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Spectroscopy and photodynamics of gas phase ions

Faulk, James Donald, Ph.D.
Case Western Reserve University, 1991
SPECTROSCOPY AND PHOTODYNAMICS OF GAS PHASE IONS

by

JAMES DONALD FAULK

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

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May 17, 1991
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GRADUATE STUDIES

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SPECTROSCOPY AND PHOTODYNAMICS OF GAS PHASE IONS.

Abstract

by

JIM FAULK

In this work five studies are presented in which the spectroscopy and photodynamics of gas phase ions were investigated using photodissociation in an ion cyclotron resonance mass spectrometer.

In chapter III photodissociation measurements in the ICR ion trap were used to find the collisionless relaxation rate of thiophenol ions prepared with 2-3 eV of excess internal energy. Three techniques based on the kinetic differences between one-photon and two-photon dissociation were used to measure this rate. It was concluded that about 0.3 s is required for excited thiophenol ion to relax from 2.5 to 0.5 eV of internal energy.

In chapter IV the optical absorption spectrum of the radical cation of 2-methyl-1-pentene-3-yne was investigated by photodissociation spectroscopy between 605 and 538 nm and between 515 and 458 nm. Both the 0-0 and the 1-0 components of a vibrational progression were observed in the photodissociation spectrum. The position of the 0-0 peak was in perfect agreement with the corresponding peak in the photoelectron spectrum of the neutral. The Franck-Condon factors for the 0-0 and 1-0 transitions were similar for the photodissociation and photoelectron spectra, suggesting similar geometries of the neutral and ground state ion,
which was in accord with the expectations from the simple MO picture.

In chapter V the optical absorption spectrum of gas phase ferrocene cation was measured by photodissociation spectroscopy between 570 nm and 643 nm. The photodissociation process was loss of a cyclopentadienyl ring from the parent cation. Some structure was observed in the photodissociation spectrum and a possible assignment of the three apparent maxima is proposed involving electronic transitions from low-lying electronic states. A lower limit of 5.4 eV was set on the dissociation threshold by light intensity dependence measurements at 308 and 266 nm, and time-resolved photodissociation measurements at 308, 266 and 240 nm.

In chapter VI time-resolved photodissociation (TRPD) in the ion cyclotron resonance ion trap was used to observe the slow dissociation of tri-t-butylbenzene ion at four wavelengths between 615 and 532 nm. Dissociation rates of the order of 5x10^3 to 3x10^4 s^-1 were found for thermalized ions. An excellent fit to the observed curves was obtained by convoluting an RRKM rate-energy curve with the thermal distribution of ion internal energies at 375 K. RRKM parameters for the best fit were E_0 = 1.2±0.1 eV and ΔS^‡ = -7±7 cal/K.

In chapter VII dissociation of thiophenol molecular ion to yield competitive product ions of m/z 84 (C₄H₄S⁺) and 66 (C₅H₅⁺) was studied by time-resolved photodissociation in the ICR ion trap. Rate constants of 1.3x10^5 s^-1 for m/z 84 formation and 8x10^4 for m/z 66 formation were measured at 308 nm (4.20 eV ion internal
energy). At 355 nm (3.66 eV ion internal energy) a rate constant of 2.8×10^3 s^{-1} for m/z 84 formation was measured, with m/z 66 not observed at this wavelength. RRKM modeling of these dissociations was successful, using a very loose transition state (ΔS^†(1000 K) = 14 eu) and a critical energy of 3.2 eV for m/z 66 formation; and a tighter transition state (ΔS^†(1000 K) = 2.74 eu) and a critical energy of 2.9 eV for m/z 84 formation. Using TRPD as an ion-thermometric tool, collisional cooling of hot thiophenol ions was observed, and a collisional cooling rate constant of 4×10^{-10} cm^3·molecule^{-1}·s^{-1} was measured.
ACKNOWLEDGMENTS

I especially want to thank my thesis advisor Dr. Robert Dunbar for his patience and encouragement during my thesis work. Dr. Dunbar provided invaluable guidance and assistance both in the empirical and theoretical aspects of gas phase ion spectroscopy and photodynamics. Dr. Hun Young So provided much needed advice and assistance in the laboratory during the early part of my studies.

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LIST OF ABBREVIATIONS

ICR- Ion cyclotron resonance
PDS- Photodissociation spectroscopy
PD- Photodissociation
PES- Photoelectron spectroscopy
RRKM- Statistical rate theory
QET- Quasiequilibrium theory
PEPICO- Photoelectron photoion coincidence
IP- Ionization potential
TTBB- Tri-t-butylbenzene
TBB- t-butylbenzene
DTBB- Di-t-butylbenzene
TRPD- Time resolved photodissociation
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CHAPTER ONE

INTRODUCTION
The study of gas phase ions is interesting for several reasons. First, it is possible to adjust experimental conditions so that ions in the gas phase are virtually free from interactions of the type encountered in condensed phases. One can therefore prepare ions with a specific internal energy (or in some cases in a specific electronic, vibrational and rotational state) and then follow their behavior on a time scale of seconds without the complication of ion-neutral interactions. However, if desired, it is also possible, using a mass spectrometer, to study ion-neutral interactions by controlling the frequency and intensity of ion-neutral collisions. These advantages have been exploited on many occasions to measure the properties of isolated ions, such as Freiser and Beauchamp’s study of acidities and basicities of gas phase ions. Second, mass spectrometers are used extensively as analytical tools. It is therefore important to understand unimolecular ion fragmentation processes that are of fundamental importance in interpreting and predicting mass spectra. Third, there is much interest in the type of chemistry occurring in outer space and planetary atmospheres, much of it involving ions. For instance, interest in interstellar dust cloud chemistry has prompted several studies on radiative association reactions between ions and neutrals.
TRAPPING MASS SPECTROMETRY:

Gas phase ions have traditionally been studied using magnetic sector, quadrupole and time of flight mass spectrometers in which the time between ion formation and ion detection is on the order of microseconds. This of course limits one to the study of processes with time constants shorter than about $10^{-5}$ seconds. An ion trapping mass spectrometer, such as the ion cyclotron resonance (ICR) spectrometer which can trap ions for several seconds (2 to 5 s being typical), allows the study of slower processes.

