following way: The internal energy of the molecule is distributed statistically among
Table III. Infrared radiative rates for diatomic ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \omega_e )</th>
<th>( v = 1 )</th>
<th>( v = 2 )</th>
<th>( \text{krad (s}^{-1}\text{)} \text{ experimental} )</th>
<th>( \text{krad (s}^{-1}\text{)} \text{ calculated} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(^+)</td>
<td>( 2376.7 \text{ cm}^{-1} )</td>
<td>10.5(^a)</td>
<td>21.7(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(^-)</td>
<td>( 2620 \text{ cm}^{-1} )</td>
<td>571(^c)</td>
<td>-910(^c)</td>
<td>510(^d)</td>
<td>917(^d)</td>
</tr>
<tr>
<td>HCl(^+)</td>
<td>( 1605 \text{ cm}^{-1} )</td>
<td>333(^a)</td>
<td></td>
<td>217(^e)</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) reference 11  
\(b\) reference 12  
\(c\) reference 13  
\(d\) reference 14  
\(e\) reference 15  
\(f\) reference 16
the vibrational modes. That part of the energy which is
distributed in radiating modes dissipates radiatively, but the
energy populating the more numerous reservoir modes has no means of
being dissipated by photon emission. A further reduction in the
cooling rate of polyatomic relative to diatomics comes from the
fact that many reservoir modes have low frequency and are heavily
populated, while the most strongly radiating modes have high
frequency and are sparsely populated. These factors combine to
give the expectation that radiative cooling rate constants of
polyatomics should be one, two or even three orders of magnitude
slower than those of strongly allowed diatomics.

The expectation that the cooling rate constant for polyatomics
will be strongly temperature dependent arises from similar
considerations. The high-frequency normal modes with large
radiative intensity coefficients tend to be frozen out at low
internal temperatures so that, containing little energy, they
contribute little to the photon emission rate. As the internal
temperature increases these modes become populated and the rate of
photon emission rises sharply, resulting in an increased cooling
rate constant.

The quantitative treatment of these questions proceeds most
easily by defining the internal temperature of the molecule for a
given amount of internal energy. The mode populations are
calculated from Boltzmann factors, and the roles of the reservoir
modes and the radiating modes in determining the radiative cooling
rate are readily derived. This treatment confirms the qualitative
expectations given above, first that the cooling rate constants should be orders of magnitude slower for polyatomics than for diatomics, and second that the cooling rate constant for polyatomics should show strong dependence on the temperature (or internal energy) of the molecule.

Radiative cooling measurements of polyatomic ions from our laboratory have divided into a high-energy group and a low-energy group, following the different types of experiments used, as shown in Table IV. The low-energy group, to which the present n-butylbenzene experiment adds another value, has internal energies in the region of a few tenths of an electron volt above thermal (-500 K), and show radiative cooling rate constants between 0.28 and 1 s⁻¹. The high-energy group has energies 2-3 eV above thermal (-1500 K), and shows radiative cooling rate constants of 3 to 16 s⁻¹. As expected from the different radiative characteristics of the different ions, there is variation among the cooling constants in each group, but overall the results give excellent confirmation of the theoretical expectations. The cooling rate constants are two or three orders of magnitude slower than the strongly radiating diatomic ions; and there is a decrease of an order of magnitude in the typical cooling rate constant when going from the 1500 K to the 500 K internal temperature regime. Both of these observations are in good quantitative accord with the expectations from the full theoretical analysis.⁹
<table>
<thead>
<tr>
<th>Compound</th>
<th>Radiative relaxation rate (s⁻¹)</th>
<th>Internal energy (eV)</th>
<th>Internal temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butyl benzene</td>
<td>0.8</td>
<td>0.67</td>
<td>500</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>0.4</td>
<td>0.4</td>
<td>600</td>
</tr>
<tr>
<td>styrene</td>
<td>0.65</td>
<td>0.45</td>
<td>590</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>1.0</td>
<td>0.44</td>
<td>630</td>
</tr>
<tr>
<td>ferrocene</td>
<td>0.28</td>
<td>0.7</td>
<td>600</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>5.7</td>
<td>2.71</td>
<td>1765</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>5.3</td>
<td>2.54</td>
<td>1680</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>3.6</td>
<td>2.41</td>
<td>1615</td>
</tr>
<tr>
<td>iodobenzene</td>
<td>2.9</td>
<td>2.10</td>
<td>1470</td>
</tr>
<tr>
<td>m-iodotoluene</td>
<td>4.6</td>
<td>2.0</td>
<td>1300</td>
</tr>
<tr>
<td>cyanobenzene</td>
<td>16</td>
<td>2.54</td>
<td>1570</td>
</tr>
<tr>
<td>benzene</td>
<td>5.6</td>
<td>2.54</td>
<td>1750</td>
</tr>
</tbody>
</table>

a) this work
b) reference 3a
c) reference 3b
d) reference 3c
e) reference 3d
f) reference 2
CONCLUSION

Competitive photodissociation of n-butylbenzene ions has proven to be a successful thermometric tool to study the dynamic process of cooling of vibrationally hot ions. The sensitivity of the branching ratio of fragment ions m/e 91 and m/e 92 is high enough to observe changes of a few hundredths of an electron volt. This provides sufficient resolution to study the rate of infrared radiative emission by trapped polyatomic ions. A radiative relaxation rate of 0.8 s\(^{-1}\) was found for n-butylbenzene ions with an internal temperature of 500 K.

Polyatomic ions having internal temperatures near thermal have radiative relaxation rate constants on the one-second time scale. This is consistent with predictions\(^9\) based on infrared absorption intensity measurements. Radiative cooling measurements have been made for a number of polyatomic ions in different limited temperature ranges, and these results fit well into the current theoretical understanding of these processes. It would be interesting to study the rate of radiative relaxation in a single ion as a function of internal temperature over a broad temperature range. Study of a consistent molecular system over the entire internal energy regime from 0.1 to 3 eV would give a more comprehensive test of the current theory for radiative relaxation processes.
REFERENCES


   d) Faulk, J. D.; Dunbar, R. C. J. Am. Chem. Soc., submitted for publication


8. see footnote 10 of reference 3b.

9. A possible explanation for the energy shift at this low pressure is heating by infrared irradiation of the filament. Due to the large cross section of n-butylbenzene ions in the infrared, pumping by infrared multiphoton absorption could account for the energy shift. At higher pressures energy relaxation by collisional cooling may compete with the filament heating showing no effect of the filament.


CHAPTER IV

SPACE CHARGE EFFECTS ON RELATIVE PEAK HEIGHTS
IN FT-ICR SPECTRA
INTRODUCTION.

The thermometric technique of competitive photodissociation used in chapter III is based on the accurate measurements of the branching ratio of the photoproducts of n-butylbenzene. It is well known that the relative peak heights in Fourier-transform ion cyclotron resonance (FT-ICR) spectra do not always reflect accurately the ratios of ion abundances. For ions far apart in mass, incorrect peak height ratios have been convincingly ascribed to selective z-axis ejection artifacts. However, peak height ratios can also show large inaccuracies for ions close in mass, for which this mechanism is insignificant. The interaction of ions through their Coulomb repulsion, often referred to as space charge interaction, provides an alternative mechanism for distorting the relative intensities of FT-ICR spectra. We describe here experimental results and computer simulations which indicate that space charge interactions account for the inaccurate ratios of close-lying mass doublets. Wang and Marshall have described analogous calculations and experiments examining the space-charge interaction and the resulting minor peak broadening for ions of the same mass; the present consideration of the intensity ratios for mass doublets represents quite a different situation.
EXPERIMENTAL SECTION

The m/z 91 to 92 branching ratios and other experimental results were obtained on a homebuilt Fourier transform ion cyclotron resonance (FT-ICR) spectrometer. The ICR instrument contains a 2.5 cm cubical cell in a magnetic field of 1.4 Tesla, controlled by an IonSpec FT-ICR data system. At an indicated pressure of 3x10^{-8} torr, ions were produced by the electron impact fragmentation of n-butylbenzene at a nominal electron energy of 15 eV. Typical emission currents were 0.05 - 0.10 uA. Ions were trapped for 100 - 250 ms at a trapping plate voltage of 4 V (except where noted otherwise).

The r.f. amplitude was measured peak to peak at the transmitter plates. Peak heights were used to obtain the branching ratio rather than peak areas. The widths of the peaks (FWHM) were observed to be the same, so the question of whether to measure peak heights or areas was not significant.
EXPERIMENTAL RESULTS

Figure 1 shows measurements of the 91/92 peak height ratio (fragment ions of n-butylbenzene) as a function of r.f. excitation amplitude, using chirp excitation. Concurrent measurements using impulse excitation, low ion number and low trapping voltage, conditions which were expected to approach closely to an accurate ratio measurement, gave a ratio of 1.0, which was taken to be the true ratio for these ionizing conditions. (Our confidence that this latter measurement gave true ratios was reinforced by a similar measurement of the bromine 79/81 isotope ratio in bromobenzene ions as 1.02, which is correct.)

It is seen that at low r.f. amplitudes the observed 91/92 ratio is substantially too high (about 1.4), while at high r.f. amplitudes it drops sharply below 1.0. We ascribe the dropoff in ratio at excitation amplitudes above 2000 V/m to preferential cyclotron ejection of m/z 91 ions. However, below 2000 V/m there is no reason to expect cyclotron ejection of ions of either mass, and we attribute the increase in ratio from 1.0 to 1.4 to ion-ion Coulomb repulsion ("space charge effects"). The conditions resulting in the ratios shown in Fig. 1 were taken as the basis for comparison with the computer simulations of space charge effects described below, and a goal of the simulations was to see if reasonable parameter choices would lead to a good match with this set of experimental results.

If we postulate that space charge repulsions are the cause of the inaccurate peak ratios of close mass doublets, there are
FIG. 1. Experimentally obtained peak height ratio of m/z 91 and 92 as a function of chirp excitation amplitude.
EXPERIMENTAL MASS DISCRIMINATION

91/92 PEAK HEIGHT RATIO vs. P-P R.F. AMPLITUDE (V/m)
various predictions that can be experimentally tested: this model predicts that the ratio should become more accurate as the ion-ion repulsions are reduced by (1) reducing the number of ions in the trap, (2) reducing the trapping voltage to give a shallower, broader trapping well along the z direction, and (3) increasing the excitation amplitude. Some limited experiments were done to test these predictions. Fig. 2 shows the effect of increasing the number of ions by increasing the electron beam pulse length. (The lowest value, 5 ms, corresponds to the data of Fig. 1.) It is seen that the ratios generally move farther above the correct value of 1.0 as the number of ions increases, for any given r.f. excitation amplitude. The longest beam pulse (100 ms) combined with a low r.f. level (1420 V/m) gave an extreme mass discrimination of about a factor of 6.

It was found hard to do convincing experiments varying the trapping potential, since this gave variations in ion trapping and detection conditions which were not easily standardized. It was observed, however, that increasing the trapping voltage from 1.5 to 3.5 V gave a large increase in the observed bromine isotope ratio for bromobenzene ions (an increase of as much as a factor of three at low r.f. amplitude).

Finally, as is clear in Figs. 1 and 2, low r.f. excitation amplitudes gave the greatest mass discrimination. At the lowest r.f. levels, where the signal was approaching the noise level, mass discrimination was typically very severe.
FIG. 2. Experimental peak height ratio of m/z 91 to 92, similar to Fig. 1, with the number of ions in the trap controlled by using various lengths of the electron beam pulse: 5 ms ( ), 10 ms ( ), 25 ms ( ), 100 ms ( ).
EFFECT OF ION NUMBER

91/92 PEAK HEIGHT RATIO

P-P R.F. AMPLITUDE (V/m)
COMPUTER MODELLING

Convincing support for the space-charge mechanism of mass discrimination for close-lying peaks can be gained through computer simulation of the experiments. The goal is to show that Coulomb repulsion, using physically reasonable parameter values, does actually lead to mass discrimination in the observed direction, with the right magnitude, and having the correct dependences on ion density and r.f. level. Accordingly, we undertook extensive computer simulations of these effects, and the success of these simulations provides the strongest indication we can give for the relevance of the Coulomb repulsion model of mass discrimination.

The effect of Coulomb interactions during excitation was modeled for the system consisting of two ion clouds (masses 91 and 92). The trajectory of each ion cloud was calculated by numerical integration of Newton’s second law for motion of an ion experiencing the repulsion of a charge cloud at relative position \( r \),

\[
F = ma = qE + (qv/c \times B) + (1/4\pi\varepsilon_0)qq_2/r^3 \quad (1)
\]

were \( F \) is the force on an ion of mass \( m \) and charge \( q \), \( E \) (Volts/m) is the instantaneous electric field along the \( x \) axis, \( v \) (m/s) is the velocity, \( B \) (Tesla) is the magnetic field along the \( z \) axis, and \( q_2 \) is the charge of the repelling ion cloud. The cyclotron motion of the ion is in the \( x-y \) plane since the direction of the magnetic field is along the \( z \) axis. Each of the two ion clouds was represented as a single point having the charge of the total number
of ions in the cloud.

Two assumptions were made in the model to simplify the calculations. First, the initial thermal velocity of the ions was neglected. The contribution of the thermal velocity of the ions to the overall signal is essentially zero. The direction of the thermal velocity of each ion is random, so that the net velocity vector of all the ions in the ion cloud is zero. A signal induced on the receiver plates of the ICR cell can only be produced by the coherent motion of a packet of ions in a cyclotron orbit. While the random thermal motion of the ions thus makes no direct contribution to the signal, it may affect the ion trapping and the signal strength through various mechanisms involving ion-ion collisions, coupling of z-axis and cyclotron motions, and other non-linear terms in the equation of motion\(^2\). We did not see that these possibilities would be important in the present context, and did not try to include them in the modelling.

Second, a simplified picture was adopted to model the distribution of ions along the z axis and in the x-y plane. The initial relative position of the interacting ions has a significant effect on the role of Coulomb repulsion in the ion trajectories. Table 1 shows calculated final cyclotron radii for ion pairs having five different initial orientations, giving somewhat varying Coulomb contributions to the mass discrimination. An average over these five orientations gives a result quite similar to that obtained for the single case of ions both lying along the z axis. Taking this to be a generally good approximation, the calculations
TABLE 1. Ratios of m/z 91 and 92 final cyclotron radii calculated using different initial ion positions. 50 V rf amplitude, 0.20 ms chirp excitation m/z 95 - 88, 5000 ions in each cloud. m/z 91 are placed at (0,0,0).

<table>
<thead>
<tr>
<th>Initial position of m/z 92 (mm)</th>
<th>Calculated 91 radius / 92 radius (mm / mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0, .15)</td>
<td>8.27 / 6.23 = 1.32</td>
</tr>
<tr>
<td>(.15, 0, 0)</td>
<td>8.54 / 6.27 = 1.36</td>
</tr>
<tr>
<td>(-.15, 0, 0)</td>
<td>7.96 / 6.37 = 1.25</td>
</tr>
<tr>
<td>(0, .15, 0)</td>
<td>8.62 / 6.23 = 1.38</td>
</tr>
<tr>
<td>(0, -.15, 0)</td>
<td>8.26 / 6.33 = 1.30</td>
</tr>
<tr>
<td></td>
<td>average = 1.32 ±0.01</td>
</tr>
</tbody>
</table>
were simplified by positioning the two ion clouds initially along the $z$ axis in all further simulations.

The numerical integration was carried out by straightforward iteration of the difference equations corresponding to Eq. 1:

$$\begin{align*}
x_1^{i+2} &= 2x_1^{i+1} - x_1^i + \frac{q_1 E_x}{m_1} \Delta t^2 + \frac{q_1 B}{m_1} (y_1^{i+1} - y_1^i) \Delta t - \frac{q_1 q_2}{4 \pi \varepsilon_0 m_1} \frac{x_2^{i+1} - x_1^{i+1}}{R^3} \\
y_1^{i+2} &= 2y_1^{i+1} - y_1^i - \frac{q_1 B}{m_1} (x_1^{i+1} - x_1^i) \Delta t - \frac{q_1 q_2}{4 \pi \varepsilon_0 m_1} \frac{y_2^{i+1} - y_1^{i+1}}{R^3}
\end{align*}$$

and a similar pair of equations with labels 1 and 2 interchanged.

Here $x_1^i$, $x_1^{i+1}$, and $x_1^{i+2}$ give the position of ion 1 after zero, one and two time steps (with similar notation for the $y$ coordinate), $q_1$ is the charge of ion 1, $q_2$ is the total charge of ion cloud 2, $m_1$ is the mass of ion 1, $R$ is the distance between ion 1 and ion cloud 2, and $\Delta t$ is the time step for the integration.