There are several advantages in studying ions with an ICR spectrometer. The most obvious one is the ability to observe very slow ion processes. MacMahon et al. have trapped ions for several hours to study slow radiative stabilization of ion molecule complexes formed at low pressures.

Another advantage is the ability to thermalize the ions at a known temperature before beginning the experiment. Since this feature of trapping mass spectrometry is exploited extensively in the work presented here, it deserves further discussion.

Ion Thermalization: Ions in an ion population formed by low energy electron impact invariably have some superthermal (excess) internal energy that is difficult to characterize. To study ion processes (most of which are energy dependent) requires that parent ions be prepared with well characterized internal energy. This is done by allowing the initially "hot" ion population to reach thermal equilibrium with the environment during a one or two second thermalization time after ion formation. The resulting thermal
population will have a distribution of internal energies that corresponds to the temperature of the environment and is accurately represented by a Boltzmann distribution taken over all internal degrees of freedom. The environment, consisting of the walls of the ICR cell and all neutral molecules and ions in the cell, is heated by the glowing filament to somewhere around 350-400 K.

The two principle mechanisms by which "hot" ions are thermalized are: i) collisional charge transfer with thermal parent neutral, giving a thermal ion on nearly every collision and ii) less efficient radiative relaxation where energy is lost by emission of infrared photons. Ion relaxation will be discussed in more detail in chapter III.
PHOTODISSOCIATION:

A convenient and useful technique used to study gas phase ions is photodissociation (PD), where a known amount of energy is supplied to the ion in the form of a visible, infrared or UV photon. All of the work described in the following chapters involves the interaction of ions with visible or UV photons. There are several advantages to using this approach.

First, most processes that ions undergo are in some way energy dependent. It is therefore desirable to prepare ions with known internal energy. This is most conveniently done by supplying a photon of known energy to ions in a population having a known distribution of thermal energies. The fate of an ion prepared in this way can be followed as a function of time and photon energy. In chapters VI and VII photodissociation was used to measure the energy dependence of the rate of unimolecular fragmentation of thiophenol and tri-t-butylbenzene cations respectively. In chapter III it was used to measure the rate of radiative energy loss from the thiophenol cation.

Second, every feature in the photodissociation spectrum must correspond to a feature in the optical absorption spectrum. It is therefore possible to probe the electronic structure of an ion by following the wavelength dependence of the extent of photofragmentation. This aspect of PD was exploited in chapters IV and V where PD spectra were obtained of 2-methyl-1-penten-3-yne and ferrocene cations, respectively.

Lastly, PD of gas phase ions corresponds in a direct way to
photo-phenomena occurring naturally in the upper atmosphere and in interstellar dust clouds.

We are interested in photodissociation occurring from the ground electronic state of an energized parent ion. The energy is initially deposited through absorption of one or more photons each of which corresponds in energy to an allowed electronic transition of the molecular ion. For most of the ions we study this is in the visible or UV range. The lifetime and fate of the resulting electronically excited ion (M\(^+\dagger\)) depends on the relative rates of several competing processes (see scheme I): i) direct fragmentation from the excited electronic state (k\(_F\)), ii) visible or UV fluorescence (k\(_{h\nu}\)), and iii) internal conversion from an excited electronic state to the vibrationally excited ground electronic state (M\(^+\ast\)) (k\(_{I,C}\)).

![Scheme I](image)

**Options available to an electronically excited parent ion, M\(^+\dagger\).**

In open shell cations the most likely process is usually internal conversion since in most open shell cations internal conversion is much faster than fluorescence from excited electronic states\(^5\) and direct fragmentation does not occur unless repulsive electronic states are accessed by one of the absorbed photons.

**One-Photon Dissociation.** The fate of the vibrationally excited
electronic ground state ion resulting from internal conversion \( (M^{**}) \) depends on the relative rates of three competing processes. If it does not absorb another photon (two photon absorption will be discussed later) it will branch into two channels. These are shown in scheme II as loss of excess vibrational energy by radiative or collisional relaxation (with a rate \( k_r + k_c[M] \)), or fragmentation with a rate \( k_f \) that depends, according to RRKM theory, on the internal energy in excess of the fragmentation threshold. RRKM theory is discussed later in this chapter under Ion Fragmentation Dynamics.

Scheme II

One photon dissociation from the electronic ground state, where \( I(\lambda) \) is the light intensity at \( \lambda \) (in units of photons \( \cdot s^{-1} \cdot cm^{-2} \)).

If we assume that \( k_f >> (k_r + k_c[M]) \) and that the lifetime of \( M^{**} \) is very short compared to that required for ion detection, then \( M^+ \) is the only parent ion species with a kinetically significant life time and its abundance is given by a simple exponential:

\[
[M^+] = [M^+]_0 \exp(-\sigma(\lambda) \cdot I(\lambda) \cdot t)
\]

from which it follows that

\[
D = \sigma(\lambda) \cdot I(\lambda) \cdot t \quad (1)
\]

where \( t \) is the light on time and \( D \) is the extent of dissociation.

The photodissociation cross section, \( \sigma(\lambda) \) (in units of area),
is a product of two terms, the optical absorption cross section and the quantum yield for dissociation $\Phi(\lambda)$. Although the value for $\Phi(\lambda)$ is usually close to 1 it can be reduced by a competing process such as fluorescence. If $\Phi(\lambda) < 1$, the photodissociation spectrum ($\sigma(\lambda)$ vs. $\lambda$) is the lower limit for the optical absorption spectrum of the ion. If $\Phi = 1$, the photodissociation spectrum is the same as the optical absorption spectrum. Since every feature in the photodissociation spectrum must correspond to a feature in the optical absorption spectrum the wavelength dependence of the extent of dissociation was used as a probe of the parent ion optical absorption spectrum in the work with 2-methyl-1-pentene-3-yne and ferrocene cations in chapters VI and V.

Experimentally the extent of photodissociation is given by $D = \ln(M^+_0/M^+)$, where $M^+_0$ is the light off parent ion abundance and $M^+$ is the light on parent ion abundance.

**Two Photon Dissociation.** In their work on benzene cation Freiser and Beauchamp discovered that fragmentation can occur at photon energies below the fragmentation threshold. The kinetic scheme they proposed for this process (still accepted today) is given below.

\[
\begin{align*}
M^+ & \xrightarrow{k_c[M] + k_f} M^+ \xrightarrow{I \cdot \sigma_1} M^{+\dagger} \xrightarrow{I \cdot \sigma_2} M^{+\dagger} \xrightarrow{M^{++}} \text{Fragments} \\
\end{align*}
\]

Scheme III

Two photon dissociation from the electronic ground state.
The first photon is absorbed by the ground state ion \( M^+ \) at a rate of \( \sigma_1 \), forming the electronically excited ion \( M^{*+} \). This undergoes rapid internal conversion to the vibrationally excited electronic ground state cation, \( M^{**} \). Radiative and collisional relaxation of the excess vibrational energy of this intermediate compete with absorption of the second photon which occurs at a rate of \( \sigma_2 \). The resulting electronically excited cation \( M^{**} \) undergoes internal conversion to the electronic ground state cation \( M^{***} \) now with an excess vibrational energy equal to the energy content of two photons minus that lost by collisional and or radiative relaxation from \( M^{**} \). RRKM fragmentation then occurs with a rate governed by the vibrational energy in excess of the fragmentation threshold for the lowest energy fragmentation pathway. At internal energies equivalent to the energy content of two photons this rate is usually much faster than collisional or radiative energy loss.

If in the above scheme we assume that \( M^+ \) and \( M^{**} \) are the only parent ion species with kinetically significant lifetimes their time dependence for continuous irradiation is described by:

\[
\frac{d[M^+]}{dt} = -\sigma_1[M^+] + (k_T + k_C[M])[M^{**}] \tag{2}
\]

\[
\frac{d[M^{**}]}{dt} = \sigma_1[M^+] + (\sigma_2 - (k_T + k_C[M]))[M^{**}] \tag{3}
\]

Integration of these gives:

\[
\frac{[M^+] + [M^{**}]}{[M^+]_0} = \frac{\lambda_-}{\lambda_- - \lambda_+} \exp(-\lambda_- t) - \frac{\lambda_+}{\lambda_- - \lambda_+} \exp(-\lambda_+ t) \tag{4}
\]
where \([M^+]_0\) is the light off parent ion abundance and \(\lambda_+\) and \(\lambda_-\) are given by

\[
\lambda_{\pm} = \frac{1}{2} (I\sigma_1 + I\sigma_2 + (k_R + k_C[M])) \\
(1 - \frac{[(I\sigma_1 + I\sigma_2 + (k_R + k_C[M]))^2 - 4I^2\sigma_1\sigma_2]^{1/2}}{(I\sigma_1 + I\sigma_2 + (k_R + k_C[M]))^2})
\]

This can be expanded in terms of the quantity,

\[
\begin{bmatrix}
I^2\sigma_1\sigma_2 \\
(I\sigma_1 + I\sigma_2 + (k_R + k_C[M]))^2
\end{bmatrix}
\]

to give

\[
\lambda_+ = \frac{I^2\sigma_1\sigma_2}{(I\sigma_1 + I\sigma_2 + (k_R + k_C[M]))} + \Delta
\]

and

\[
\lambda_- = I\sigma_1 + I\sigma_2 + (k_R + k_C[M]) - \frac{I^2\sigma_1\sigma_2}{(I\sigma_1 + I\sigma_2 + (k_R + k_C[M]))} - \Delta
\]

where \(\Delta\) is very small and will not be considered further.

For times long enough for the initial transient behavior (represented by the second term in equation 4) to die out \((t >> 1/\lambda_-)\)

equation 4 simplifies to:

\[
\left[ \frac{[M^+] + [M^{+*}]}{[M^+]_0} \right]_{\text{long time}} = \frac{\lambda_-}{\lambda_+} \exp(-\lambda_+ t)
\]

\((5)\)

In the low light intensity high pressure limit, defined by \(I\sigma_1/(k_R + k_C[M]) << 1\) and \(I\sigma_2/(k_R + k_C[M]) << 1\), the coefficient of the exponential in equation 5 is nearly equal to 1. This gives the two photon dissociation equation that is most often used:
\[
\frac{[M^+] + [M^{**}]}{[M^+]_0} = \exp(-\lambda_4 t)
\]

\[
D = -\ln \left[ \frac{[M^+] + [M^{**}]}{[M^+]_0} \right]
\]

\[
= \left[ \frac{I^2 \sigma_1 \sigma_2}{I \sigma_1 + I \sigma_2 + (k_T + k_C[M])} \right] t
\]

The assumptions involved in deriving equation 6 are 1) high parent neutral pressure and low light intensity and 2) irradiation times long enough for the initial transient photodissociation behavior to die out.

**Light Intensity Dependence.** The light intensity dependence of photodissociation can often provide an indication of the number of photons required for dissociation. Dissociation requiring only one photon will, as shown in equation 1, always exhibit a linear dependence on light intensity.

\[
D = \sigma(\lambda)I(\lambda)t = -\ln(M^+/M^+_0)
\]

Interpretation of the light intensity dependence of multiphoton photodissociation is less straightforward since it depends on the relative rates of photon absorption and of internal energy relaxation. Using the two photon case as an example, it is apparent from equation 6 that the intensity dependence of a two photon process will vary from being proportional to \(I^2\) for low intensities and rapid internal energy relaxation (where \(k_T + k_C[M]\)
I(\sigma_1 + \sigma_2)) to being proportional to I at higher intensities and slower internal energy relaxation (where \(k_r + k_c[M] < I(\sigma_1 + \sigma_2)\)). Such variability in light intensity dependence has been observed in photodissociations requiring more than two photons: while modeling the photodissociation of naphthalene, a process requiring four visible photons, Kim and Dunbar showed the exponential light intensity dependence to be equal to 4 only in the limit of low light intensity (slow photon absorption rate) and rapid energy relaxation but to decrease to less than 2 at higher intensities.