Some attention was necessary in the choice of the time step $\Delta t$. If $\Delta t$ was chosen too large, accumulated errors in the numerical integration resulted in gradually increasing ion orbits in the absence of any electric force. $\Delta t$ was empirically chosen to limit the drift of the orbiting radii to less than 0.5 percent with each successive cycle. This criterion was comfortably satisfied by a $\Delta t$ value (1.1 ns) which give a complete cyclotron orbit for an
ion of mass 91.5 in 4,000 time steps. Inspection of ion motion plots like those shown below indicated that this time step was satisfactorily short even during the initial period of rapid ion acceleration under the influence of Coulomb repulsion.

EXCITATION SCHEMES. Three excitation schemes were modeled to compare the effect of the Coulomb interaction on the peak ratio:

1. Chirp (frequency sweep) excitation\(^8,9\):

\[
E(\text{chirp})_x = E_0 \left(\frac{0.72}{2.54 \times 10^{-2} \text{m}}\right) \sin(\omega_1 t + 0.5at^2)
\]  

where \(E_0\) is the amplitude of the r.f. voltage applied to the receiver plates, 0.72 is a correction factor to the potential in a cubic cell [10], 2.54x10\(^{-2}\) m is the length of a side of the cubical cell, \(\omega_1\) is the starting frequency in radians/s, \(t\) is time in seconds, and \(a\) is the sweep rate in radians/s\(^2\). The parameters were chosen to match the experimental conditions corresponding to Fig. 1, with a mass range from 95 to 88 swept in 200 \(\mu\)s.

2. Impulse excitation\(^11,12\). This was modeled as a constant electric field turned on for 1 \(\mu\)s in the \(x\) direction.

\[
E(\text{impulse})_x = E_0 \left(\frac{0.72}{2.54 \times 10^{-2} \text{m}}\right) \quad 0 < t < 1 \mu\text{s}
\]  

3. SWIFT excitation\(^13,14\). SWIFT is not actually a specifically defined excitation waveform, but describes a family of
waveforms having the desired excitation spectrum. In the preferred implementation, the phases of the Fourier components are scrambled in such a way that the excitation r.f. amplitude is spread out reasonably uniformly over the duration of the excite pulse. This was mimicked by the sum of two sinusoidal waveforms at the specific frequencies for m/z 91 and 92:

\[ E_{\text{SWIFT}} \propto = E_0 (0.72/2.54 \times 10^{-2} \text{m}) (\sin \omega_1 t + \cos \omega_2 t) \]  

(6)

which accelerated the ion clouds for 200 \(\mu\)s.

**COMPUTER MODELLING RESULTS**

The first set of calculations investigated whether the inclusion of the Coulombic term affected the trajectory of the ions in a way that would explain the mass discrimination seen in Fig. 1. Figures 3 a,b and 4 a,b are sets of plots that show the trajectories of ion clouds m/z 91 and 92 with the absence and inclusion of the Coulomb repulsion term respectively. Each ion cloud contained the charge of 5,000 ions and was accelerated by a chirp excitation waveform of amplitude \(E_0 = 40\) \(\text{V}\) sweeping through m/z 95 - 88 in 200 \(\mu\)s. The separation of the ion clouds was 0.125 mm along the z-axis.

The inclusion of Coulomb repulsion between the two ion clouds clearly has a direct effect on the final cyclotron orbital radius after chirp excitation. FT-ICR peak heights are expected to be proportional to the final cyclotron radii of the two ion clouds after excitation\(^{15}\). The difference in the calculated cyclotron
FIG. 3. Trajectory plots of the ion clouds calculated in the model, without Coulomb interaction. a) m/z 91, b) m/z 92.
FIG. 4. Plots identical to Figure 2 except Coulomb interaction between the ion clouds is included. a) m/z 91, b) m/z 92.
radii is large enough to account for the mass discrimination seen in the peak ratios for the set of data shown in Figure 1. Table 2 shows the calculated dependence of the final cyclotron orbital radii on the chirp excitation amplitude.

Excellent quantitative agreement between the experimentally determined peak heights (electron beam length 5 ms) and the calculated final cyclotron orbital radii is seen in Table 2. The ratios for each excitation amplitude correspond well up to $E_o = 70$ V. At $E_o = 80$ V the calculated cyclotron radius of 91 exceeds 12 mm. This matches the cyclotron radius at which the orbiting ion cloud would begin to collide with the walls of the cell. This is seen in the observed dropoff in the experimental signal strength near this amplitude. The calculation predicts that m/z 91 has a larger radius than m/z 92, which is in agreement with the observation that it is preferentially ejected at high r.f. amplitudes.

Table 3 shows the mass discrimination produced using the three types of excitation schemes: chirp, Eq. (4), impulse, Eq. (5), and the simulated version of SWIFT excitation, Eq. (6). The ion clouds each contained the charge of 5,000 ions with a z-axis separation of 0.125 mm. It is seen that mass discrimination is most severe for chirp excitation, smaller but still significant for simulated SWIFT excitation, and smaller still for impulse excitation.

FURTHER MODELLING STUDIES

To probe further the modelled space charge effect a series of
TABLE 2. Experimental peak ratios and calculated cyclotron orbital radii for m/z 91 and 92 as a function of r.f. amplitude (chirp excitation)

<table>
<thead>
<tr>
<th>$E_0 (V)$</th>
<th>Experimental 91/92 (arbitrary units)</th>
<th>Calculated 91 radius / 92 radius (mm / mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>3.29 / 2.35 = 1.40</td>
<td>6.78 / 4.75 = 1.42</td>
</tr>
<tr>
<td>50</td>
<td>3.96 / 3.08 = 1.38</td>
<td>8.52 / 6.19 = 1.38</td>
</tr>
<tr>
<td>60</td>
<td>4.95 / 3.48 = 1.32</td>
<td>9.42 / 7.82 = 1.20</td>
</tr>
<tr>
<td>70</td>
<td>5.26 / 4.74 = 1.11</td>
<td>10.59 / 9.26 = 1.14</td>
</tr>
<tr>
<td>80</td>
<td>4.12 / 5.27 = 0.78</td>
<td>12.55 / 10.49 = 1.19</td>
</tr>
<tr>
<td>90</td>
<td>2.68 / 5.48 = 0.49</td>
<td>13.55 / 12.22 = 1.10</td>
</tr>
</tbody>
</table>
TABLE 3. The effect of Coulomb repulsion on calculated cyclotron orbital radii using three different excitation schemes.

<table>
<thead>
<tr>
<th>Excitation scheme</th>
<th>$E_0$</th>
<th>Pulse width</th>
<th>Calc. 91/92 Coulomb off (mm / mm)</th>
<th>Calc. 91/92 Coulomb on (mm / mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chirp m/z 95-88</td>
<td>50v</td>
<td>0.2ms</td>
<td>7.27 / 7.05</td>
<td>= 1.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.52 / 6.19</td>
</tr>
<tr>
<td>simulated SWIFT</td>
<td>20v</td>
<td>0.2ms</td>
<td>7.27 / 7.26</td>
<td>= 1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.06 / 7.93</td>
</tr>
<tr>
<td>impulse</td>
<td>400v</td>
<td>0.001ms</td>
<td>7.44 / 7.46</td>
<td>= 1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.66 / 7.24</td>
</tr>
</tbody>
</table>


FIG. 5. Ratio of the calculated cyclotron orbital radii as a function of r.f. excitation amplitude. (■) ratio of cyclotron radii for m/z 92 and 134, (●) ratio of cyclotron radii for m/z 91 and 92.
FAR-MASS RATIO VS. NEAR-MASS RATIO

CYCLOTRON ORBITAL RADIUS RATIO

EXCITATION AMPLITUDE $E_0$ (V)

91/92

92/134
calculations was made to observe the response of the ratio of the final cyclotron orbital radii to changes in various parameters. Fig. 5 compares the space charge effect for the close-lying 91/92 doublet and the widely mass-separated 92/134 doublet. The ions were excited by identical chirp excitation waveforms of pulse length 200 μs sweeping through m/z 200 - 50. Each ion cloud contained the charge of 3000 ions with an initial separation of 0.15 mm along the z-axis. The effect on the cyclotron orbital radii ratio of m/z 91/92 was very dependent on the number of ions, while the effect on the 92/134 ratio was small. (The discrimination of up to 1.07 in the 92/134 ratio was largely independent of the Coulomb interaction, and represents numerical errors in the simulation.)

Fig. 6 probes the effect of a shortened (but higher-amplitude) chirp excitation pulse length on the ratio of the final cyclotron orbital radii of the ion clouds of m/z 91 and 92. To compensate the shortened pulse length the excitation amplitude was correspondingly increased in order to keep the final cyclotron radius of the ion clouds relatively constant at 7 mm in each run. Once again a charge of 3000 ions was given to each ion cloud with an initial z-axis separation of 0.15 mm. Chirp excitation was used, sweeping through m/z 95 - 88. As the length of the chirp waveform was shortened the mass discrimination between m/z 91 and 92 decreased.

The effect of reducing the total number of ions was modelled by decreasing the total charge in each ion cloud. Figure 7 shows
FIG. 6. Ratio of the calculated cyclotron orbital radii of m/z 91 and 92 as a function of r.f. excitation pulse length. The excitation amplitude was lowered as the pulse length was lengthened to produce final cyclotron orbits of approximately 7 mm.
91/92 VS. R.F. PULSE LENGTH

91/92 ORBITAL RADI RATIO

EXCITATION PULSE LENGTH (us)
FIG. 7. Ratio of calculated cyclotron orbital radii of m/z 91 and 92 as a function of r.f. excitation amplitude. (▲) 3,000 ions in each cloud, (■) 1,500 ions in each cloud, (●) 500 ions in each cloud.
the dependence of the 91/92 cyclotron orbital radius ratio on the r.f. excitation amplitude. Three cases were modelled: 3,000 ions, 1,500 ions, and 500 ions in each cloud. Chirp excitation of pulse length 200 μs swept through m/z 95 - 88, with an initial separation of the ion clouds of 0.15 mm along the z-axis. Reduction in the total charge steadily reduced the extent of mass discrimination.

Lower ion densities were mimicked by increasing the initial z-axis separation of ion clouds while keeping the total number of ions the same (as would be expected for a reduced trapping voltage). Each ion cloud contained the charge of 3,000 ions, accelerated by a chirp excitation waveform sweeping through m/z 95 - 88 for 200 μs at $E_0 = 40$ V. Figure 8 shows the lessening of the mass discrimination between m/z 91 and 92 as the ion clouds approach distances where the short range Coulomb interactions have little effect.

The simulations successfully modelled the qualitative increase in mass discrimination for increasing ion number, increasing trapping voltage, and decreasing excitation amplitude. However, the ion trajectories found in these simulations did not account quantitatively for the large mass discrimination seen at very high ion numbers and trapping voltages, as in the 100 ms data in Fig. 2. This may reflect the limitation in modelling the ion clouds as point charges.
FIG. 8. Ratio of calculated cyclotron orbital radii of m/z 91 and 92 as a function of initial separation of the ion clouds along the z-axis.
EFFECT OF ION SEPARATION

Initial Z Separation ($10^{-4}$ m)

91/92 Orbital Radii Ratio

Points on the graph indicate the relationship between initial Z separation and orbital radii ratio for different separations.
DISCUSSION

From the trajectory calculations we see that Coulomb repulsion significantly affects the motion of the ions during excitation. Fig. 3 a,b show ion clouds, m/z 91 and 92, without Coulombic interaction, spiralling out from the center of the cell in a uniform manner as one would expect during excitation by an oscillating electric field. In Fig. 4 a,b the cyclotron motion during the chirp excitation is perturbed by the inclusion of Coulomb repulsion, resulting in altered final cyclotron orbits. Once the ion clouds have reached the final cyclotron orbital radii ion motion is unperturbed by Coulomb interactions.

The motion of the ion clouds during the chirp excitation is very complicated and it is not easy to interpret the simulation results. The relative phases of the ion clouds' cyclotron motions are not easily followed. Rather than attempt to understand in detail the interaction of the Coulomb force with the other forces during the excitation, we have focussed on the space charge effects reflected in the calculated final cyclotron orbital radii. Using this criterion, the excellent agreement seen in Table I between simulated and observed space charge effects gives us confidence that we understand the mechanism of the 91/92 ratio distortion in an entirely satisfactory way, at least when the perturbation is relatively small.

The trajectory calculations have emphasized and clarified several features of the effect of space charge interactions on peak heights in FT-ICR spectra. First, mass discrimination by space
charge effects is most important for ions close in mass. Second, the artifact can be minimized by using a short, high-amplitude excitation waveform. Both of these characteristics come naturally from the fact that the Coulomb perturbation of the ion motion depends on the length of time over which the interacting ions are close together during excitation. Third, the artifact is minimized by using low numbers of ions and by spreading the ions out along the z axis, both of which reduce the magnitude of the Coulomb forces.

Coulomb repulsion as a mechanism for mass discrimination is only significant for ions close in mass. Two ions of different mass that are initially travelling coherently in their cyclotron orbits will gradually fall out of phase, and move apart in space, due to their difference in cyclotron frequency. The cyclotron motions of ions far apart in mass dephase quickly. Ions at m/z 92 and 134 travelling with the same cyclotron orbital radius will be separated by 1 radian after about 2 μs, which is short compared with a typical chirp excitation pulse length of 200 μs. Once the ions have dephased in the first 2 μs of excitation the short range Coulomb forces become negligible with respect to the force of the r.f. electric field. The dephasing period for ions m/z 91 and 92 is 62 μs, and the motion of the ions is perturbed by Coulomb repulsion during a significant fraction of the excitation. The simulations clearly show this distinction between close-lying and far-apart mass doublets, as illustrated in Fig. 5.
The length of the excitation waveform strongly determines the extent of mass discrimination. Fig. 6 shows that as the chirp waveforms become shorter and higher in amplitude the mass discrimination decreases. Once again the basic principle is that the length of time in which Coulomb repulsion significantly perturbs the motion of the ions determines the degree of mass discrimination. For a given extent of dephasing of the cyclotron motions of the interacting ions, the spatial separation between them is proportional to their cyclotron radii. If the excitation pulse length is shortened the ions reach large cyclotron radii sooner, allowing dephasing to move them apart more quickly.

Impulse excitation uses a very short high-amplitude excitation waveform\textsuperscript{11,12}. Ideally the length of the impulse excitation is chosen to be much less than one cycle of the cyclotron orbit of the ions in the ion trap cell. Impulse excitation in principle instantly increases the momentum of the ion cloud from rest producing all ions travelling in a large cyclotron orbit. At this large orbit a small angular separation due to dephasing will result in a large linear separation, minimizing Coulomb repulsion effects.

In obtaining accurate peak heights, SWIFT addresses the problem of the nonuniform frequency domain power spectrum produced by chirp excitation\textsuperscript{9}. The ideal excitation scheme accelerates all the ions to the same cyclotron orbital radius. The amplitude of the image current produced on the receiver plates will then simply be proportional to the total number of ions in each ion cloud. The SWIFT excitation waveform is derived from the inverse Fourier
transform of the desired frequency domain power spectrum\textsuperscript{13,14}. Various algorithms have now been developed for the production of the SWIFT waveform.

We did not attempt to produce an actual SWIFT waveform for the investigation but simply mimicked one. The sum of two sinusoidal waveforms which we used preserves the desired characteristics that the two ions are accelerated simultaneously, and the duration of the excitation is the same as the chirp waveform which we are comparing with.

Unfortunately, SWIFT will only remedy the problem of accurate peak heights to the extent that the mass discrimination artifact is produced by the nonuniform power spectrum of the excitation waveform. Even if the excitation waveform is designed to produce a flat power spectrum the problem of Coulomb repulsion between ion clouds can still perturb the motion of the ions and mass discrimination may still persist. As Table 3 shows, the simulated SWIFT waveform we used gives less discrimination than the chirp, which seems to be particularly bad in this respect, but the SWIFT waveform by no means eliminates the discrimination. Moreover, for SWIFT pulses longer than the 200 \(\mu s\) we used, we would expect the discrimination to be more severe, following the arguments given above.

Mass discrimination due to ion repulsion can also be reduced by minimizing the magnitude of the Coulomb force existing between the two ion clouds. Experimentally, reducing the total number of
ions and lowering the trapping potential both help to remedy the ion intensity ratio problem. Fig. 7 shows that a reduced number of ions reduces the mass discrimination.

Lowering the trapping potential while keeping the number of ions the same reduces the ion density [16]. The lowered d.c. voltage on the trapping plates produces a shallower potential well allowing the trapped ions to spread out along the z axis. The total number of ions will remain the same but at a lower ion density. This was modelled by keeping the total number of ions in each cloud the same while increasing the initial separation between ion clouds. Fig. 8 shows the reduction in mass discrimination as the initial ion cloud separation increases.
CONCLUSION.

The use of competitive photodissociation as a thermometric technique requires the accurate measurement of the branching ratio of the photoproducts. Although FT-ICR spectrometry provides low pressure conditions which are excellent for the study of infrared photoprocesses the problem of mass discrimination detracts from our confidence in the ion thermometry technique. Most of the problems with accurate peak ratios we have observed in this chapter have been attributed to space charge interactions that influence the motion of the ions during excitation.