If, in a multiphoton process, one of the photon absorption steps is rate limiting then it will be the only kinetically significant step and will control the overall kinetics for the dissociation. The light intensity dependence in this case will be linear as can be seen from equation 6. Therefore a non-linear light intensity dependence always implies a multiphoton process, but a linear light intensity dependence is uninformative: it may correspond to a one-photon process, or it may correspond to a multiphoton process with one of the photon absorption steps being rate limiting.
ION FRAGMENTATION DYNAMICS:

**Kinetic Shift.** Fragmentation thresholds are usually derived from appearance potential measurements using techniques such as PEPICO. However, such measurements are subject to a phenomenon called kinetic shift which causes the measured appearance potential to be above the actual activation energy by an amount ranging from zero to several eV. (The activation energy is represented by $E_0$ in figure 1). This difference reflects the internal energy in excess of the activation energy that is necessary to produce a detectable amount of photoproduct between the time of parent neutral irradiation and photofragment ion detection, usually about $10^{-5}$ s. This problem becomes more severe as the number of internal degrees of freedom increases.

The TRPD experiment avoids this difficulty by taking full advantage of the ICR's ability to trap ions for extended periods. Photofragmentations are observed for times long enough to see products from even the slowest fragmentations. We have therefore sought to apply this technique to fragmentations where kinetic shift is expected to be a problem: to fragmentations of large parent ions where the large vibrational state density is expected to slow down the fragmentation rate (see chapter VI and reference 9) and to fragmentations that require significant structural rearrangement where the expected large negative value of $\Delta S^\#$ (the entropy of activation) would result in a large kinetic shift (see chapter VII and reference 10).

Another difficulty, one which cannot be experimentally
compensated for, is intrinsic kinetic shift. Any process that removes or de-energizes energized parent ions at a rate comparable to the fragmentation rate can compete with fragmentation for available parent ions. Infrared radiative relaxation often competes with slow fragmentations. Loss of one infrared photon from an energized parent ion that is just above the activation energy can reduce its internal energy below the value required for fragmentation. If the rate of energy loss by photon emission is greater than the rate of fragmentation, as it often is for ions whose internal energy is just above the activation energy, the internal energy must be greater than the actual activation energy before fragmentation becomes fast enough to occur. It is usually considered fast enough when the fragmentation rate is 10% or more of the photon emission rate.

However, in the Time Resolved Photodissociation (TRPD) experiment of chapters VI and VII the value for the activation energy, $E_0$, is obtained from RRKM modeling of several rate energy points without requiring that the ions be near threshold after photon absorption, therefore the intrinsic kinetic shift need not be a problem; It is often possible to increase the photon energy, within the limits of the ion's electronic absorption spectrum, thereby increasing the fragmentation rate to values high enough that radiative relaxation no longer competes with fragmentation.

Competitive Fragmentation. Products formed from the same population of photoexcited parent ions but by different fragmentation channels (different transition states) will be formed
in competition for available parent ion; the faster fragmentation will deplete the population of available parent ions faster than will the slower fragmentation. In a competitive unimolecular fragmentation the abundance of the parent ion, $M$, and the products, $P_I$, are given by:

$$P_I = \frac{k_1 M_0}{k'} (1 - e^{-k't})$$

$$M = M_0 e^{-k't}$$

where $k'$ is the sum of the rate constants for the competing channels. The appearance curves of competitively formed products have the same shape. Their rise time reflects the kinetics of the disappearance of the photoexcited parent ion (not the kinetics of the appearance of the individual product ions). The rate constant derived from the shape of the daughter ion appearance curve will be the parent ion disappearance rate constant, that is to say, the sum of the constants for the competing channels. The rate constant for each individual channel is obtained by multiplying the measured rate, $k'$, by the branching ratio for the channel in question. The branching ratio for product ions B and C relative to A is the ratio of rates of formation, $k_B/k_A$ and $k_C/k_A$, or as can be seen from equation 7, the ratio of ion abundance at long times, $B/A$ and $C/A$.

**RRKM Theory**.\(^2,12,13\) RRKM theory involves the following assumptions. 1) The available vibrational energy is randomized over all vibrational degrees of freedom much faster than dissociation. 2) Energy randomization is statistical. 3) The
vibrational modes or oscillators are loosely coupled and exchange energy easily.

For the work presented in this thesis the kinetic scheme for the fragmentation of a molecular ion \( M^+ \) according to RRKM theory is

\[
\begin{align*}
\text{hv} & \quad M^+ \quad \rightarrow \quad M^{++} \\
M^{++} & \quad k_a \quad \rightarrow \quad M^{+\#} \quad \rightarrow \quad \text{Products}
\end{align*}
\]

The molecular ion is energized by absorption of a photon to form the energized molecular ion \( M^{++} \), which then fragments.

Figure 1 illustrates the energetics of this step. The molecular ion is energized by a photon (\( h\nu = E \)) to form \( M^{++} \) which differs from \( M^+ \) only in that it has the additional vibrational energy \( E \). However before fragmentation can occur the energized ion must structurally rearrange to the geometry of the transition state, \( M^{+\#} \). This process concentrates a sufficient amount of vibrational energy in the reaction coordinate to allow the system to pass over the barrier which occurs with a time constant on the order of one vibrational period, about \( 10^{-13} \) sec. The reaction coordinate is chosen to be a vibrational mode that corresponds to the bond breaking process. The various energies are defined in the figure caption. Both RRKM theory and Absolute Rate theory make the assumption that the steady state concentration of \( M^{+\#} \) crossing the barrier in the forward direction is the same as it would be if an equilibrium existed between \( M^{++} \) and \( M^{+\#} \) with no net reaction occurring. This gives \( k_a \ [M^{++}] = k^\# \ [M^{+\#}] \) and
\[ k_a = \frac{1}{2} \frac{k^*}{[M^{++}]} \frac{[M^+]^{\text{eqilibrium}}}{[M^{++}]} \] (8)

The factor of 1/2 arises because at equilibrium the concentration of complexes crossing in the forward direction is 1/2 the total concentration of complexes. This equilibrium hypothesis has been defended by arguing that the energized ions about to assume the geometry of the transition state and cross the barrier in the forward direction do not know that there are no ions crossing in the reverse direction and so assume the geometry of the transition state at the rate they would if a true equilibrium was set up.