The actual motion of ions in an FT-ICR spectrometer is complicated and can differ from the motion of a single ion in a cyclotron orbit. Space charge interactions among the ions further complicate the motion of the ions. Using ion trajectory calculations we have studied the effects of interionic repulsion under various conditions. The effect of Coulomb repulsion on the final cyclotron orbital radius after excitation provides satisfactory understanding of the mass discrimination seen in spectra of close-mass ions. The trajectory calculations, reinforced by experimental observations, indicate that space charge effects can be minimized by (1) using low ion densities, (2) using low ion numbers, and (3) using an excitation scheme that accelerates the ions in a very short period of time. The first two criteria would favor the use of large cells, low trapping voltages and small numbers of ions; even better should be cells elongated along the z direction\textsuperscript{17}, and cells with screened trapping plates\textsuperscript{18},
to spread the ions out along the z axis. The third criterion would suggest impulse excitation as the best excitation scheme for accurate peak ratios, with other excitation profiles being progressively worse as the acceleration period for the ions of interest grows longer.
REFERENCES


16. In considering that the ions are more compressed along the z axis at higher trapping voltage, we have assumed that the initial oscillations along the z axis have damped out, settling the ions to the center of the trap. It can be questioned whether z-axis relaxation is complete in these low pressure experiments; but we see substantial relaxation of the z-axis motion judging from the increase and levelling off of the FT-ICR signal strength within a few hundred ms after the electron beam pulse (see Ref. 2). The z-axis relaxation is believed to be effected by Coulomb repulsions between ions along the z axis.


CHAPTER V

THE KINETICS OF INFRARED LASER PHOTODISSOCIATION OF

N-BUTYLBENZENE IONS AT LOW PRESSURE
INTRODUCTION

The photodissociation of gas-phase ions by light from infrared lasers is attracting increasing attention in ion-trapping mass spectrometry, using both the ion cyclotron resonance (ICR) ion trap\textsuperscript{1,2} and the quadrupole ion storage (QUISTOR) ion trap\textsuperscript{3}. Infrared radiation is seen as promising both for characterizing ions by vibrational spectroscopy, and also for inducing ion fragmentation close to the lowest dissociation threshold. This latter application has the potential for giving incisive quantitative information about low-energy fragmentation thresholds and kinetics, and toward this goal we have undertaken studies to improve our understanding of IR-induced fragmentation kinetics. It will become clear that the approach adopted here is particularly relevant to large ions and molecules which lie within the quasicontinuum at ambient temperature, which meshes well with the current trend toward study of larger ions in ion trapping mass spectrometers.

It has often been thought that there should be a useful analogy between infrared multiphoton decomposition (IRMPD) reactions and thermally-induced reactions, since the chemistry in both cases proceeds by stepwise accumulation of energy in the internal degrees of freedom of the molecule. However, in the widely studied case of IRMPD by pulsed lasers, thermal analogies have not been found to be useful. We have recently been exploring the possibility that this point of view may be much more accurate and useful in the case of slow IRMPD using cw
laser irradiation, with encouraging success on both theoretical and experimental sides.

Our theoretical understanding is based on a paper\textsuperscript{4} (referred to hereafter as I) which discussed the kinetics of IR photodissociation of a polyatomic molecule by low-intensity continuous-wave infrared laser light under collision-free conditions. The point of view was explored that such dissociations are very similar to thermal dissociations, and can be fruitfully viewed from a thermal point of view.

As portrayed in I, a population of molecules under collision free conditions in contact with a black body source will result in a Boltzmann distribution of energies at the given temperature of the source. This will also be true for the special case where the molecules absorb and emit IR photons only at a single frequency, $\hbar \nu$. This specific situation is identical to a molecule irradiated by a monochromatic laser at the frequency $\hbar \nu$ and of intensity defined by the Planck relation

$$I(\hbar \nu) = I_0(\hbar \nu) \left[ \exp(\hbar \nu/kT) - 1 \right]^{-1}$$

One normally uses this relationship to determine the intensity of a specific frequency for the given temperature of the black body source. For our purposes a given laser intensity will be equated to a particular temperature which will give rise to the distribution of internal energies for the population of molecules.
Real molecules do not absorb and emit photons at the single frequency of the laser light. However as shown in I the temperature range reached in this study freezes out high frequency C-H bond stretches. The IR spectra of medium sized molecules show active modes in the 1000 cm\(^{-1}\) region which is where the CO\(_2\) laser line is found (940 cm\(^{-1}\)). Deviations from a Boltzmann distribution by the steady state distribution of the population of molecules were found to be minimal in numerical simulations.

The outstanding experimental environment for trying out these ideas is the photodissociation of ions in a low-pressure ion-trapping device. We describe here such a study of the CO\(_2\)-laser photodissociation of n-butylbenzene ions in the ion cyclotron resonance (ICR) ion-trapping mass spectrometer. The pressures used were sufficiently low to make collisions unimportant in the kinetics, so that this constitutes an excellent system for testing our understanding of isolated-molecule IR-laser dissociation kinetics.

Infrared multiphoton decomposition (IRMPD) of polyatomic molecules has been extensively studied.\(^5\) While most work has been done with pulsed infrared lasers, there has been a substantial growth of interest in IRMPD chemistry using continuous-wave (cw) lasers, following initial experiments by Woodin et al.\(^6\) showing that the ICR ion trap is eminently well suited for study of this chemistry. Thorne and Beauchamp\(^1\) gave an excellent review of this area which is still timely. An important distinction discussed there exists between molecules which do or do not lie in the
quasicontinuum at ambient temperature. We will assume that n-
butylbenzene ion lies in the quasicontinuum at room temperature, so
that absorption of even the first IR photon from the laser is not
constrained by the possible low density of resonant final states.
We thus rule out any low-energy bottlenecking behavior. The
assumption of the quasicontinuum at ambient temperature
(corresponding to 0.3 eV internal energy) is amply justified by
estimates of the vibrational state density for n-butylbenzene at
this energy.

Although the thermal analysis discussed in I does not
necessarily require it, modeling of the kinetics is greatly
simplified by making a stronger assumption about the laser pumping
process, namely that there is no variation in IR absorption cross
section with the internal temperature of the ion from 373 to 1000 K
(except for a minor extent of temperature dependence arising from
the properties of the resonant vibrational mode considered as a
harmonic oscillator, as detailed below). This assumption about
pumping rates seems eminently reasonable for such a large molecule
and receives additional support form the excellent agreement of the
data with the kinetic behavior predicted by this kinetic model.

In considering the kinetic we will adopt the "sudden death"
assumption,\(^1,7\) namely that there is a threshold ion internal energy
\(E_t\), below which the rate of unimolecular dissociation of the ion is
negligible slow, and above which it is so fast that it may be
considered as instantaneous (compared to the up-pumping and
relaxation rates). The very steep rate-energy curve (extrapolated form that reported by Baer et al.8) for dissociation of n-butylbenzene ion in the rate region relevant to the IRMPD kinetics (10-100 s\(^{-1}\)) makes this a very good approximation.

The extensive study and understanding of pulsed-laser IRMPD chemistry gathered over the last two decades\(^5\) has considerable relevance to cw laser chemistry. In one comparison of pulsed and cw excitation, the IRMPD behavior was found to be qualitatively similar.\(^9\) However, we emphasize here a fundamental difference distinguishing cw laser experiments at low light intensities from all pulsed experiments, namely the fact that infrared radiative deexcitation of the ions competes strongly with laser pumping, so that the dissociation rate reflects a balance between these processes. As pointed out in I, one consequence of this is that it becomes practically useless to speak of laser fluence as the governing variable in determining IRMPD yield: the yield varies enormously with laser intensity, even when the fluence is held at a constant value.

An induction time is usually observed in cw IRPMD, that is a time after turning of the laser before any dissociation is observed. Thorne and Beauchamp\(^1\) pointed out that the induction time should be approximately inversely proportional to laser intensity, (that is, there shold be an approximate fluence threshold for the first appearance of photoproducts) if the time it takes the laser to pump ions up to near the threshold \(E_c\) is short compared with all relaxation processes. This was shown to be true
for diethyl ether proton-bound dimer ion dissociation at the laser intensities and pressures of their study. We will see that this approximation is also moderately well followed for the present data.

Salomon and Brauman\textsuperscript{10} used logarithmic reaction fluence (LRF) plots to analyze IRMPD results in a study of CH$_3$OH$^-$ (dissociation) and C$_7$H$_7^-$ (detachment). This approach, along with other methods involving plots of decomposition yield versus fluence, does not seem very useful for data taken with low laser intensities as in the present study. Based on the considerations discussed above, the steepness of the LRF plot for cw IRMPD will be strongly dependent on laser intensity when infrared radiative relaxation or collisional relaxation are comparable to or faster than the laser pumping rate. Moreover, the presence of an induction time will make the LRF plot non-linear with respect to the length of the laser irradiation time. Thus inspection of LRF plots does not give a clear signal about the characteristics of the IRMPD mechanism, and they seem much less useful than direct plots of dissociation versus time at various laser intensities.

With IR laser excitation, only the lowest energy fragmentation pathway for n-butylbenzene ions is observed, giving m/z 92 product ions:

$$C_4H_9C_6H_5^+ \rightarrow C_7H_8^+ + C_3H_6.$$ \hspace{1cm} (1)

The photoelectron-photoion coincidnece (PEPICO) study of Baer et al.\textsuperscript{8} gives the clearest picture of the kinetics of this
unimolecular decomposition as a function of ion internal energy. The critical energy for dissociation derived in this study was 0.99 eV, and extrapolating their rate-energy curve to low rates via RRKM fitting suggests that the decomposition rate becomes significant (10-100 s⁻¹) at an ion energy of the order of 1.25 eV. Beginning with thermal ions with about 0.3 eV of internal energy, the ions must thus accumulate about 8 or 9 infrared photons of additional energy from the CO₂ laser (940 cm⁻¹) in order to dissociate.
EXPERIMENTAL

The CO₂-laser photodissociation experiment was done on the Fourier-transform ion cyclotron resonance (FT-ICR) spectrometer used in other recent work of our group. Briefly, the homebuilt ICR system has a 2.5 cm cubical cell in a magnetic field of 1.4 Tesla, controlled by an IonSpec FT-ICR data system. A homebuilt cw CO₂ laser produced IR light at 940 cm⁻¹ with a power of about 9 W. The IR beam was attenuated with a stepped attenuator consisting of a variable stack of AgCl plates. The beam was unfocussed, and we estimate very roughly that its diameter at the position of the ions was 3 mm.

Fig. 1 shows the pulse sequence used. Ions were first produced by a 200 ms electron beam pulse at 12.5 eV nominal electron energy. All fragment ions at m/z 91 and 92 were immediately ejected from the cell. The ions were then thermalized for 1 s or more to allow vibrationally excited ions to cool to thermal equilibrium by radiative and collisional processes. After thermalization the CO₂ laser was turned on. When the chosen period of laser irradiation was finished, ICR excitation and detection were carried out, with the time required for ICR analysis being brief (2 ms) compared with the time scale of the experiment. The ICR detection was broadband, detecting simultaneously both the parent and daughter ions, to monitor the progress of m/z 134 depletion and m/z 92 production as a function of laser irradiation time. All experiments were done at an indicated pressure of 9x10⁻⁹ Torr.
FIG. 1. The pulse sequence used for the FT-ICR measurements.
1.3 s thermalization
detect delay 0-1s

ELECTRON BEAM
EJECT M/Z 91 & 92
EJECT M/Z 91 & 92
DETECT QUENCH

cw-CO2 LASER
940 cm⁻¹ 1-9W

TIME
RESULTS

The extent of dissociation of parent ions as a function of time after turning on the laser was recorded at a series of laser power levels. A typical time plot is displayed in Fig. 2. After the points were plotted in logarithmic form, each time plot was decomposed (as illustrated in Fig. 4 of I) into an induction time, \( r_{\text{ind}} \), and a reaction rate, \( k_{\text{diss}} \), by drawing a line through the linearly decreasing portion of the data. \( k_{\text{diss}} \) was assigned as the slope of the linearly decreasing portion, and \( r_{\text{ind}} \) was assigned from the point at which this sloping line intersects the initial signal level.

In Table 1 the resulting values of \( k_{\text{diss}} \) and \( t_{\text{ind}} \) are shown as a function of laser power for the most extensive data set. The induction time is seen to decrease markedly with increasing laser power, while \( k_{\text{diss}} \) increases sharply with increasing power. This is qualitatively consistent with our picture of the reaction process, in which the cool molecules are initially pumped up the ladder of internal energies to a near-steady-state distribution with a peak below the dissociation threshold, after which the laser pumps them over the dissociation threshold at a steady rate. The agreement of the data with this qualitative picture is expanded and validated below by more detailed fitting of the data to the computer simulation of the kinetics. Finally it is pointed out that the thermal-dissociation point of view gives a satisfactory quantitative understanding of these kinetics.

It was observed that in the absence of laser irradiation ion
FIG. 2. Illustrative data for dissociation versus time.
CO$_2$ Laser Dissociation of n-Butylbenzene Ion

![Graph showing the dissociation of n-Butylbenzene ion with laser irradiation time. The x-axis represents Laser Irradiation Time (sec), and the y-axis represents Ion Signal. The graph includes two sets of data points: circles for m/z 134 and squares for m/z 92.](image-url)
Table 1

Dissociation rate constants and induction times derived from the observed dissociation curves.

<table>
<thead>
<tr>
<th>I (W)</th>
<th>$k_{\text{diss}}$ ($s^{-1}$)</th>
<th>$\tau_{\text{ind}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.3</td>
<td>0.31</td>
</tr>
<tr>
<td>2.3</td>
<td>1.3</td>
<td>0.155</td>
</tr>
<tr>
<td>2.9</td>
<td>1.1</td>
<td>0.115</td>
</tr>
<tr>
<td>3.3</td>
<td>2.1</td>
<td>0.075</td>
</tr>
<tr>
<td>3.7</td>
<td>2.0</td>
<td>0.075</td>
</tr>
<tr>
<td>4.0</td>
<td>3.0</td>
<td>0.095</td>
</tr>
<tr>
<td>4.5</td>
<td>3.5</td>
<td>0.070</td>
</tr>
<tr>
<td>4.9</td>
<td>4.0</td>
<td>0.070</td>
</tr>
<tr>
<td>6.0</td>
<td>6.2</td>
<td>0.040</td>
</tr>
<tr>
<td>6.9</td>
<td>6.0</td>
<td>0.050</td>
</tr>
<tr>
<td>9.2</td>
<td>10.5</td>
<td>(a)</td>
</tr>
</tbody>
</table>

(a) Too short for meaningful measurement within the precision of laser timing.
dissociation still proceeds at a very low rate, about 0.16 s\(^{-1}\).

This could be considered to be thermal dissociation at ambient temperature, but we reject this possibility, because the analysis given below, which is in satisfactory agreement with all other features of the data, leads us to expect a thermal dissociation rate less than 0.001 s\(^{-1}\) at 375 K. Instead, we attribute this zero-power dissociation to photodissociation by visible radiation from the incandescent filament, which illuminates the ion could continuously at a distance of 1.3 cm. It is therefore appropriate to subtract this rate of 0.16 s\(^{-1}\) from the IR-laser-induced dissociation rated, which we have done in the quantitative analysis below. This correction is noticeable only for the lowest-power point (1.4 W).
COMPUTER SIMULATION

Random Walk Simulation Procedure

The laser irradiation and dissociation process was modeled by a random walk sequence similar to the events believed to take place in the physical system. The conceptual model is the often-used energy-grained master equation. The simulated random-walk model, comparable to that introduced by Gillespie, was discussed in detail in I, and will only be briefly summarized here. At each time step in the evolution of the molecule, one or more of three events may occur:

1. Photon absorption. The internal energy of the molecule increases by one quantum of energy $\omega_0$. Probability proportional to the light intensity $I_{rw}$, to the absorption coefficient $k_{n,n+1}$, and to the probability of occupation of the lower level (n) of the absorbing mode.

2. Induced emission. The internal energy decreases by one quantum of energy $\omega_0$. Probability proportional to the intensity $I_{rw}$, to the induced emission coefficient $k_{n+1,n}$, and to the probability of occupation of the upper level (n+1) of the emitting oscillator.

3. Spontaneous emission. The internal energy decreases by one quantum of energy $\omega_{rad}$ from n to n-1. Probability proportional to the radiative rate constant, $k_{rad,n}$, and to the probability of occupation of the upper level (n+1) of the
emitting oscillator.

At each time step the occurrence or non-occurrence of each of these processes is random, with the probabilities indicated above. To find the total probability of absorption or emission of a photon at each step, the probabilities of these three processes are summed over all the levels of the emitting and absorbing normal modes. The thermodynamic approximation is used to evaluate the occupation probabilities of the levels of these modes\textsuperscript{12}. We use the fact that $k_{n,n+1} = k_{n+1,n}$, and we assume (corresponding to harmonic oscillator behavior) that $k_{n,n+1} = n k_0$, and $k_{\text{rad},n} = n k_{\text{rad},1}$. The molecule thus undergoes a random walk on the energy axis. Over a large number of time steps the statistics of occupation of each point on the energy scale will reflect either the time-distribution of energies of a single molecule, or the energy distribution of a population of molecules observed at a single time.

Two types of simulation were carried out. In the temperature simulation, the molecule was allowed to evolve randomly over about $10^4$ time steps, and the statistics of occupation of the levels on the energy axis were recorded. The temperature was assigned from the average energy $E$ of the distribution according to the canonical energy-temperature function given in Table 2. In this way a curve was constructed of the population temperature (in the absence of reaction) as a function of laser intensity $I_{\text{lw}}$, at a fixed value of $k_{\text{rad}}$, as shown in Fig. 3.
Table 2
Average Energy \( \langle E \rangle \) as a function of temperature \( T \) for a canonical ensemble of n-buylbenzene molecule.\(^a\)

<table>
<thead>
<tr>
<th>( T )</th>
<th>( \langle E \rangle )</th>
<th>( \langle E' \rangle )(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>400</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>500</td>
<td>0.61</td>
<td>0.60</td>
</tr>
<tr>
<td>600</td>
<td>0.86</td>
<td>0.80</td>
</tr>
<tr>
<td>700</td>
<td>1.13</td>
<td>0.93</td>
</tr>
<tr>
<td>800</td>
<td>1.42</td>
<td>1.01</td>
</tr>
</tbody>
</table>

\(^a\)Calculated using the mode frequencies given by Baer et al., Ref. 8.

\(^b\)\( \langle E' \rangle \) is the average energy of the truncated Boltzmann distribution at temperature \( T \), obtained from the canonical Boltzmann distribution by removing all molecules with internal energy greater than 1.23 eV.
FIG. 3. Internal temperature of the ion as a function of laser intensity. The laser intensity scale marked $I_{RW}$ is the intensity used in the random walk simulations, and the line plotted shows the temperatures calculated in the simulations.
In the reaction simulation, the molecule was initially set at an energy of 0.3 eV (corresponding to thermalized ions) and was allowed to evolve until it reached or exceeded the threshold energy (1.23 eV) for the first time. The reaction profile was constructed from the statistics of the extent of reaction versus time. The profiles were plotted for a series of $I_{rw}$ values (again at fixed $k_{rad}$). Each time profile was decomposed into an induction time and a reaction rate constant in exactly the same way as was done for the experimental reaction profiled, and this set of values for $k_{rw}$ and $r_{rw}$ versus $I_{rw}$ was used in the fits to the experimental data described below.

The reaction threshold energy $E_T$ was chosen based on the raee-energy curve for dissociation given by Baer et al. Since their measurements did not extend below a dissociation rate of about $10^5$ s$^{-1}$, extrapolation was necessary, and was done using an RRKM fitting curve similar to that assumed by Baer et al. The kinetic shift for such a large molecule is significant, and we estimated that the dissociation rate would be comparable to the relaxation rate at an internal energy of 1.23 eV. For ions with internal energy less than this, dissociation is not expected to compete successfully with IR radiative relaxation. This chosen $E_T$ value is greater by 0.24 eV than the activation energy of 0.99 eV assigned by Baer et al., which is thus the kinetic shift assumed in our analysis.

In the rigorous thermal analysis of $I$, it was assumed that IR photons were absorbed and emitted at the same frequency. However,
in the simulation of the specific n-butylbenzene case, it seemed more realistic to assign the spontaneous emission photon frequency somewhat lower than the laser frequency (940 cm$^{-1}$). The IR absorption spectrum of n-butylbenzene in the mid-IR is dominated by a series of strong absorptions between 500 and 900 cm$^{-1}$. In the simulation a spontaneous emission frequency of 705 cm$^{-1}$ was used, to represent an approximate average of these allowed IR transitions. Emission from the strong C-H stretches near 3000 cm$^{-1}$ can be neglected, since these modes have almost no probability of occupation at the internal temperatures relevant to this study. Looking at the IR absorption spectrum, there appear to be no allowed IR transitions at frequencies below 500 cm$^{-1}$ whose intensity is large enough to give significant IR radiative cooling. The laser photon energy of 940 cm$^{-1}$ was used for the absorption and stimulated emission steps.

The simulation results are displayed in the figures. Fig. 3 shows the internal temperature vs. laser intensity; Fig. 4 shows the dissociation rate constant vs. laser intensity; and Fig. 5 shows the induction time vs. laser intensity.

**Fit to the Numerical Simulation**

The central problem in quantitative interpretation of IRMPD experiments like these is making the correspondence between the laser intensity and the internal energy or internal temperature of the molecules under laser pumping at the given intensity. This may
FIG. 4. Simulated values $k_{rw}$ of the dissociation rate constant as a function of laser intensity $I_{rw}$. 
Simulated Dissociation Rates

\[ k_{rw} \]

\[ I_{rw} \text{ (Simulated Laser Power)} \]
FIG. 5. Simulated values $\tau_{rw}$ of the induction time.
be achieved if auxiliary information is available. For instance, if the dissociation can be observed as a thermal process at at least one temperature, as in the experiments of Mautner, the temperature scale for IRMPD experiments can be anchored. Or if another thermometry technique can be used in conjunction with the IRMPD experiment, the temperature-scale problem may be solved; An illustration of this approach on n-butylbenzene ion from our laboratory using auxiliary ion thermometry will be described in chapter VI.

However, if, as in the present experiments, only IRMPD data are available, it is probably not possible to make the temperature correspondence from $k_{\text{diss}}$ vs. $I_{\text{laser}}$ data alone. We will show here how the fitting process can be completed using the additional information provided by the induction times, if we assume that the laser pumping of the molecules upward from thermal energy occurs uniformly, without bottlenecking or other irregular variations in pumping rate as a function of internal energy. This assumption is built into the model used in the random walk simulations. We can proceed to interpret the data by fitting the experimental data to the simulated kinetic results, using the simulation to provide calculated values of $k_{\text{rw}}$ and $\tau_{\text{rw}}$ vs. $I_{\text{rw}}$ to correlate with the experimental values.

The random walk simulation produces values for the induction time $\tau_{\text{rw}}$ and the dissociation rate $k_{\text{rw}}$ as a function of the laser intensity $I_{\text{rw}}$ and the radiative relaxation rate $k_{\text{rad, rw}}$. In order to relate these results to the experimental valued, there are three
unknown parameters to be assigned; (a) the laser pumping rate $I_{wall}$ experienced by the molecules at zero laser power due to background wall and filament radiation; (b) the scale factor $B$ relating the intensity used in the simulation to the real laser intensity, $B = dI_{rw}/dI_{laser}$; (c) the ratio $R$ of the real time scale to the time scale used in the simulation. When the correlation between simulated and observed results has been established, the intensity used in the simulation will be related to the laser power in the actual experiments by

$$I_{rw} = B(I_{wall} + I_{laser}).$$

(2)

The time scale of the simulation will be fixed relative to the experimental time scale by the time-scale ratio $R$, which will be defined so that unit time interval in the simulated decays corresponds to $R$ seconds in the actual experiments.

The computer modeling leads to a criterion which is very helpful in the process of assigning the quantitative correspondence between the experimental and the simulated kinetics. At zero laser power the ions equilibrate at the temperature of the cell (taken as $375$ K for the present experiments). The simulations give directly a relation between the laser pumping intensity $I_{rw}$ and the equilibrium temperature of the pumped ions. From the plot of $T$ versus $I_{rw}$ (Fig. 3), setting $T = 375$ K, along with $I_{laser} = 0$ in Eq. (2), this gives an immediate value for $BI_{wall}$ of 0.052. There
remain two adjustable parameters, B and R, to be fixed to complete the correspondence between simulated and experimental results.

If the experimental data are free of scatter and the kinetic model assumed in the simulation is exactly correct, there is a straightforward procedure for fixing these parameters, based on the fact that comparing the induction time to the dissociation rate gives an absolute determination of the light intensity seen by the molecules. The ratio of the induction time \( t \) to the dissociation time constant \( k^{-1} \) is a dimensionless quantity which depends on the laser intensity. Call this dimensionless ratio \( W \). There is a unique relation between \( W \) and \( I_{rw} \), which is determined from the simulation results as shown in Fig. 6. By measuring the ratio \( W \) for each experimental point, and reading the corresponding \( I_{rw} \) value from Fig. 6, the pumping rate \( I_{rw} \) can be assigned corresponding to each experimental laser power \( I_{laser} \).

A plot generated by this approach of \( I_{rw} \) versus \( I_{laser} \) for this data set is shown in Fig. 7\(^{15} \). From Eq. (2), this plot should be a straight line with intercept \( BL_{wall} \) and slope B. In principle, this plot thus fixes two of the unknown parameters, B and \( L_{wall} \). However, the substantial scatter of the points in Fig. 7 (arising because these points combine the scatter of \( k_{diss} \) and \( t_{ind} \)) makes this fit quite uncertain. It is better to take \( BL_{wall} \) to be 0.052 as noted above, and with the intercept thus fixed, the slope of the line gives B with good accuracy. The third parameter R then follows directly from a plot of \( k_{rw} \) versus \( k_{diss} \).

It is found that this approach gives a quite tightly
FIG. 6. Simulated curve for the dimensionless ratio $W = \tau_{rw} k_{rw}$. 
Calculated Ratio $W$

Ratio $W = \frac{\tau}{k-1}$
FIG. 7. Relation of simulated to the experimental laser intensity. The points were determined from the curve of FIG. 6 as described in the text. The line is the best estimate of the relation as discussed in the text.
constrained fit of the simulation to the data. The parameters best relating the simulation to the experiment are \( I_{\text{wall}} = 1.2 \text{ W} \), \( B = 0.043 \text{ W}^{-1} \) and \( R = 4.9 \times 10^{-2} \text{ s} \). The line predicted by this fit is plotted on Fig. 7. In Fig. 8 and Fig. 9 are shown the experimental and simulated values of \( k_{\text{diss}} \) and \( r_{\text{ind}}^{16} \), respectively. As can be seen from these three figures, the fit between experiment and simulation is satisfactory within the data uncertainties. It is clear that the kinetic model adopted in making the simulations is entirely satisfactory to account quantitatively for the values and trends of the experimental results.
FIG. 8. Dissociation rate constants $k_{\text{diss}}$ as a function of laser intensity $I_{\text{laser}}$. The circles show the experimental data points for $k_{\text{diss}}$, corresponding to the intensity scale marked $I_{\text{laser}}$. The solid line shows the calculated rate constants $k_{rw}$ from the simulations, using Eq. (2) to relate the simulated laser intensity to the experimental intensity.
Dissociation Rates

Dissociation Rate (s⁻¹)

Laser Power (W)
FIG. 9. Induction times $r_{\text{ind}}$ as a function of laser intensity.

The solid line is again the calculated values from the simulations.
Induction Times

Induction Time $\tau_{\text{diss}}$ (ms)

Laser Power (W)
DISSCUSSION

The comparison of experimental results with the kinetic model assumed for this reaction (implemented in the random-walk computer simulation), shows that the assumed picture of this slow IRMPD process gives a satisfactory account of the reaction kinetics. This appears to be the first quantitative kinetic study of a slow cw IRMPD reaction under collision free conditions, so there is no base of experience to indicate whether this kinetic picture is followed in other dissociations. A superficially similar process, the slow IR multiphoton electron detachment from benzyl anion, has been investigated at a level of detail similar to the present study, but with contrasting results. Wight and Beauchamp\textsuperscript{16} found the ratio $W$ of induction time to reaction time constant to be independent of laser power over their range of powers. As indicated in Fig. 6, the computer modeling predicts a very marked variation of $W$ with laser power in the vicinity of $W = 0.1$, which was the region studied by Wight and Beauchamp. Our analysis thus confirms their conclusion that their system is not described by this simple kinetic model, and a bottleneck in the IR pumping rate, or some other irregular feature of the kinetics, is present.

Salomon and Brauman\textsuperscript{10} also observed the benzyl anion reaction with cw CO$_2$ laser irradiation, although they did not report time plots, and they also concluded, based on non-linear logarithmic fluence plots, that there is an irregular feature in the IRMP photodetachment kinetics of benzyl anion. They considered rotational hole-burning to be the effect responsible. Unexpectedly
they observed no induction time under the conditions of their experiments. In view of the rather high pressures of all of the benzyl anion experiments (3 - 8x10^-7 Torr) there is some question about how comparable they are to the present experiments, although Wight and Beauchamp found no pressure dependence of the photodetachment yields. It is also not clear whether electron photodetachment and photodissociation are comparable processes.

The Thermal Picture

Our picture of the slow IRMPD reaction is that after the induction period, a steady-state condition is reached balancing pumping of infrared photons by the low-powered cw CO_2 laser and the infrared radiative deexcitation of the ions. The kinetics is governed by the internal energy distribution of the ion population in this steady state. If the distribution can be characterized by a Boltzmann distribution (actually, a Boltzmann distribution truncated at energy E_T), the kinetics will be simply the kinetics of thermal decomposition. We will show that the present reaction approximates this situation closely enough to make a useful link between the computer-modelled analysis and a thermal analysis of the data.

The hoped-for advantages of a successful thermal treatment of such a reaction include: the use of the parameters of activation energy and frequency factor to provide a compact and economical description of the kinetics; the elimination of the need for
elaborate computer modeling in interpreting data; and the idea that in some sense the description of the reaction in thermal terms should be more general, and less model-dependent, than its description in terms of a set of computer-modeling parameters.

We will test the thermal point of view for this reaction using the temperature versus laser-intensity function given by Fig. 3, which is linked to the experimental laser intensities via Eq. (2). Fig. 10 shows the data plotted in Arrhenius form using this temperature function. The solid curve on the figure is an estimated smooth fit to the data. The activation energy for a thermal reaction is defined to be

\[ E_a = R \frac{d\ln k}{d(1/T)} \] (3)

We can take slope of the line in Fig. 10 and calculate the formal activation energy \( E_a^{\text{slope}} \) as a function of laser intensity. To test whether the thermal picture of this reaction is a valid description, we can compare these formal activation energies with those predicted from the thermal analysis described in I, for which the key result is the modified Tolman theorem, Eq. (17) from I:

\[ E_a^{\text{Tolman}} = \langle E_{\text{diss}} \rangle - \langle E' \rangle + \hbar \nu (q-1) - \hbar \nu \alpha/(1+\alpha), \] (4)

where \( E_a^{\text{Tolman}} \) is the activation energy predicted by the kinetic analysis in the thermal picture, \( \langle E_{\text{diss}} \rangle \) is the average energy of the dissociating molecules, given in I as
\[ <E_{\text{diss}} > = E_T - h\nu \quad \frac{l}{\ln \alpha} + \frac{\alpha}{1-\alpha} \quad (5) \]

which has the value 1.27 eV for this case. \( <E'> \) is the average energy of the thermal population truncated at \( E_T \), \( h\nu (q-1) \) is the average canonical energy of a single vibrational mode at the frequency \( h\nu \) of the IR photons, and \( \alpha \) is the ratio of the thermal population at energy \( E_T \) to the population at \( E_T - h\nu \). We will take the photon energy \( h\nu \) to be 800 cm\(^{-1} \), a value intermediate between the absorbed and emitted photons.

In Table 3 the parameters and results of the thermal analysis are given at several temperatures within the range of the present data. As the table shows, the last two terms in Eq. (4) are indeed small corrections to the basic Tolman theorem. The last two columns of the table compare the activation energies derived from the slope of the Arrhenius plot (Fig. 10) with the values predicted by the modified Tolman theorem. It is seen that these numbers are in quite good agreement.
Table 3

Thermal analysis of data for dissociation rate versus laser intensity.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>I_{laser}(W)</th>
<th>$&lt;E'&gt;$</th>
<th>$h\nu(q-1)$</th>
<th>$h\nu\alpha/(\alpha+1)$</th>
<th>$E_a^{\text{slope}}$(eV)</th>
<th>$E_a^{\text{Tolman}}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>2.0</td>
<td>0.71</td>
<td>0.01</td>
<td>0.04</td>
<td>0.45</td>
<td>0.53</td>
</tr>
<tr>
<td>650</td>
<td>3.3</td>
<td>0.88</td>
<td>0.01</td>
<td>0.05</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>750</td>
<td>4.5</td>
<td>0.98</td>
<td>0.01</td>
<td>0.05</td>
<td>0.27</td>
<td>0.25</td>
</tr>
</tbody>
</table>
FIG. 10. Arrhenius plot of $k_{\text{diss}}$ as a function of temperature. The solid line is an assumed smooth curve through the data which was used to calculate the slopes and $E_a$ slope values as shown in Table 3.
Relation between computer-modeling and thermal treatments.