Using Absolute Rate theory a value for \( k_a \) can be derived from equation 8:

\[ k_a = \frac{W^*(E-E_0)}{h N^*(E)} \] (9)

where \( W^*(E-E_0) \) is the number of vibrational states up to the energy \( E-E_0 \) at the transition state \( M^+\# \), \( N^*(E) \) is the density of vibrational states at the energy \( E \) of the energized ion \( M^{++} \) and \( h \) is Planck's constant (numerically equal to the inverse of the speed of light in cm s\(^{-1}\)).

The RRKM rate is calculated according to equation 9 by a computer program called RRKMDISS. The program requires complete lists of the vibrational frequencies for the molecular ion and the proposed transition state, a trial value for \( E_0 \) and the range of total internal energies (E) over which the rate calculation is to be done. It first uses the vibrational frequencies and a Steepest
Descents state counting procedure\textsuperscript{14} to calculate \( N^*(E) \) and \( W^*(E-E_0) \) at \( E \) values 1000 cm\(^{-1}\) apart over the specified energy range. The RRKM rate is then calculated at each energy in the range.

The shape of this rate-energy curve is governed by the values of only two activation parameters: the activation energy \( E_0 \) and the activation entropy \( \Delta S^\# \). The value for \( \Delta S^\# \) is determined by the change in the vibrational frequencies in going from the energized ion to the transition state. The shape of the rate-energy curve is not sensitive to the exact frequency changes made, only to the value of the parameter \( \Delta S^\# \).

Fragmentations that require loosening the vibrational frequencies in the transition state (loose transition state) have a more positive \( \Delta S^\# \). Tighter transition states have more negative \( \Delta S^\# \).

It is convenient at this point to make a distinction between the different reaction energies and bonding energies involved in unimolecular ion fragmentation.

1) Activation Energy (Thermochemical Activation Energy): This is the energy \( E_0 \) from the ground vibrational state of reactants to the top of the barrier in figure 1.

2) Appearance Energy (Threshold Energy, Fragmentation Threshold): As discussed in the Kinetic Shift section, fragments may not be formed fast enough to be detected unless the parent ion internal energy is above the actual thermochemical activation energy by an amount called the kinetic shift. The minimum parent ion internal energy at which fragments can be detected is the Appearance Energy.

3) Dissociation Endothermicity: The energy from ground state
reactants to ground state products. This may be different from the Thermochemical Activation Energy if there is an activation barrier for product recombination, i.e., a reverse activation barrier. In this case the Dissociation Endothermicity will be smaller than the Thermochemical Activation Energy by the reverse activation barrier. In the absence of a reverse activation barrier it will be numerically equal to the Thermochemical Activation Energy.
ARRANGEMENT OF THESIS:

This thesis is divided into three sections; (i) photophysics, (ii) spectroscopy and (iii) photochemistry of gas phase ions. The first section made up of chapter III deals with the photophysical process of radiative relaxation of excess vibrational energy from thiophenol cation in which no chemical change is induced by photon absorption. The second section composed of chapters IV and V deals with the spectroscopy of 2-methyl-1-penten-3-yne and ferrocene cations. The last section, chapters VI and VII, examine the photochemical phenomenon of photo-induced unimolecular fragmentation of tri-t-butylnbenzene and thiophenol cations.
REFERENCES:


1. Energy diagram of unimolecular fragmentation according to:

\[ h\nu \rightarrow M^{+\ast} \rightarrow M^{+\#} \rightarrow \text{Products} \]

In the diagram: \( E \) is the total internal energy of the ion (photon energy plus thermal); \( E_0 \) is the thermochemical activation energy for fragmentation; \( E_v \) and \( E_v^{\#} \) are the vibrational energy of the energized ion \( M^{+\ast} \) and the transition state \( M^{+\#} \) respectively; \( E_r \) and \( E_r^{\#} \) are the rotational energies of the energized ion and transition state respectively; \( E_X \) is the energy in the reaction coordinate for the fragmentation.
\[ E = E_v + E_r \]
\[ E^\# = E^\#_v + E^\#_r + E^\#_x \]
CHAPTER TWO

INSTRUMENTATION
The advantages of studying gas phase ions in an ICR mass spectrometer and some of the experimental and theoretical considerations involved in such studies were discussed in the last chapter. This chapter describes some of the tools we use to study gas phase ions. Most of the discussion will be centered around the ICR mass spectrometer but the light sources and associated components will also be mentioned.
DESCRIPTION OF CELL:

Figure 1 is a diagram of the trapping cell used in our instrument. It is operated in a pulsed mode; that is, a pulse sequence much like the one shown in figure 2 is repeated continuously. It is therefore convenient to describe the trapping cell in terms of this pulse sequence.

**Ion Formation.** Ions are initially formed by electron impact during the electron beam (or grid) pulse. The electrons originate from an electron plasma around the rhenium filament while it is being heated to glowing by passing 2 to 3 amps of DC current. The electron kinetic energy is adjusted by biasing the filament voltage negative relative to the trapping plate voltage. The electrons are accelerated from the filament toward the trapping plate along the magnetic field lines and pass into the cell through a hole in the center of the trapping plate. In this arrangement the electron beam is very collimated all along its path by the magnetic field lines so all of it passes through the hole in the center of the trapping plate and through the center of the cell. This means that the newly formed ions are spread out along the z axis but are in the center of the xy plane of the cell. They are also formed with thermal or near thermal kinetic energies because most of the excess electron kinetic energy is carried off by the departing electrons. To pulse the beam we have inserted a grid, a metal plate with a hole in it through which the electrons can pass, between the filament and the trapping plate. The electron beam is pulsed on by grounding the grid which is normally kept 8 volts more negative
than the filament. The electron beam pulse is usually tens of milliseconds long.

**Ion Trapping.** During the trapping period, which begins at the start of ion formation and may last for several seconds, ions are trapped in the ICR cell in all three dimensions because of two effects: i) the cyclotron motion of a charged particle in a magnetic field and ii) the effect of an electrical potential well on a charged particle.