The computer modelling does not contain any assumptions that would bias the laser-pumped ion population toward a Boltzmann-like distribution, and it should give a good description of the kinetics at all laser intensities. As described in I, theory leads us to expect a Boltzmann distribution, and a valid treatment, at low laser intensities. The good agreement of the observed activation energies with the expectation from the thermal treatment (in the form of Tolman’s theorem) confirms that the present experiments do indeed lie in the regime of laser intensities where the assumptions of the thermal treatment are valid. If the experiment had been done at higher laser intensities the computer modelling should still accurately simulate the kinetics, but the internal energy distribution would no longer be usefully approximated as a Boltzmann distribution.

The observed fact that the Tolman-theorem analysis gives a good fit to the present data confirms that the thermal picture gives a useful description of the dissociation kinetics. On the other hand, the observed fact that the computer-modelled kinetics gives a good fit to the data confirms the assumptions made above about the physical processes involved in the IRMPD dissociation of n-butylbenzene ions.
CONCLUSION

We have examined the IRMPD results for n-butylbenzene ion from two perspectives. First, we have asked whether the observed results conform to the anticipated simple mechanism of slow IRMPD, which we defined by making assumptions about photon absorption, stimulated emission and spontaneous emission processes. The assumed mechanism was embodied in a computer simulation scheme, and the parameters of the simulation were adjusted to fit the observed induction times and dissociation rates. The concept of temperature was introduced in this process only to the extent that the simulation parameters were required to be such that in the absence of laser irradiation the ion population conforms to a Boltzmann distribution at the cell temperature of 375 K. The analysis from this point of view was successful, in the sense that the model mechanism was readily parametrized to give quite good agreement with the observed kinetics. It was concluded that the simple IRMPD mechanism gives a good description of the n-butylbenzene ion dissociation kinetics. However, in chapter VI we will see that this simple mechanism will not be adequate to describe the thermometric data for the infrared multiphoton absorption process. Refinements to our assumptions about infrared photon absorption and emission will be made.

The second perspective was the examination of whether and when the conceptual framework of thermal kinetics provides a useful alternative description of IRMPD kinetics, as the theory described in I had suggested it should do for slow continuous IRMPD. For the
present data, we verified that the Tolman theorem does indeed give the correct relationship between the observed slope of the rate-versus-intensity curve and the dissociation threshold energy. This confirms that the thermal picture gives a valid description of the dissociation kinetics under the conditions of low, continuous laser irradiation and dominant infrared radiative energy relaxation.

In terms of the ultimate goal of determining dissociation thermochemistry from IRMPD data, the present results are promising, but have not given a fully satisfactory solution. The central problem, assigning the internal energy (or temperature) of the ions as a function of laser intensity, still presents a substantial obstacle, whether we use a computer-modeling analysis or a thermal analysis. The present paper showed a route to temperature assignment using the observed induction times combined with the dissociation rates to parameterize the computer-modelled analysis. The assumption that the induction times reflect simple, temperature-independent pumping without bottlenecking appears to be valid for n-butylbenzene ion, and may be justifiable for other large ions, although this question leaves some residual uncertainty in applying this approach to unknown systems. Perhaps more satisfactory is the possibility of using an auxiliary thermometric approach to determine the ion temperatures as a function of laser intensity, followed by a Tolman's theorem analysis of the dissociation rates to extract the dissociation threshold energy. The application of auxiliary thermometry to the case of CO2 laser
pumping of \( n \)-butylbenzene ion will be done in chapter VI.

A final point about the activation energies deserves emphasis. In most situations involving thermal kinetics, the activation energy represents a reasonable estimate of the energy barrier to reaction. However, as is seen at once from Table 3, the activation energies in the present case are only a fraction, 1/4 to 1/3, of the effective barrier \( E_c \), and are less than 1/2 of the true critical energy \( E_0 \) (0.99 eV). This is a result of the special nature of low-pressure IRMPD kinetics, and the consequence is that an analysis such as the Tolman's theorem analysis given here is essential if one wants to relate the observed activation energies to the dissociation thermochemistry.
REFERENCES


14. It was shown directly in Uechi, G.T.; Dunbar, R.C. J. Chem. Phys. 93, 1626, (1990) that the n-butylbenzene ions actually do equilibrate to about 350-375 K in our ICR cell at low pressure.

15. In comparison with other data sets obtained with better thermalized ions, the data set of Table 1 evidently corresponds to incompletely thermalized ions, making the induction times somewhat shorter than in other data sets. Accordingly the computer-simulated curve in Fig. 9 was generated by a set of induction-time simulations in which the ions were assumed to start with 0.25 eV of excess energy at the beginning of laser irradiation. In fitting
this data set to the computer simulations, the W calibration curve of Fig. 5 was appropriately modified to correspond to these revised simulations.

CHAPTER VI

THERMOMETRIC STUDY OF CO$_2$ LASER HEATING AND RADIATIVE COOLING OF N-BUTYLBENZENE IONS
INTRODUCTION

New scientific opportunities for studying slow kinetic processes of isolated molecules have been made available by the ability to trap ions for long periods under essentially collision-free conditions. Among the slow processes whose kinetics are of interest to our group are the absorption of infrared radiation from low-intensity light sources\(^1\), the cooling of collision-free molecules by infrared emission\(^2\)\(^-\)\(^4\)\(^,\)\(^8\), and the slow dissociation of ions by multiphoton infrared absorption\(^5\)\(^,\)\(^6\). Such processes are of interest in the modelling of interstellar photophysics and photochemistry\(^7\), as well as in understanding the behavior of ions in low-pressure ion-trapping mass spectrometers. New techniques generally described as Ion Thermometry\(^2\)\(^-\)\(^4\)\(^,\)\(^8\) offer powerful, but not yet well exploited, experimental approaches to studying these kinetic questions.

Ion Thermometry is the attractive idea of being able to probe the internal energy of an ion at any given time. Our laboratory has developed two particularly effective ways of doing this through photodissociation by a laser pulse: these are the methods of time-resolved photodissociation\(^3\)\(^,\)\(^8\), and competitive photodissociation\(^2\)\(^,\)\(^4\). Both of these have been used for measuring the cooling of initially hot ions. Equally interesting is the possibility of using thermometry to watch the rising ion internal energy during pumping by a laser.

A great many experiments have observed the kinetics of ion dissociation under IR laser irradiation, but thermometry offers the
more powerful possibility of making direct observations of the heating of the molecule when the laser is turned on, as well as determining the internal energy of the ion population after it reaches steady state and undergoes dissociation. In the present study, these possibilities were applied to the n-butylbenzene ion, whose IR dissociation kinetics have previously been explored in some detail by less direct approaches\(^9\); the present results clearly illustrate the deeper and more confident understanding of the photophysical kinetics gained by direct thermometric measurements.

Competitive photodissociation of n-butylbenzene ions has proven to be a successful thermometric tool. The branching ratio of photofragments m/z 91 and 92 as a function of ion internal energy is well established\(^{10}\). The ion internal energy can be probed by inducing dissociation by the absorption of a visible photon and measuring the ratio of photofragments by Fourier-transform ion cyclotron resonance (FT-ICR) spectroscopy.

Three experiments were done in this work. First, the kinetics of n-butylbenzene ion dissociation were observed using IR multiphoton absorption by a low-powered cw-CO\(_2\) laser. Second, the vibrational heating of the ions during the irradiation of the CO\(_2\) laser was monitored thermometrically. Third, once the ions were sufficiently heated the laser was turned off and the rate of vibrational cooling was followed thermometrically to obtain the IR radiative rate of these heated ions.
EXPERIMENTAL

**Instrumentation.** The CO$_2$-laser photodissociation experiment was done on a Fourier-transform ion cyclotron resonance (FT-ICR) spectrometer. The instrument contains a 2.5 cm cubical cell in a magnetic field of 1.4 Tesla and controlled by an IonSpec data system. The experiments were run at 0.8 V trapping potential with all other plates at 0 V. A homebuilt cw-CO$_2$ laser produced light at 940 cm$^{-1}$ with power of up to 10 W. The IR beam entered the instrument through a NaCl window along an axis perpendicular to the magnetic field. The intensity of the CO$_2$ laser was measured on a Coherent Radiation thermopile power meter. The diameter of the IR beam was unfocussed and estimated to be about 4 mm. A Lumenics Nd-YAG pulsed laser pumped a dye laser running Coumarin 440 dye with 355 nm light producing 10 nanosecond visible laser pulses at 440 nm. This visible laser pulse, with a 5 mm diameter, entered the cell along the axis orthogonal to both the magnetic field and the direction of the IR laser beam.

The pressure was measured from the ion pump current, which was calibrated by observing the loss of m/z 78 ions produced by electron impact of n-butylbenzene. This ion is known to be highly reactive and was assumed to react at the ion-molecule collision rate.

**Dissociation.** The dissociation of n-butylbenzene ions by infrared multiphoton absorption has been described in a recent investigation.
The sequence of events for this experiment is the same as in chapter V. Ions were produced by electron impact ionization of nominal electron energy, 12.5 eV, and allowed to thermalize during a 2 s cooling period at 9×10^{-9} torr. All fragment ions, m/z 91 and 92, were ejected from the cell immediately after electron impact ionization and at the end of the cooling period assuring complete isolation of parent ions. IR multiphoton absorption was initiated by turning on the cw-CO$_2$ laser. Dissociation was monitored by a broad band detection of both parent ions, m/z 134, and fragment ions, m/z 92 produced by the irradiation of the cw-CO$_2$ laser.

**Ion Thermometry.** The use of the branching ratio of n-butylbenzene ion's photoproducts has also been previously described in chapter III$^4$. Specific to this work, the source of visible photons for competitive dissociation was a Lumonics Nd-YAG pumped dye laser. The dye used was Exciton Coumarin 440 giving 10 nanosecond pulses of energy between 5 to 10 mJ. These short pulses allowed better time resolution in probing the dynamics of IR multiphoton absorption and vibrational cooling. Laser power was kept at a level that produced less than ten percent total dissociation. This was to assure the production of m/z 91 ions was from parent ions directly and not from the subsequent photodissociation of m/z 92 ions. Fig. 1 shows the sequence of pulses in which competitive photodissociation was used to probe the photochemistry induced by cw-CO$_2$ laser irradiation.

Since this thermometric technique depends on the branching
FIG. 1. Sequence of pulses using competitive photodissociation to thermometrically probe the heating of n-butylbenzene ions by continuous irradiation from a cw-CO$_2$ laser.
PULSE SEQUENCE

2 s trapping for thermalization

Internal energy probe delay
0 - 5 s

ELECTRON BEAM
EJECTION M/Z 91 & 92
EJECTION M/Z 91 & 92
QUENCH

440 nm
DETECT

0.4 - 1 s

cw-CO2 LASER
10.6 um 1-3 W

TIME
ratio of m/z 91 and 92, confidence in acquiring accurate peak ratios was needed. We have already discussed this in chapter IV. Briefly, the relative peak heights of close lying mass doublets are very sensitive to the r.f. excitation amplitude of a chirp waveform. The accuracy of the measured peak ratio is not always assured. The mass discrimination has been attributed to space charge effects and was minimized by the use of impulse excitation at low ion densities.

**Heating Curves.** Infrared multiphoton absorption was observed by monitoring the internal energy of the n-butylbenzene ions during the irradiation by the cw-CO\textsubscript{2} laser. Once the cw-CO\textsubscript{2} laser was turned on the average internal energy of the ions was probed by detecting the ratio of the fragment ions due to the absorption of 440 nm photons. To obtain an accurate branching ratio all fragment ions must be produced by the absorption of the visible photons. Any fragment ions remaining in the cell either due to an incomplete ejection of earlier pulses or those produced by IR multiphoton dissociation were ejected before the visible laser pulse. Detection was done immediately after photodissociation. This sequence of three events (ejection, visible laser pulse, and detection) took place within 10 ms. Since this was fast on the time scale of the absorption of the infrared photons, the CO\textsubscript{2} laser beam did not have to be shut off while the average internal energy was probed.

**Cooling Curves.** Once the ions were heated to an average internal
energy of approximately 0.8 eV, the CO₂ laser was turned off. The cooling of these hot ions was monitored by again probing the internal energy obtained by competitive photodissociation from the absorption of 440 nm photons.

The cooling of the internal energy of the ions occurs by both collisional and radiative processes. In order to determine the IR radiative rate, cooling curves were obtained at varying pressures. By extrapolating to zero pressure the collisional contribution to cooling was removed giving the IR radiative rate.
RESULTS

Typical light off and light on spectra of m/z 92 ions produced by IR multiphoton absorption are shown in Figs. 2a,b. Plotting the peak height of the parent ion, m/z 134, for increasing irradiation periods by the CO₂ laser gives a dissociation curve seen on Fig. 3. Dissociation was only carried out to 80 percent parent ion abundance. By using a logarithmic axis, the rate of dissociation was obtained from the slope of the linear portion of the curve. By extrapolating this linear region back to 100 percent ion abundance the induction period for IR multiphoton absorption is determined. This is the period of time for the ions starting at thermal energy to heat up to the dissociation threshold energy by the sequential absorption of IR photons.

Figs. 4a,b are the spectra showing the photofragment ions produced by competitive photodissociation after the irradiation by the 440 nm laser pulse. It is the branching ratio of these fragment ions that probes the average internal energy of the parent n-butylbenzene ion cloud.

The calibration curve that allows one to convert the branching ratio into the average ion internal energy is the same one used in chapter III. The branching ratio resulting from competitive photodissociation corresponds to the energy of the absorbed photon plus the internal energy of the excited ion just prior to photon absorption. The internal energies graphed in Figs. 6, and 7a-d do not include the energy of the 440 nm photon (2.82 eV).

Using the thermometric technique of competitive photodissoc-
FIG. 2. Spectra of m/z 92 production by infrared multiphoton dissociation, a) CO$_2$ laser light off, b) CO$_2$ laser light on.
FIG. 3. Plot of the dissociation of n-butylbenzene ions with increasing irradiation of CO₂ laser light.
DISOCIATION BY INFRARED ABSORPTION

PERCENTAGE REMAINING

CO₂ LASER ON (ms)
FIG. 4. Spectra of the competitive photodissociation products used for ion thermometry, a) broad band detection of parent and photoproducts, b) photoproducts only.
iation to probe the internal energy of the ions during CO\textsubscript{2} laser irradiation, Fig. 5 shows the average ion internal energy increasing until a steady state value is reached. By overlaying Figs. 3 and 5, Fig. 6 shows the heating of the n-butylbenzene ions in relation to the IR multiphoton dissociation. The left axis corresponding to the solid circles displays the rise in parent ion internal energy as the ions sequentially absorb IR photons. The right axis corresponding to the solid triangles shows the abundance of the parent ions during dissociation by IR multiphoton absorption. What is striking is that the induction period, determined by the IR multiphoton dissociation curve, precisely corresponds to the time it takes the ions to reach the steady state energy seen on the heating curve.

Figs. 7 a-d is the set of curves showing the internal energy relaxation curve of n-butylbenzene ions at 1x10\textsuperscript{-8}, 3x10\textsuperscript{-8}, 1x10\textsuperscript{-7}, and 3x10\textsuperscript{-7} torr. Since collisions can contribute to the cooling rate even at the lowest pressure studied the radiative rate was obtained by extrapolating to zero pressure. Fig. 8 is the graphical analysis of the collisional contribution to vibrational cooling of these n-butylbenzene ions heated by the cw-CO\textsubscript{2} laser. The data obtained in our previous investigation are also included in the analysis. With an initial excess internal energy of 0.50 eV the infrared radiative rate is 1.1 s\textsuperscript{-1}.

Although the ions in this work were prepared with 0.2 eV more internal energy than the ions studied in our previous work, due to the high heat capacity of n-butylbenzene this corresponds to an
FIG. 5. Thermometric data showing the increase in internal energy during cw-CO₂ laser irradiation.
HEATING BY INFRARED ABSORPTION

ION INTERNAL ENERGY (eV)

CO$_2$ LASER ON (ms)
FIG 6. An overlay of the heating curve, Fig 5, with the dissociation curve, Fig 3.
FIG. 7. Thermometric cooling curves at a) $1 \times 10^{-8}$ Torr, b) $3 \times 10^{-8}$ Torr, c) $1 \times 10^{-7}$ Torr, d) $3 \times 10^{-7}$ Torr.
COOLING CURVE AT 1X10^-8 TORR

INTERNAL ENERGY (eV)

COOLING TIME (s)
COOLING CURVE AT 3×10⁻⁸ TORR

INTERNAL ENERGY (eV)

COOLING TIME (s)
COOLING CURVE AT 1.5x10^{-7} TORR

INTERNAL ENERGY (eV)

COOLING TIME (s)
COOLING CURVE AT 3X10^{-7} TORR

INTERNAL ENERGY (eV)

COOLING TIME (s)
increase of only 70 K. The graphical analysis in fig. 8 shows that the points from this study and those from chapter III all fall on the same line within experimental error indicating a common infrared radiative rate.
FIG. 8. Graphical analysis for the pressure dependence of the cooling rate constants.
Pressure dependence of $k_{\text{cool}}$
MODELLING AND MASTER-EQUATION SIMULATIONS

Our previous kinetic analysis of the CO$_2$-laser multiphoton dissociation (IRMPD) of n-butylbenzene ion (chapter V) was carried out based on the observed induction times and dissociation rate constants as a function of laser power. The rates of ion heating and cooling were derived indirectly through modelling, and the IRMPD rates were shown to be well treated within a thermal approximation, involving Arrhenius plotting of the rate data. The present experiments are a major step forward in developing understanding of this system, since they make available for the first time direct information on the heating and cooling rates. It is thus interesting to revisit the questions of how the kinetics should be understood and modelled in terms of the microscopic photophysical and photochemical rates.

The previous analysis of IRMPD of n-butylbenzene ion (chapter V and references 1 and 8) was based on the simplest possible picture of the up-pumping and relaxation properties. The picture, which we may term the simple harmonic photophysical model, takes the molecule as a collection of weakly coupled harmonic oscillators, among which the internal energy flows randomly and on a time scale faster than all other relevant time scales. Many of the modes (reservoir modes) are infrared inactive, neither absorbing nor radiating significant IR radiation. Some modes are IR active, radiating energy as harmonic radiators according to their IR oscillator strengths, and according to their degree of
excitation above their ground states. Some of these radiator modes have infrared absorption intensity at the IR laser frequency, and undergo absorption and induced emission of IR photons, again according to the harmonic oscillator rules. Previous work, in particular chapter 5 and reference 8, described in some detail the modelling of IR laser-pumping and radiative cooling kinetics with this simple harmonic photophysical picture (simple IRMPD mechanism).

In our previous modelling of n-butylbenzene ion IRMPD, this picture was used. In particular, radiative relaxation was assumed to occur through a single harmonic radiator mode, and laser pumping was assumed to proceed with a constant photon absorption cross section independent of internal energy. Since it was found possible to fit all the previous data within this simplest picture, there was no reason to introduce more elaborate assumptions. However, the more detailed picture given by the present experiment is no longer entirely compatible with this first set of assumptions, which must be refined.

The nature of the problem is as follows. The relaxation curve of Fig. 7a gives the absolute rate of radiative cooling of the ion, while the initial portion of the pumping curve of Fig. 6 gives the absolute rate of photon absorption at early times before relaxation and dissociation become important. If the simple harmonic photophysical model is used with these known rates, simulation predicts that the ions will rise to high energies much too fast for agreement with experiment. This model predicts an induction time which is too short and a dissociation rate which is too large. For
instance, using parameters which match Fig. 7a and the initial part of the heating curve of Fig. 6, this model predicts that more than half of the ions will have dissociated after 200 ms, whereas experiment shows that only 6% of them have actually dissociated at this time.

The present experiments thus tell us that at high internal energies either the relaxation is faster, or the up-pumping is slower, than was assumed in the simple harmonic model. Agreement with experiment can be achieved by modifying the photophysical model in either of these ways.

**Modified photon absorption kinetics:** A few simple models for modifying the photon absorption rate curve were explored. It was found that agreement with experiment requires up-pumping in the 0.2-0.6 eV region to be two or three times faster than in the 0.6 to 1.2 eV region, but the curve cannot drop off too steeply in the dissociation region around 1.25 eV or the dissociation reaction is suppressed entirely. A straightforward two-rate assumption worked as well as anything else: The absorption strength of the laser-absorbing molecular vibration was assigned a constant value for internal energies up to 0.5 eV, rolled off smoothly from 0.5 to 0.7 eV, and had a constant value 3 times smaller for energies above 0.7 eV. The simulations using this absorption curve (and the corresponding induced emission curve), along with the harmonic-oscillator model for the spontaneous emission rates, can be designated Model I.
**Modified relaxation kinetics:** There are strong constraints on modifying the radiative rate at high internal energies, because the observed cooling curve (Fig. 7a) shows that the harmonic model is obeyed well up to internal energies of 0.7-0.8 eV. In order to satisfy this constraint, and also produce agreement with the data of Fig. 6 for up-pumping and dissociation rates, the radiative rate must climb very steeply above 0.7 eV. The simulation was successful using an ad-hoc radiative rate curve which followed the harmonic model up to 0.6 eV, and then curved rapidly upward, reaching values more than 10 times the harmonic model in the dissociation region. The simulations using this radiative rate curve, while retaining the harmonic model for absorption and induced emission, can be designated Model II.

The calculation of the absorption and induced emission strengths for the harmonic oscillator model as a function of ion internal energy (assuming the absorbing mode to be at the laser frequency of 940 cm\(^{-1}\)) has been described in chapter V and reference 1. Similarly, the calculation of the rate of spontaneous emission from a single emitting harmonic oscillator (taken to be at 705 cm\(^{-1}\)) has been described. Table 1 shows the absorption, induced emission and spontaneous emission rates used in the present master-equation modelling for a number of ion internal energies.

While previous modelling of this system assumed a single dissociation threshold energy of about 1.25 eV, the present work modelled the dissociation more realistically using a set of dissociation rates as a function of internal energy. The
unimolecular dissociation rates were measured by Baer et al. for ion internal energies down to 1.73 eV (where the measured value was 7.5x10^4 s^{-1}. We extrapolated the rate energy curve of Baer et al. down to the lower energies required in this work using an RRKM calculation with a critical energy E_0 of 0.99 eV. The dissociation rates used are shown in Table 1. Simulation using this realistic rate-energy curve for the dissociation gave substantially better agreement with the data than could be obtained with any comparable simulation using a fixed dissociation threshold.

The solution of the coarse energy grained master equation to obtain the kinetics of low-intensity IR pumping, cooling and dissociation has been described in detail (chapter V and references 1 and 8). Both random-walk kinetic simulations and matrix-algebra solutions of the master equation have been successful, and the latter approach was used here. The J matrix (transport matrix) is written which includes the rate constants for up-pumping, stimulated emission and spontaneous emission between energy levels, along with dissociative loss rates from the higher energy levels. It describes the time evolution of the ion population by the master equation

\[
\frac{dN}{dt} = -J \cdot N
\]

where N is the vector for the occupation of energy levels by the ion population. J is diagonalized, and the time evolution of the system is written in terms of its eigenvalues and eigenfunctions. An energy level spacing of 235 cm^{-1} was used. The laser photon
energy at 940 cm\(^{-1}\) corresponded to a change of 4 energy levels. Radiative relaxation was assumed to occur at 705 cm\(^{-1}\) (a decrease of 3 energy levels.) The coefficients were derived from the simple harmonic photophysical model, and then modified as discussed above, to give the J matrix contributions illustrated in Table 1.

For illustration, results are shown in the Figures for the Model I simulations. Fig. 7a shows the simulated cooling curve, and Fig. 6 shows the simulated heating curve and the curve for the loss of ions by dissociation. The fits to the experimental results are entirely satisfactory, and while they might be improved by further refinement of parameters, this would serve no useful purpose.

Fig. 9 shows the simulated internal energy distributions as the ion population is pumped from the initial thermal distribution up to dissociation. At 0 ms irradiation time, the distribution is that of the 350 K population, with an average energy of 0.3 eV. When laser pumping begins, the distribution at first broadens and moves rapidly up the energy ladder (as indicated at 24 ms). As the ions rise in energy relaxation speeds up and pumping slows down, and the population distribution begins to bunch up and narrow (60 ms). By 360 ms the population has settled into the steady state distribution with an average energy of 0.8 eV, approximating a thermal distribution at 580 K, and dissociation gradually depletes the population. As seen at 720 ms, the population decays steadily by dissociation at long times, but the distribution does not change shape.
FIG 9. Simulated time progress of the internal energy distributions during irradiation by the cw-CO$_2$ laser.
N-Butylbenzene Ion Heating Curves

Fraction of Ions

Internal Energy (eV)
DISCUSSION

Infrared Multiphoton Absorption. Three physical processes occur during the irradiation of the trapped ions by the cw-CO₂ laser. First, photon absorption increases the ion internal energy. Second, infrared photon emission stimulated by the laser radiation reduces the ion internal energy. Third, spontaneous emission also reduces the ion internal energy. The trapped ions are initially at thermal equilibrium with the walls of the cell. Once the CO₂ laser is turned on the average internal energy of the total ion population increases until reaching steady state between photon absorption and photon emission. The steady state energy distribution for the ion population at the low laser intensities used approximates a Boltzmann distribution with a truncated high energy tail due to the dissociation pathway.

The lowest energy dissociation pathway of n-butylbenzene is the fragmentation to m/z 92. This results in diminishing the total number of ions as the ions gain enough energy to dissociate. When the ion cloud has reached equilibrium with the IR laser radiation, the average internal energy of the ion population remains constant while the reaction channel slowly depletes the total number of ions.

The master-equation modelling described above yields the time progression of the actual distribution of ion internal energies during the irradiation by the cw-CO₂ laser, as displayed in Fig. 12. After initial heating is accomplished (the induction time), the ions remain at the laser-produced steady-state temperature
while the dissociation pathway slowly depletes the population until the reaction is complete. The observed up-pumping kinetics shown in Fig. 6 are completely in accord with this picture.

**Infrared Radiative Cooling.** For a polyatomic ion with a number of normal modes, some IR active and some inactive, the rate of cooling is a complicated function of the ion internal energy (within the simple harmonic photophysical picture). However, over a limited energy range, and given some reasonable assumptions about the distribution of mode frequencies (Case iii of Section III in Ref. 12), it can be true to an excellent approximation that the rate of radiative energy loss is propotional to the internal energy, so that the internal energy decays exponentially in time. Previous work in chapter III has suggested that this approximation is good for n-butylbenzene ion in the 0.6 to 0.3 eV region.

The cooling curve of Fig. 6 allows us to extend this conclusion, since the energy range in this experiment is wider (0.8 to 0.3 eV). An exponential cooling curve gives an excellent fit to these data, and there is no indication of faster relaxation at higher energy. The relaxation rate fitted to Fig. 6 is somewhat faster than that fitted to the relaxation at the same pressure in chapter III (1.1 s\(^{-1}\) versus 0.8 s\(^{-1}\)) but this difference is not experimentally significant, and the two studies are concordant.

One of the conditions leading to approximate exponential cooling, as noted above, is that the infrared emission comes from only one active normal mode (or from several modes in the same
frequency region.) The low frequency ring modes in n-butylbenzene are populated while the high frequency CH stretching modes are frozen out at the temperatures studied. At the internal temperatures relevant to this work (below 700 K), we expect harmonic behavior of the active ring modes to be quite well followed. N-butylbenzene contains 66 vibrational modes where the majority are infrared inactive modes that contribute to the heat capacity of the molecule. Anharmonic behavior is typically only expected for modes in a very highly excited state. Even near dissociation around 2 eV, the amount of energy typically tied up in any one mode is small, and even at the highest internal energies less than half the ions will have even one quantum of excitation in a 700 cm\(^{-1}\) mode at any given time. Given these conditions the simple harmonic model predicts the behavior for photon emission well.

**Kinetic Modelling.** The master-equation simulations with both photophysical models gave similar agreement with the data. Considering the number of adjusted quantities it is not surprising that the data could be fitted, but the successful fit does substantiate the overall ability of the master equation to model the pumping and relaxation processes in this system.

It is easy to see how the photon absorption rate can drop off by a factor of 2 or 3 at higher internal energies as required by Model I. Assuming the CO\(_2\) laser frequency to lie near an IR absorption maximum for the ion, heating of the ion can reduce the photon absorption cross section by shifting and/or broadening the
absorption peak to reduce the intensity at the laser frequency.

On the other hand, it is also possible to justify at least speculatively the rapidly rising radiative rates at higher internal energies required by Model II. The first excited electronic state of the ion lies of the order of 0.5 eV above the ground state (as indicated by the splitting of the 9 eV feature in the photoelectron spectrum), which is the energy region where Model II requires the IR-radiative relaxation to begin climbing. Although it is forbidden in benzene ion, the optical transition between these electronic states is weakly allowed in this case, due to symmetry breaking by the butyl substituent (approximate C$_2$V symmetry). Occupation of this excited electronic state is strongly disfavored by the statistics of molecular state densities relative to the ground electronic state. Nevertheless, relaxation by electronic fluorescence might be so efficient for those ions which did cross over to this state by reverse internal conversion, that this relaxation mechanism could conceivably give the large radiative rates required by Model II. This mechanism, while thus conceivable, does not seem quantitatively attractive, and we prefer the approach of Model I for reconciling the simulations with experiment.

The revision indicated here in the photophysical kinetic parameters has some significance for the analysis of chapter V and Ref. 8. The change in up-pumping rates embodied in Model I will have at most a minor effect on the thermal analysis outlined in
chapter V and Ref. 6, because the up-pumping rate curve is unchanged in the high-energy region which is important for the validity of the thermal approach. Given Model I, some readjustment of the detailed fit of chapter V will be needed because the induction times are somewhat smaller than in the simple harmonic photophysical model, but the intensity dependence of the dissociation rate, and the Arrhenius plot relating the results to the activation energy, should be essentially unchanged. If, on the other hand, the relaxation curve is modified as in Model II, the assumptions made in the thermal analysis are no longer reasonable approximations, and a more extensive reconsideration of the analysis of chapter V and Ref. 6 would be necessary.
CONCLUSIONS

Heating by infrared photon absorption, cooling by infrared photon emission, and dissociation by multiphoton absorption have all been studied in the FT-ICR ion trap. The heating, cooling and dissociation kinetics observed in this experiment showed the time dependent behavior expected. However our initial intent laid out in chapter V to obtain dissociation thermochemistry by the thermal analysis of the cw IRMPD data appears to be unsuccessful. The major surprise was that the simple harmonic photophysical picture (simple IRMPD mechanism) was unable to account quantitatively for the relative rates of these processes. The most likely explanation was considered to be an "inverse bottleneck" such that the rate of laser up-pumping drops off by a factor of two or three at high internal energies.

In chapter V our ability to determine the ion temperatures as a function of laser intensities, was based on the assumption of the absence of a bottleneck during laser up-pumping. Since an inverse bottleneck for n-butylbenzene is suspected a generalized thermal analysis for the cw-IRMPD kinetics of various gas-phase ions does not seem to be feasible. We would have liked to have applied a thermal analysis to the cw-IRMPD kinetics of various ions. However it is reasonable to assume bottlenecks to be found in other ions.

Although dissociation thermochemistry could not be obtained from the cw-IRMPD data, the thermometric data provided valuable information on the infrared photophysical processes of laser up-pumping and radiative cooling. First, from the analysis of the
thermometric data an "inverse bottleneck" has been suspected. Ions as large as n-butylbenzene at room temperature are expected to be in the quasicontinuum where incoherent pumping of infrared ions take place. One would not expect a bottleneck under these conditions but the sequential absorption of photons. However for n-butylbenzene this was not the case. Second, the thermometric study of radiative cooling showed that the exponential decay of internal energy occurred at energies higher than those studied in chapter III. This gives further validity for the simple harmonic photophysical model of infrared photon emission from polyatomic ions.\textsuperscript{12}
Rates from the Master Equation J Matrix (s\(^{-1}\))

<table>
<thead>
<tr>
<th>Internal Energy (eV)</th>
<th>Radiate (at 705 cm(^{-1}))</th>
<th>Pump (at 940 cm(^{-1}))</th>
<th>Stimulated Emission (at 940 cm(^{-1}))</th>
<th>Dissociate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model I(^a)</td>
<td>II</td>
<td>Model I</td>
<td>II(^a)</td>
</tr>
<tr>
<td>.14</td>
<td>1.7</td>
<td>0.8</td>
<td>52</td>
<td>38</td>
</tr>
<tr>
<td>.29</td>
<td>5</td>
<td>2.4</td>
<td>52</td>
<td>38</td>
</tr>
<tr>
<td>.44</td>
<td>8</td>
<td>4</td>
<td>53</td>
<td>39</td>
</tr>
<tr>
<td>.58</td>
<td>12</td>
<td>6</td>
<td>22</td>
<td>40</td>
</tr>
<tr>
<td>.73</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>41</td>
</tr>
<tr>
<td>.87</td>
<td>18</td>
<td>58</td>
<td>19</td>
<td>42</td>
</tr>
<tr>
<td>1.02</td>
<td>22</td>
<td>125</td>
<td>19</td>
<td>43</td>
</tr>
<tr>
<td>1.08</td>
<td>23</td>
<td>165</td>
<td>19</td>
<td>43</td>
</tr>
<tr>
<td>1.14</td>
<td>24</td>
<td>215</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>1.19</td>
<td>26</td>
<td>275</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>1.25</td>
<td>27</td>
<td>350</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>1.31</td>
<td>28</td>
<td>440</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>1.37</td>
<td>29</td>
<td>540</td>
<td>20</td>
<td>45</td>
</tr>
</tbody>
</table>

\(^a\)For reference, note that these columns show the matrix element contributions from the simple harmonic photophysical model, before the ad hoc alterations to fit the experimental results.
Table 2.
Relaxation results for IR-laser excited ions

<table>
<thead>
<tr>
<th>Initial energy (eV)</th>
<th>Final thermal energy (eV)</th>
<th>Radiative relaxation rate (s⁻¹)</th>
<th>Collisional relaxation rate (collisions⁻¹)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.30</td>
<td>0.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

ᵃAssuming a collision rate constant of 1.4x10⁻⁹ cc molecule⁻¹ s⁻¹.
REFERENCES


8. Faulk, J.D.; Dunbar, R.C. submitted for publication.


CHAPTER VII

RADIATIVE ASSOCIATION REACTIONS OF SILICON CATIONS

WITH BENZENE, NAPHTHALENE, AND ANTHRACENE
INTRODUCTION

Radiative association reactions are a class of reactions where the collision complex of an ion and a neutral molecule in the gas phase is stabilized by the emission of a photon. Association reactions have been observed under very low pressure conditions (on the order of a few collisions per second) where the stabilization by an inelastic third body collision is unlikely. These reactions have been attributed to the emission of an infrared photon. Once again FT-ICR provides the essentially collisionless conditions to study a class of reactions which are governed by the rate of infrared photon emission.