The cyclotron motion is responsible for trapping ions in the \( x, y \) plane perpendicular to the lines of magnetic field. Ions with a charge, \( q \), moving with linear velocity, \( v \), in a magnetic field of strength, \( B \), experience a Lorentz force that is perpendicular to both the velocity vector and the lines of magnetic field and is given by \( F = q \cdot v \cdot B \).\(^1\) The ions therefore move along a curved path which, because a centripetal force must balance the Lorentz force, eventually closes to form a circular orbit of radius \( r \). Equating these two forces we get:

\[
\frac{m \cdot v^2}{r} = q \cdot v \cdot B
\]

\[
v/r = \omega = q \cdot B/m
\]

where \( m \) is the ion mass and \( \omega \) is the ion cyclotron resonance frequency. At thermal velocities, around 200 m/s, the orbit radius is on the order of a few tenths of a mm. Since the ions are all formed in the center of the \( xy \) plane of the cell their cyclotron motion traps them there for the duration of the trapping time.

Although the ions are constrained in the \( xy \) plane by their circular orbit, they can still drift freely along the \( z \) axis
parallel with the magnetic field. Ions are trapped along this
direction by applying a positive DC potential, typically 2-4 volts,
to trapping plates situated on either end of the cell and
perpendicular to the z axis. Positive ions are trapped in the
minimum of the electrical potential well halfway between the two
trapping plates. The result of the ion trapping is an ion cloud
that is within 1 mm of the center of the cell in the x, y and z
directions.

Ion Ejection. During the trapping time ions of one mass or
range of masses can be removed from the cell by resonant ejection,
wherein a pulse of radio frequency radiation, equal in frequency to
the ion's cyclotron frequency, is applied to the cell and absorbed
by the ions. This increases the ion's orbital radius until it hits
one of the plates where it is neutralized and effectively removed
from the cell.

Ion Detection. Toward the end of the trapping period the ions
are detected by the excite/detect pulse sequence. The ions have
thermal velocities with a cyclotron orbital radius of several
tenths of a mm. Since they were all formed at the center of the
cell they are confined to a volume of not more than 1 mm in
diameter at the center of the cell.

To detect the ions it is necessary to first excite them to a
larger orbit that will carry them closer to the cell plates. This
is accomplished by irradiating the ions with an RF waveform, having
a frequency equal to \( \omega \), the ion's cyclotron frequency. This
resonant RF signal is applied to the two transmitter plates, for
several tens of microseconds, during the excite pulse as discussed in the Excite Circuit section. Because the ions absorb energy from the resonant signal they are accelerated and their linear velocity, \( v \), increases. This causes the ions to follow a path that spirals outward while the resonant RF excite signal is applied to the transmitter plates. The excite pulse length is adjusted to bring the ion's orbit close to the cell plates without touching them, a necessary condition for ion detection.

As the positive ions pass near the receiver plate electrons are attracted to it because of the electric field of the ions and an induced current (image current) flows through a wire attached to the receiver plate.\(^2\) This image current is typically around 0.1 nanoamp for 1000 ions and is given by \( I = N \cdot q \cdot v/d \), where \( q \) is the charge per ion, \( N \) is the number of ions, \( v \) is their velocity toward the cell plate and \( d \) is the separation of the cell plates.\(^2\) Because of their circular motion the ions pass first near one receiver plate then near the other. This induces, on the receiver plates and in the attached detect circuitry, a sinusoidally varying current having a frequency equal to the ion's cyclotron frequency and an amplitude proportional to the number of ions. Measuring this amplitude and frequency during the one or three millisecond detect pulse, as described in the Detection Circuit section, gives the mass and abundance of the ions.

**Ion Removal.** At the end of the trapping period all the ions are removed from the cell in preparation for the next trapping cycle by the quench pulse. One trapping plate is momentarily pulsed
to +20 volts while the other is pulsed to -20 volts.
ELECTRONICS:

**Excite Circuit.** The excitation circuit is shown in figure 3. A 4066 gate chip is used to gate the Rf excitation waveform generated by the WaveTek oscillator. In order to excite the ion cyclotron motion coherently the Rf excitation waveform applied to one transmitter plate must differ in phase by 180 degrees from that applied to the other transmitter plate, with both waveforms having the same resonant cyclotron frequency. This is accomplished by passing the gated Rf through a phase-splitter circuit which outputs two waveforms having the same frequency but one half the amplitude of the original Rf waveform, and differing in phase from each other by 180 degrees.

**Detection Circuit.** This circuit is shown in figures 4 and 5. The cyclotron motion of ions induces a sinusoidally varying current signal called the ion image current. These signals, one on each receiver plate, differ in phase from each other by 180 degrees but have equal amplitude and frequency:

\[ I_s(t) = \frac{N \cdot q \cdot v}{d} \sin(\omega_s t + \pi/2) \]

But \( v = \omega \cdot r \), so

\[ I_s(t) = \frac{N \cdot q \cdot \omega_s \cdot r}{d} \sin(\omega_s t + \pi/2) \]

Using equation 1 this becomes:

\[ I_s(t) = \frac{N q^2 r B}{m d} \sin(\omega_s t + \pi/2) \]
The first step in signal processing is to convert these current signals into voltage signals by passing each to ground through a 1 Meg ohm resistor. The voltage appearing across the resistor lags the current signal by 90 degrees because of the capacitive impedance of the remaining circuitry:\textsuperscript{3}

\[ V_s(t) = \frac{N \cdot q \cdot r}{d \cdot C} \sin \omega_s t \]

where \( C \) is the capacitance of the detect circuitry and \( \omega_s \) is the ion signal frequency. Note that, although the image current signal is inversely proportional to the ion mass, the voltage signal is independent of mass because of the capacitive nature of the detection circuit.\textsuperscript{3}

The two voltage signals, also differing in phase by 180 degrees, are each amplified by a JFET op-amp and then subtracted using a 715 op-amp configured as a difference amplifier. The resulting voltage signal has the same frequency as but twice the amplitude of the two input voltage signals. This is then multiplied with a reference signal by a Teledyne Philbrick 4456 multiplier chip giving a product signal:

\[ V_s(t) \cdot V_r(t) = 2A \sin \omega_s t \cdot [B \sin \omega_r t] \]

\[ = A \cdot B \left( \cos(\omega_s - \omega_r) t - \cos(\omega_s + \omega_r) t \right) \]

with \( A = \frac{N \cdot q \cdot r}{d \cdot C} \) and \( B \) equaling the amplitude of the reference signal. This reference signal, which is produced by the WaveTek excitation Rf generator, must be phase shifted by a variable angle \( \phi \) relative to the excite Rf because the ion signal lags the excitation signal by 180 degrees. The high frequency term of the
product signal (with the sum of frequencies in the argument) is filtered from the lower frequency term using a 10 kHz cutoff low pass filter to give:

\[ \text{Filtered } V_S(t) \cdot V_R(t) = A \cdot B \cos(\omega_S - \omega_R)t \] (2)

The process of multiplying by a reference signal and filtering out the high frequency component is called signal heterodyning.