Interest in gas phase ion chemistry has been prompted by the field of astrochemistry. To interpret the vast amounts of spectra obtained from satellites and telescopes very elaborate models containing numerous chemical reactions have been developed\(^1,2\). Many of the reactions used in these models have not yet been well studied in the laboratory, so many reaction rates as well as the actual chemistry that takes place are not well known. Studies in high pressure selected-ion flow tube (SIFT) mass spectrometers have been done to investigate the kinetics of these gas phase reactions\(^3-9\). However the actual conditions in the interstellar medium are at very low molecular densities and the chemistry that takes place may not be similar to that seen under the high pressure (0.35 Torr of Helium buffer gas) conditions in a SIFT mass spectrometer. The low pressure conditions that one is able to obtain in a Fourier
transform ion cyclotron resonance (FT-ICR) ion trap spectrometer (10^{-9} - 10^{-8} Torr) may be more suited to determine kinetic data applicable to the interstellar chemistry.

The abundance of silicon is known to be large in interstellar clouds. SiO^{10} is easily detected and at least one model containing 300 gas phase reactions\(^1\) has been developed to account for the silicon chemistry in these clouds. Spectra from nebulae have suggested the existence of polycyclic aromatic hydrocarbon (PAH) molecules in these interstellar sources\(^{11-13}\). To investigate the chemistry that may be occurring between silicon ions and the PAH molecules we studied the gas phase reactions between silicon ions and benzene, naphthalene, and anthracene.
EXPERIMENTAL

A pulsed TEA-CO₂ laser was focussed on a silicon wafer attached to the tip of the sample autoprobe, to produce singly charged silicon ions by laser desorption. Silicon ions were easily and reproducibly produced at low laser energies of 5 - 10 mJ/pulse after "cleaning" the silicon surface by repetitive CO₂ laser irradiation at higher energies to remove K⁺ ions. Ground state Si⁺(²P) ions were assured since no reaction was observed with deuterium, which has been reported to scavenge metastable Si⁺(⁴P) ions.

The ions were trapped in the source region of the dual cell in the Extrel FT/MS 200 at 0.4 - 0.6 V for periods ranging from 25 ms to 5 s. The association reactions were studied by observing the time evolution of Si⁺ (m/z 28) depletion and product ion formation. Benzene and napthalene were introduced into the mass spectrometer through the sample batch inlet. A constant pressure of neutral reagent molecules was achieved by maintaining the pressure in the batch inlet. As the batch inlet became depleted of sample the valve to the sample vial had to be continually opened to restore the initial pressure. This may have produced fluctuations in the pressure in the cell resulting a margin of error in the pressure readings. Anthracene was introduced into the cell simply by placing a sample adjacent to the silicon wafer on the tip of the sample autoprobe. The pressure readings from the ion guages were calibrated by a proton transfer between protonated methane ions and the reagent neutral molecules. This was done after the time
evolution of the silicon ions was obtained.

Collision induced dissociation experiments were done on the product ions to probe their structures. After allowing the silicon ions to react, the product ion of interest was isolated by selective ejection of all other ions. Argon gas was introduced into the cell by a pulsed valve and was used as a collision gas. The isolated product ions were excited to higher kinetic energies and allowed to collide with the argon gas to induce dissociation.

Since the silicon ions and the silicon containing product ions were reactive to water, great precautions were taken to assure that the argon gas was sufficiently dry. This was done by a liquid nitrogen trap placed between the container of the argon and the sample batch inlet. A simple electron impact spectrum of the argon gas did not show the presence of the water vapor. The amount of water was detected by exposing Si+ ions to the argon and detecting the fraction of SiOH+ ions produced. Although completely dry argon gas was never obtained conditions were obtained where less than 10 percent of the Si+ ions reacted with water.
RESULTS

Association reactions: The reaction scheme for silicon ion, Si⁺, with an aromatic hydrocarbon, ArH is as follows:

\[
\begin{align*}
\text{Si}^+ + \text{ArH} & \rightarrow \text{SiArH}^{2+} \rightarrow \text{SiArH}^+ + \text{hv} \quad (i) \\
& \rightarrow \text{SiAr}^+ + \text{H} \quad (ii) \\
& \rightarrow \text{ArH}^+ + \text{Si} \quad (iii)
\end{align*}
\]

Ground state silicon ions were all found to be reactive to the three aromatic neutral molecules. Three types of reactions were found to take place: radiative association Eq. (i), combination with H loss Eq. (ii), and charge transfer Eq. (iii). The product ions with their relative abundances are listed as follows:

\[
\begin{align*}
\text{Si}^+ + \text{C}_6\text{H}_6 & \rightarrow \text{SiC}_6\text{H}_6^+ \quad (m/z\ 106) \quad 15\% \quad (1) \\
& \rightarrow \text{SiC}_6\text{H}_5^+ \quad (m/z\ 105) + \text{H} \quad 85\% \quad (2)
\end{align*}
\]

\[
\begin{align*}
\text{Si}^+ + \text{C}_{10}\text{H}_8 & \rightarrow \text{SiC}_{10}\text{H}_8^+ \quad (m/z\ 156) \quad 20\% \quad (3) \\
& \rightarrow \text{SiC}_{10}\text{H}_7^+ \quad (m/z\ 155) + \text{H} \quad 37\% \quad (4) \\
& \rightarrow \text{C}_{10}\text{H}_8^+ \quad (m/z\ 128) + \text{Si} \quad 43\% \quad (5)
\end{align*}
\]

\[
\begin{align*}
\text{Si}^+ + \text{C}_{14}\text{H}_{10} & \rightarrow \text{SiC}_{14}\text{H}_{10}^+ \quad (m/z\ 206) \quad 35\% \quad (6) \\
& \rightarrow \text{C}_{14}\text{H}_{10}^+ \quad (m/z\ 178) + \text{Si} \quad 65\% \quad (7)
\end{align*}
\]

Collision induced dissociation (CID). The structures of the adduct
ions were probed by observing the fragmentation pattern produced by CID.

Benzene adduct:

\[ \text{SiC}_6\text{H}_5^+ \text{ (m/z 105)} \rightarrow \text{SiC}_2\text{H}^+ \text{ (m/z 53)} + \text{C}_4\text{H}_4 \]  
\[ (8) \]

Napthalene adducts:

\[ \text{SiC}_{10}\text{H}_8^+ \text{ (m/z 156)} \rightarrow \text{SiC}_{10}\text{H}_7^+ \text{ (m/z 155)} + \text{H} \]  
\[ (9) \]
\[ \text{SiC}_{10}\text{H}_7^+ \text{ (m/z 155)} \rightarrow \text{SiC}_8\text{H}_5^+ \text{ (m/z 129)} + \text{C}_2\text{H}_2 \]  
\[ (10) \]

Anthracene adduct:

\[ \text{SiC}_{14}\text{H}_{10}^+ \text{ (m/z 206)} \rightarrow \text{SiC}_{14}\text{H}_9^+ \text{ (m/z 205)} + \text{H} \]  
\[ (11) \]
\[ \rightarrow \text{SiC}_{12}\text{H}_8^+ \text{ (m/z 180)} + \text{C}_2\text{H}_2 \]  
\[ (12) \]
\[ \rightarrow \text{Si}^+ \text{ (m/z 28)} + \text{C}_{14}\text{H}_{10} \]  
\[ (13) \]
\[ \rightarrow \text{C}_{14}\text{H}_{10}^+ \text{ (m/z 178)} + \text{Si} \]  
\[ (14) \]

One should note the common features about the CID products. First, the SiArH\(^+\) adduct ions of napthalene and anthracene both lost hydrogen, producing the SiAr\(^+\) ions. Second, the SiAr\(^+\) ions of naphthalene and anthracene lost acetylene while SiC\(_6\)H\(_5\)^+ produced SiC\(_2\)H\(^+\) which may have a structure similar to acetylene. The anthracene adduct ion was unique in producing the Si\(^+\) precursor ion and the charge transfer product, anthracene ion.
DISCUSSION

Our first aim in this chapter was to study the radiative association reactions between ground state Si\(^+\) ions and neutral aromatic hydrocarbons. All three aromatic molecules formed the association product ions, SiArH\(^+\) (where ArH is the neutral aromatic hydrocarbon molecule), as seen in Eqs. (1), (3), and (6). The reactions were done at pressures less than 3x10\(^{-8}\) Torr at which ion-neutral collisions are about one per second. The association rates are on the order of the collision rate. Any contribution by collisional stabilization should be minimal since a third body collision is very unlikely at this pressure. Infrared radiative stabilization is the only reasonable mechanism for the association reaction. These low pressure conditions mimic those found in the interstellar clouds where molecular densities are low. Hydrogen gas has the highest density at approximately 10\(^4\) cm\(^{-3}\), but even at this density the rate of collisions experienced by ions is on the order of one per day.

Thermochemistry.

A thermochemical analysis is needed to predict the structures of the adduct ions as well as to interpret the CID experiments. Unfortunately a complete listing of heats of formation and bond energies is not available for all ions produced in this study. The information that is available will be used to draw reasonable conclusions.
First, the binding energies for weakly bound adduct ions will be considered. These ions have the silicon atom $\pi$-bonded to the aromatic ring. The current theoretical understanding for radiative association complexes allows one to estimate lower bounds for binding energies\textsuperscript{19}. The values given below are estimates of the minimum binding energy that would be needed to give a stabilized association product for one out of a hundred collisions.

\begin{center}
\begin{tabular}{lc}
\textbf{Ions} & \textbf{Predicted Binding Energy} \\
\text{SiC}_6\text{H}_6^+ & 2.2 \text{ eV} \\
\text{SiC}_{10}\text{H}_8^+ & 1.4 \text{ eV} \\
\text{SiC}_{14}\text{H}_{10}^+ & 1.2 \text{ eV} \\
\end{tabular}
\end{center}

Second, the other structure for the adduct ions that will be considered is a $\sigma$-bonded structure where the silicon ion inserts into the C-H bond of the aromatic ring. The bond dissociation energies for Si$^+\cdot\text{H}$ and Si$^+\cdot\text{CH}_2$ were found to be 3.27 and 4.51 eV respectively\textsuperscript{14,15} from a study of Si$^+$ with methane and ethane. The bond dissociation energy for C-H in benzene neutrals is 4.78 eV\textsuperscript{20}. Using the thermochemical information given here we can estimate an upper bound to the exothermicity of Eq. (i).

\[
\Delta H = D^0(\text{Si}^+\cdot\text{H}) + D^0(\text{Si}^+\cdot\text{C}) - D^0(\text{Ar}\cdot\text{H}) \\
= 3.27 \text{ eV} + 4.51 \text{ eV} - 4.78 \text{ eV} \\
= 3.0 \text{ eV}
\]
Two new bonds, the Si\(^+\)-H and the Si\(^+\)-C bonds, are formed while the C-H bond of the aromatic ring is broken (the C-H bond energy is assumed to be similar for benzene, naphthalene and anthracene). This energy is 0.8 eV more stable than the values listed as "predicted binding energies". Under conditions where the association reaction favors the thermodynamically more stable complex we would expect the \(\sigma\)-bonded structure to be produced rather than the weakly bound \(\pi\)-bonded structure.

The fragmentation of the adduct ions seen in the CID experiments appears to be similar to the fragmentation of aromatic ions. The photodissociation of benzene ions has been studied giving the following activation energy values\(^\text{16}\):

\[
\begin{align*}
\text{C}_6\text{H}_6^+ & \quad \rightarrow \quad \text{C}_6\text{H}_5^+ + \text{H} & 3.65 \text{ eV} & \quad (15) \\
\rightarrow & \quad \text{C}_6\text{H}_4^+ + \text{H}_2 & 3.74 \text{ eV} & \quad (16) \\
\rightarrow & \quad \text{C}_6\text{H}_3^+ + \text{C}_2\text{H}_2 & 4.13 \text{ eV} & \quad (17) \\
\rightarrow & \quad \text{C}_6\text{H}_2^+ + \text{C}_3\text{H}_3 & 4.19 \text{ eV} & \quad (18)
\end{align*}
\]

Using these data we will predict the fragmentation pattern for proposed structures for the adduct ions produced in this work.

**Structure Elucidation of SiArH\(^+\) by CID**

To better understand the chemistry of the association reactions the structures of the product ions were probed by collision induced dissociation (CID). We will analyze the CID fragmentation pattern by 1) assuming a particular structure for the adduct ion, 2)
predicting the fragmentation pattern for that structure from the thermochemical data provided, then 3) comparing our predicted fragmentation pattern to the observed CID spectra.

A reasonable structure for the association product is the silicon ion weakly bound to the surface of the aromatic ring. A similar study by Bohme et al. observed the production of weakly bound silicon-benzene and silicon-naphthalene adduct ions, for which they assign a π-bonded structure between the silicon ion and the aromatic ring. Ligand switching experiments for the benzene adduct ion gave an upper bound for the bond energy of 1.89 eV. Since the adduct ions are produced by radiative association the "predicted binding energies" are lower limits. The silicon-benzene complex with 33 internal degrees of freedom has a "predicted binding energy" of 2.2 ev. This is in reasonable agreement with Bohme et al.'s value.

If our adduct ions have the same structures as postulated by Bohme et al. the collision induced dissociation fragmentation pattern should show the production of the Si⁺ ion or the ArH⁺ ion of the aromatic molecule (if charge transfer occurs in the collision complex). All fragmentations of the aromatic ring require more energy than what we expect for the binding energy of the π-bonded structure.

The CID data do not show the production of Si⁺ or ArH⁺ with the exception of the anthracene adduct ion, Eq. (13). Benzene and naphthalene must not form adduct ions with the π-bonded structure.
and another structure must be considered. The anthracene adduct ions produce both Si$^+$ and ArH$^+$ which is expected for the $\pi$-bonded structure and also product ions due to the fragmentation of the aromatic ring. Anthracene appears to produce adduct ions in the $\pi$-bonded form as well as a structure that fragments similarly to the adduct ions of benzene and naphthalene.

**CID of the naphthalene adduct ion**

To simplify the analysis we will just consider the fragmentation pattern of the SiArH$^+$, naphthalene adduct ion. As we showed above it does not fragment in a manner consistent to the $\pi$-bonded structure.

Let us consider another structure for the silicon-naphthalene adduct ion, where the silicon ion inserts into the C-H bond of the aromatic ring producing a $\sigma$-bonded structure. What can be expected for the fragmentation of this structure? Using the values for the bond energies found in the silicon complexes with methane and ethane$^{14,15}$, we will assume that their Si$^+$-H bond energy is the same for our silicon-aromatic complexes. The loss of hydrogen is the lowest energy dissociation pathway for this structure, requiring 3.27 eV.

\[
\begin{align*}
\text{\textcircled{\text{\textbackslash n}}} & \quad \text{\textcircled{\text{\textbackslash n}}} \quad \text{\textcircled{\text{\textbackslash n}}} \quad \text{\textcircled{\text{\textbackslash n}}} & \quad \text{Si}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{n-bonded} & \quad \text{o-bonded}
\end{align*}
\]

\[
\begin{align*}
\text{\textcircled{\text{\textbackslash n}}} & \quad \text{\textcircled{\text{\textbackslash n}}} \quad \text{\textcircled{\text{\textbackslash n}}} \quad \text{\textcircled{\text{\textbackslash n}}} & \quad \text{SiH}^+ \\
\end{align*}
\]
The SiAH+ adduct ion for naphthalene showed precisely the loss of H as the dissociation product from CID. At this point it is reasonable to conclude that naphthalene produces the σ-bonded adduct ions upon association with Si+. 

**Structure of Si-benzene and Si-anthracene adduct ions.**

What can be said about the structure of the adduct ions produced from benzene and anthracene? CID was not done on the benzene adduct ion due to its low abundance. But reaction of benzene with the silicon ion did produce a SiAr+ product ion resulting from the loss of hydrogen. The most reasonable structure for the SiArH+ ion for benzene which results in the loss of hydrogen is the σ-bonded structure. This will be confirmed by the CID experiments done on the SiAr+ ion for benzene.