This heterodyned signal is then integrated by the sample and hold integration circuit (shown in figure 5) which accumulates (or sums) the area under the sinusoidal signal for a time \( t \) by allowing it to build up charge on an "integrating" capacitor. At the end of accumulation this capacitor is allowed to discharge onto a second "hold" capacitor (which is actually where the signal is accumulated) across which the voltage is amplified and measured. The voltage across the "integrating" capacitor is reset to zero by grounding the capacitor during the first few microseconds of the next detect pulse before accumulation begins again.

The process of heterodyning followed by integration results in filtering out all but the sample frequency. To see this, note that the time integral of equation 2 (or for that matter any periodic signal) taken over a whole number of cycles is always zero unless \( \omega_S \) is equal to \( \omega_R \) which is true only if the instrument is on resonance (i.e., if the WaveTek signal generator is tuned to the sample frequency, \( \omega_S \)). Therefore, the output from the integration stage is a non-zero linear function of time proportional to the ion signal amplitude, \( A \), only when the reference signal frequency is
equal to the sample signal frequency:

\[ \text{Resonant Integrated Signal} = A \cdot B \cdot t \]

The voltage across the "hold" capacitor at the end of accumulation is a time independent DC voltage given by evaluating \( A \cdot B \cdot t \) at the acquisition time \( t \).

Figure 6 shows the signal waveform at several points in the detect circuit of figure 4 when the instrument is on resonance.

**Timing Circuit.** Each icr pulse sequence is initiated by a TTL signal (a +5 to 0 negative going voltage or edge) from one side of a 556 master timing chip. This clocking signal initiates the timing for the grid pulse, the excite/detect pulses and the quench pulse. All pulses are controlled by their own 556 timing chips except in the case of the excite pulse where a 74221 timing chip is used. Both types of timing chip are triggered by a +5 to 0 volt negative going edge. The length of all timed intervals and pulses are controlled by the time constants of RC circuits that are wired externally to the various timing chips. Most of these RC circuits incorporate a variable resistance (usually a 10 turn pot) giving the operator control over the lengths of pulses and timed intervals. TTL logic is used throughout the timing circuit.

The grid pulse is generated by the other side of the 556 master timing chip immediately after the clock signal and controls the circuitry which drives the grid voltage from -8 volts relative to the filament to ground allowing the electrons to pass from the glowing filament through the grid into the cell. The length of this pulse is adjustable from the front panel.
The excite/detect pulse sequence is controlled by a 74221 timing chip. As soon as it receives a negative going edge from the master clock it begins timing a delay (the excite pulse delay) for a period determined by an RC timing circuit. The length of this delay was put under computer control and the 74221 triggered by a signal from the laser for the time resolved experiments (See the section entitled “Computer Control of Experiments”). After this delay the 74221 simultaneously triggers two more TTL chips: i) It sends a positive going pulse (the excite Rf shutter pulse) to a 4066 analog switch momentarily closing it thereby completing the circuit between the excite Rf generator and the transmitter plates, giving the Rf excite pulse. ii) It also sends a negative going edge to the detect 556 timing chip beginning the detect delay period. At the end of this delay the detect 556 sends a positive going pulse (the detect gate pulse) to a 4066 analog switch momentarily closing it and completing the circuit between the low pass heterodyne filter and the integrating capacitor. The operator has control over the lengths of the excite pulse delay, the detect delay, the detect gate pulse and the excite shutter pulse from the front of the panel.

The master clock signal is also sent to another 556 timing chip to initiate the timed delay to the quench pulse. At the end of this delay the quench 556 sends a pulse to circuitry that biases one trapping plate to -20 volts and the other to +20 volts. The delay from master clock signal to quench pulse is adjustable from a pot on the front panel.
In addition the master timing signal initiates the timing for external circuitry such as that controlling the timing for firing a laser, opening a shutter, opening a pulsed valve, switching Rf for double resonance ejection of ions or sending timing pulses to a computer.
COMPUTER CONTROL OF EXPERIMENTS:

If experimental conditions give low signal to noise ratios a common solution is to signal average over many accumulated data points. This technique was required in the Time Resolved experiment in chapters VI and VII.

A block diagram of the instrument as it was configured for the Time Resolved experiment is shown in figure 7. A Heath Zenith computer is connected to the instrument through a Serial Lab Products Interface box (model SL-800). A BASIC program called TRESOLVE is used to control the interface box. As in the normal mode of operation each trapping cycle is initiated by the master clock pulse. However, the excite/detect sequence is triggered by a signal from the laser, which is coincident with laser firing and is delayed from the master clock pulse by a Laser Delay Timing Circuit. In addition the delay from the laser to the excite/detect sequence is under computer control. The operator chooses an appropriate range of delay times, the number of delay times in the range and the number of times the instrument is to scan through the time range. The program then calculates and stores values of each delay time, \( r \), which it uses to update the delay for each new trapping cycle. The sequence of events from the point of view of the interface box is as follows (the delay \( r \) has already been set in the previous trapping cycle):

1) The interface box monitors the master clock to detect the start of a new trapping cycle.
2) At the beginning of the new trapping cycle the program instructs the interface to sample the ion signal which was held over from the previous trapping cycle by the sample and hold circuit.

3) The interface box is then instructed to change the delay, $r$, to the next value calculated by the program. The laser is fired and after this updated $r$ the ions are again detected during the excite-detect sequence and the new ion signal is held over into the next trapping cycle by the sample and hold circuit.

4) The interface box monitors the master clock to detect the start of the next machine (trapping) cycle.