We already said that the CID of the anthracene adduct ion produced a fragmentation consistent with the π-bonded structure. But the CID data also shows the loss of H from the SiArH+ ion of anthracene. The association of anthracene with silicon ion appears to produce adducts having both the π-bonded and the σ-bonded structure.

**Structure Elucidation of SiAr+ by CID**

We will assume the SiAr+ ions to have the σ-bonded structure. Although it is not reasonable to assume the bond energy of silicon to the carbon of methane or ethane to be equal to the bond energy of silicon to the carbon of an aromatic ring, its value will be
taken as a lower limit of 4.51 eV. The energy to break the silicon-carbon bond is higher than the activation energy for any fragmentation channel that disrupts the aromatic ring. Thus we should expect the SiAr⁺ ions to dissociate in a manner similar to the dissociation of the ArH⁺ ions.

One characteristic feature of the dissociation of ArH⁺ is the loss of acetylene. C₂H₂ loss has been well established as dissociation products for both benzene and naphthalene ions¹⁶,¹⁷. In line with our expectation, products were observed in both the benzene and naphthalene cases which appear to correspond to the acetylene-loss channel. SiC₆H₅⁺ dissociated to produce SiC₂H⁺ Eq. (8), which may have a structure similar to acetylene. The SiC₁₀H₇⁺ ion lost acetylene, Eq. (10). The CID of the SiAr⁺ ions very strongly suggest that the silicon atom is covalently bonded to the carbon of the aromatic ring.

**H-loss reaction**

Hydrogen loss was observed for the reaction of silicon ions with benzene and naphthalene. We have already seen from the CID of the SiAr⁺ ions that the structure of these ions appear to have the silicon atom covalently attached to the carbon atom of the aromatic ring. The loss of hydrogen must occur after the rearrangement from the σ-bonded structure to the σ-bonded complex has taken place.

The reaction yields for the SiAr⁺ ion decreased as the aromatic molecule increased in size. Benzene had an 85% production of the
H-loss product ion, while none were seen for anthracene. Once the rearrangement has occurred there is a competition between hydrogen loss and infrared radiative stabilization. The σ-bonded structure for the SiArH^{2+} complex has approximately 3 eV of internal energy. Even though the complex for all three aromatic molecules would have the same 3 eV of internal energy their internal temperature will vary according to their heat capacities.

As the complexes increase in size, going from benzene to naphthalene to anthracene, the heat capacities correspondingly increase. The silicon-benzene complex, having a lower heat capacity, will have a higher internal temperature at 3 eV of internal energy than the silicon-anthracene complex which also has 3 eV of internal energy. Since the rate of dissociation for a polyatomic molecule is dependent on the internal temperature of the ion, the rate of hydrogen loss for the silicon-benzene complex will be faster than for the silicon-anthracene complex. Hydrogen loss is not seen for the silicon-anthracene complex which can be attributed to the complex’s low internal temperature which makes infrared radiative stabilization predominate over the dissociation channel.

**Charge transfer reaction**

Radiative association was not the only reaction channel observed for silicon ions with the three aromatic molecules. Charge transfer can easily occur if the ionization potential of the neutral molecule is lower than that of silicon. Charge transfer
from silicon to naphthalene is essentially thermoneutral since the ionization potentials of silicon and naphthalene are 8.15 eV and 8.14 eV respectively. Eq. (5) shows that the production of naphthalene ions by charge transfer was a major reaction channel. We see that charge transfer is a significant reaction that competes with radiative association.

One can imagine that if the charge transfer reaction was very exothermic it could completely dominate the chemistry whereby no association products would be observed. Once the collision complex, SiArH\(^{++}\), was formed charge transfer could easily take place followed by the redissociation to ArH\(^{+}\) and Si. The I.P. of anthracene is 7.5 eV which makes charge transfer with silicon ions 0.65 eV exothermic. It is not unreasonable to expect the exclusive production of anthracene ions based on the exothermicity of the charge transfer reaction.

Contrary to our expectation, Eq. (6) shows that adduct ions were formed between silicon and anthracene, in addition the production of anthracene ions from the charge transfer reaction, Eq. (7). The formation of silicon-anthracene ions could be explained if there existed a mechanism where the exothermic energy could be contained within the complex for a length of time before redissociation occurred. During this time stabilization of the complex could occur by the emission of infrared photons.

Due to the large number of internal degrees of freedom found in anthracene, which all contribute to the heat capacity of the
molecule, the 0.65 eV of exothermic energy can be contained in the silicon-anthracene complex for a sufficient length of time without redissociating. The exothermic energy from the charge transfer reaction is distributed among the many degrees of freedom resulting in a small change of the internal temperature. Since the rate of dissociation for a polyatomic molecule is sensitive to the internal temperature, a small change in the internal temperature would likewise result in only a small increase in the rate of redissociation. Infrared photon emission can effectively compete with redissociation thereby stabilizing the complex to form the adduct ion.

Based on the exothermicity of the silicon to anthracene charge transfer reaction, it seems feasible for the structure of the silicon-anthracene adduct ion to be a neutral silicon atom complexed to the anthracene ion. CID of the adduct ion of anthracene showed the production of the anthracene molecular ion, which confirms our suggested structure.

ICR vs. SIFT.

The only difference between these ICR experiments and the selected ion flow tube (SIFT) experiments of Bohme et al. is the pressure used in the two instruments since both instruments operated at room temperature (296 K). Low pressures of 1-3x10⁻⁸ Torr are used in the ICR where ion-neutral collisions take place on the order of one per second. The SIFT experiments are run in 0.35
Torr of helium buffer gas where collisions with helium atoms occur at a rate of $10^7$ per second. Since the collision rates in the SIFT experiments are seven orders of magnitude faster than in the ICR collisional stabilization will be the mechanism for the association reactions.

The structures of the adduct ions produced in the ICR were found to be different from those produced in the SIFT experiments. The CID of the adduct ions produced in this work showed fragmentation patterns consistent with the $\sigma$-bonded structure. Bohme et al. concluded that their adduct ions have the $\pi$-bonded structure. It appears that the difference in pressure for the SIFT instrument and the ICR spectrometer significantly affects the chemistry observed for the association reactions between the silicon ions and the aromatic molecules. In what way could the collision rate of the background neutrals affect the production of the adduct ions when both experiments were done at room temperature?

What must be considered is the rate of stabilization of the SiArH$^+$ relative to the rate of rearrangement to the $\sigma$-bonded structure. The collision complex, SiArH$^+$, is most likely formed initially in the $\pi$-bonded structure. Since the $\sigma$-bonded structure is more stable by 0.8 eV one would expect the rearrangement to occur. However, the activation energy associated with rearrangement reactions will retard the rate at which the $\sigma$-bonded structure will form. If the rate of stabilization by collisions is fast relative to the rate of rearrangement, as it is in the SIFT instrument, $\pi$-bonded complexes predominate. In the ICR
stabilization of the SiArH⁺ complex occurs by infrared photon emission. We saw in chapter III that typical rates for the emission of infrared photons by polyatomic molecules containing 2 to 3 eV of internal energy are 3 to 16 per second. σ-bonded complexes are observed since the rate of infrared photon emission is slow compared to the rate of rearrangement.
CONCLUSION

It is quite clear from the CID experiments that the adduct ions we have produced in this study are different from Bohme, et al. Due to the low pressure conditions in the ICR the π-bonded complex slowly rearranged into the σ-bonded complex before collisions with neutral gases stabilized the π-bonded collision complexes. Due to the high pressure of helium in the SIFT instrument, all collision complexes were stabilized before rearrangement to the more stable σ-bonded complexes could take place.

The CID of the adduct ions produced in the ICR did not show a fragmentation pattern predicted for the π-bonded structure. Fragmentation was consistent with the σ-bonded structure. C-H insertion occurred in the association reactions for silicon ions with benzene, naphthalene, and anthracene. The only exception was found for anthracene where its large number of internal degrees of freedom produced a fraction of adduct ions having the π-bonded structure.

The interest for studying these association reactions has come from understanding the formation of complex ions and molecules observed in the interstellar medium. The mechanism for interstellar association reactions has been attributed to radiative stabilization. Since the product ions formed in the ICR are primarily radiatively stabilized, one would expect the chemistry which takes place in the ICR to be consistent with interstellar chemistry. Studying association reactions under low pressure conditions in the ICR is probably a more reliable method
of understanding the reactions observed in the interstellar medium. Work done in the SIFT instruments may not accurately depict these radiative association reactions.
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CHAPTER VIII

CONCLUSION
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Four photoprocesses were studied on the Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer: infrared radiative cooling, infrared multiphoton absorption, infrared multiphoton dissociation, and infrared radiative association. Each of these processes required low pressure conditions which were easily obtained in the FT-ICR. Our object was to obtain a deeper understanding of these infrared photoprocesses and find physical models which adequately described the observed results.

Infrared radiative cooling and multiphoton absorption was studied by ion thermometry using competitive photodissociation. The thermometric technique provided a means to determine the internal energy of an ion at any given moment in time simply by measuring the branching ratio of the two competitive photoproducts. Photodissociation was initiated by the irradiation of the ions with visible laser light. N-bucylbenzene dissociated into two photoproducts, whose branching ratio is directly related to the internal energy of the parent ion. An energy resolution of hundredths of an electron volt was obtained using this technique. Since this thermometric technique is dependent on the accurate measurement of branching ratios we determined in chapter IV the experimental conditions in which mass discrimination is minimized on the FT-ICR mass spectrometer. In this way erroneous results were avoided.

Infrared radiative cooling by vibrationally excited n-
butylbenzene ions was beautifully observed by the ion thermometric technique. In chapter III, the ions were prepared by electron impact ionization and were found to contain approximately 0.67 eV of internal energy. This was only 0.35 eV above thermal equilibrium with the cell walls of the ICR ion trap. However, ion thermometry resolved the time dependence of the vibrational cooling to which an exponential decay was fit. The infrared radiative cooling rate constant was 0.8 s$^{-1}$ for n-butylbenzene in this near room temperature regime.

Radiative relaxation rate studies done in polyatomic ions having 2 to 3 eV of internal energy showed radiative cooling rates which were three to five times faster than the cooling rates measured for ions in the near-room temperature regime. With the desire to study the infrared radiative rate of n-butylbenzene ions at higher internal energies, a low powered cw-CO$_2$ laser was used in chapter VI to increase the vibrational excitation energy of the n-butylbenzene ions. Since n-butylbenzene ions dissociate once they have obtained approximately 1 eV of energy, the cw-CO$_2$ laser only excited the ions to an internal energy of 0.8 eV. The radiative cooling rate for these ions was very similar to the cooling rate for the ions observed in chapter III.

In chapter V, the dissociation of n-butylbenzene ions by infrared multiphoton absorption was studied as a prelude to the thermometric study of infrared multiphoton absorption. Dissociation was obtained by continuously irradiating the trapped
n-butylbenzene ions with the infrared light from the cw-CO$_2$ laser. Only the lowest energy photoproduce, m/z 92, was produced. The rate of dissociation showed a strong dependence on the intensity of the laser light. Our intent was to develop an analysis of these kinetic data in the framework of thermal dissociation reactions, where one normally finds the activation energy from an Arrhenius plot relating rate and temperature. In this way thermochemical data could be obtained with reasonable ease.

What is first needed for a thermal analysis is the conversion of laser intensities to an ion temperature. A computer simulation was used to do this. A simple cw-IRMPD (continuous wave-infrared multiphoton dissociation) model was used to describe the nature of photon absorption and photon emission during the cw-CO$_2$ laser irradiation. In this model the n-butylbenzene ion was taken to be a collection of weakly coupled harmonic oscillators where only a few oscillators were infrared active while the rest contributed to the heat capacity of the molecule. The infrared active modes absorbed and radiated photons according to harmonic oscillator rules.

A random walk method was used in chapter V to evaluate the internal energy of the ion population under the simulated laser irradiation. The steady state condition where an equilibrium was reached between laser up-pumping and infrared radiative relaxation, showed an internal energy distribution that was very similar to a Boltzmann distribution. Using these internal temperatures an Arrhenius plot was made to obtain the activation energy for the IRMPD of n-butylbenzene ions. By using Tolman's theorem to
evaluate the activation energy obtained in this analysis, the
thermal description for IRMPD appeared to be reasonable.

IRMPD by the low powered cw-CO$_2$ laser was further investigated
in chapter VI using ion thermometry. In particular the time
progression of the ion population's internal energy was beautifully
monitored during the cw-CO$_2$ laser irradiation. The simple harmonic
oscillator model which was used to describe the IRMPD kinetics in
chapter V gave excellent agreement with thermometric data for
radiative relaxation. However, it failed to adequately account for
the infrared multiphoton dissociation data. The predicted
induction times were too short and the predicted dissociation rates
were too fast.

The master equation describing the infrared multiphoton
absorption and dissociation processes was revised so the simulated
kinetic data would be in better agreement with the experimental
data. Rather than using an energy independent infrared absorption
cross section, a two rate absorption cross section model was
employed. A constant value was assigned for internal energies up
to 0.5 eV, then a smooth decrease to a value three times smaller at
an energy of 0.7 eV. Another revision was to use an energy
dependent dissociation rate rather than a fast dissociation rate at
a fixed threshold. Since the simple harmonic model fit the
thermometric data for radiative relaxation well, the portion of the
master equation dealing with photon emission was not altered.
These refinements were found to be satisfactory to the experimental
data.

The use of the master equation to account for the thermometric data with the dissociation kinetics was effective. However, our desire for a generalized thermal analysis for IRMPD kinetics appears to be disappointing. Appropriate temperatures can only be assigned to simulated internal energy distributions. The validity of the simulation is dependent on the accuracy of the master equation used to describe the multiphoton absorption and dissociation process. There is no reason to expect all molecular species to have a common absorption cross section for multiphoton absorption of infrared photons. With each molecule having a characteristic infrared absorption profile the internal temperature reached at a given cw-CO₂ laser intensity will also be specific to the system.

The final infrared photoprocess studied was radiative association. The interest in radiative association reactions come from the astrochemistry field where these reactions are presumed to take place in interstellar clouds. Since the density of molecules in these clouds is low ion-neutral collisions occur at a rate of one per day. The stabilization of the association complex is predominantly by the emission of an infrared photon. Our knowledge of infrared radiative cooling in polyatomic ions provided the basis for interpreting our data on these association reactions. Since the radiative cooling rates for polyatomic ions range from 0.3 s⁻¹ to 16 s⁻¹, the study of radiative association reactions necessitates working at pressures around 1-3 x 10⁻⁸ torr where the
rate of collision between an ion and a neutral molecule occurs less than one per second.

The majority of ion-neutral association reactions have been studied in selected ion flow tube (SIFT) instruments which operate at helium pressures of 0.35 Torr. At this pressure the helium atoms collide with the collision complex at a rate of $10^7$ per second. These collisions are inelastic thereby stabilizing the complexes by removing excess internal energy. Extrapolation procedures have been used to estimate radiative association rates from these high pressure experiments. The validity of obtaining radiative association rates from collisionally stabilized data may be questionable. FT-ICR provides the direct means to study radiative association reactions due to the low pressure conditions that are easily attained.

Silicon ions were allowed to associate with three aromatic molecules (benzene, naphthalene, and anthracene) at a pressure approximately $1 \times 10^{-8}$ Torr. Association products were seen for all three aromatic molecules. SIFT experiments showed the production of association products between silicon ions and benzene and naphthalene. Structures for these complexes were suggested to have the silicon ion π-bonded to the surface of aromatic molecule, based upon the ease the silicon ion transferred itself to other neutral molecules such as water and acetylene.

The structure of the association products produced in the FT-ICR was probed by collision induced dissociation. The silicon was
found to be very strongly bound to the aromatic molecule. The fragmentation pattern of the silicon-naphthalene complex produced ions that were similar to the unimolecular dissociation products of naphthalene ion. We concluded that the silicon atom in the association product ion inserted into a C-H bond of the aromatic molecule, being \(\sigma\)-bonded to the ring carbon atom. The cause for the difference in the structure of these complexes with those from the SIFT experiments come from the difference in rate at which these complexes are stabilized. The \(\sigma\)-bonded complexes are thermodynamically more stable, while the \(\pi\)-bonded complexes are kinetically more favorable.

Since ion-neutral collisions compete with infrared photon emission and with infrared multiphoton absorption from a low powered continuous wave CO\(_2\) laser, low pressure conditions are needed. The FT-ICR was found to be well suited to the study these infrared photoprocesses. The technique of ion thermometry by competitive photodissociation provided an excellent means to observe the internal energy of the trapped n-butylbenzene ions during infrared multiphoton absorption, infrared multiphoton dissociation, as well as infrared radiative cooling. The FT-ICR enabled the direct measurement of radiative association reactions and showed that extrapolations done on collisionally stabilized association data may not be suitable.


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