These steps are repeated until the ion signal has been sampled at each delay in the time range chosen, after which the delay is changed back to its initial value and the above steps repeated. In this way the time range is scanned the number of times chosen by the operator. All values of the ion signal taken at the same delay $r$ are averaged together.
VACUUM SYSTEM AND SAMPLE INTRODUCTION:

Vacuum System Description. The vacuum system is pumped by a horizontally mounted Balzers turbomolecular pump backed by a diffusion pump which itself is backed by a mechanical pump. A baffle is mounted between the turbo and the rest of the vacuum system. It can be closed to reduce the pumping speed but is usually left completely open. The distance from the turbo to the ICR cell is about 30". All vacuum connections are made with flanges of the conflat type sealed with Cu gaskets. An unobstructed optical path into the ICR cell is provided through a sapphire window mounted in the vacuum can. The entire high vacuum region is wrapped with heating tape and can be baked out at about 700 C.

Pressure Measurement. The pressure in the low pressure vacuum system is measured by an ionization gauge tube and is read off from Veeco model RG-83 ionization gauge tube controller. The gauge tube communicates with the vacuum system through a 4" long 5/8" ID tube and samples vacuum system pressure 18" from region of the cell.

Two corrections must be applied to the observed pressure readings to obtain the true pressure. i) First because there is a variation in the cross section of various neutrals for electron impact ionization, ionization gauges have different sensitivities to different molecules. The sensitivity of an ionization gauge to a molecule X is defined as \( P_X(\text{observed})/P_X(\text{true}) \). 4 Most gauges are calibrated by the manufacture to read the true pressure for nitrogen. 4 This sets the gauge sensitivity for nitrogen equal to
1. Since ionization gauges are more sensitive to larger molecules and less sensitive to smaller molecules they read high for larger molecules and low for smaller molecules. For this reason it is necessary to correct the observed pressure reading by dividing it by the sensitivity ratio, \( R_X = S_X / S(\text{nitrogen}) \); where with \( S(\text{nitrogen}) = 1 \), \( R_X = P_X(\text{observed}) / P_X(\text{true}) \). This ratio has been found to correlate well with molecular polarizability, \( \alpha \): \( R_X = 0.36\alpha + 0.30 \). Since average molecular polarizabilities can be calculated for many molecules using an empirical approach, based on the principle of additivity, this gives a convenient way to calculate the ionization gauge sensitivity for a molecule. ii) Because the cell is some distance from the point where the pressure is measured, the observed pressure (even after correction for sensitivity) may not be the actual neutral pressure inside the cell. Correcting for this requires checking the (sensitivity corrected) observed pressure against the pressure inside the cell calculated from the measured collision rate. The pressure inside the cell is calculated as follows: Assume that a reactive fragment reacts with a neutral on each collision, i.e., that the reaction rate equals the collision rate. Measure the rate of disappearance of the fragment which, by assumption, is equal to the orbiting (langevin) collision rate constant times the neutral pressure in the cell.

Sample Introduction. A sample must have a high enough vapor pressure to be introduced into the sample manifold as a vapor at room temperature with a partial pressure of at least about 0.005
Torr. The sample manifold is divided into two halves each with its own sample inlet port for a ground glass joint sample container. Each half is pumped by the same 3" diffusion pump backed by a mechanical pump and can be isolated from the other and from the manifold pumping by valves. Both halves communicate with the high vacuum region through their own leak valves.

Samples are used straight from the bottle with no purification. Air is removed from the sample by taking it through several cycles of freeze, evacuate, thaw while in the sample container on the inlet port.

The entire sample manifold is contained in an insulated box that can be baked out at about 70°C.
LASERS AND OPTICAL COMPONENTS:

Lasers, the only light sources used in this thesis, have the advantage of producing very well collimated, high intensity monochromatic light without the use of lenses, monochromator or optical filters.

A continuous Ar ion laser (Coherent model CR-12) with a choice of wavelengths at 514.5, 501, 488, 475 and 457 nm was used for much of this work. This laser could be used to irradiate the ions directly or its 514.5 nm output (5 Watts available) or all lines output (12 Watts available) could be used to pump a Coherent model 490 dye laser. The dye laser could then be used to irradiate the ions with several tenths of a Watt of monochromatic light tunable over a wavelength range of 544 to 640 nm, depending on the dye used. The output from either continuous laser could be chopped or pulsed using a notched wheel or an electrically operated mechanical shutter.

Two pulsed lasers, each producing 10 nsec pulses, were also used in the work presented in this thesis. i) The first, a Lumonics Excimer laser which when filled with a mixture of HCl and Xenon produced pulses of light at 308nm with an energy up to 40 mJ per pulse. This was sometimes used to pump a Lumonics dye laser which was used to produce monochromatic light at 538.6 nm at an energy of about 10 mJ per pulse. ii) A Lumonics YAG laser, model HY1200, which lased at 1064 nm at energies up to 1.2 J per pulse. This fundamental wavelength could be doubled (giving 532 nm at 500 mJ per pulse), tripled (giving 355 nm at 220 mJ per pulse) or
quadrupled (giving 266 nm at 80 mJ per pulse). Any of these wavelengths could be used to pump a Lumonics dye laser model 300, generating 8 nsec pulses of monochromatic light between 420 to 700 nm (depending on the dye used) at a pulse energy of up to 50 mJ. Both pulsed lasers could be triggered at a constant pulse rate from a circuit within the laser or at a rate controlled from an external timing circuit.

Two light meters were used to measure the laser output. A Coherent analog power meter using a thermocouple detector was used to measure the laser power. A Scientech surface absorbing thermocouple detector was used to measure either average power or pulse energy. The measured value was displayed by the digital LED read-out of the meter.

Spectral purity and accuracy of the laser output were checked by looking at the scattered laser output with a Schoffel monochromator model GM 250. In all cases the output consisted of a single narrow band of wavelengths less than 0.05 nm wide.

Optical filters were often used to attenuate the energy of the laser beam. This affected the beam profile less than adjusting the power to the laser would. Beam steering was done by using mirrors or right angle prisms. Quartz lenses and prisms were used with all wavelengths shorter than 400.
REFERENCES:


FIGURE CAPTIONS:

1. ICR ion trapping cell of the instrument used for the work presented in this thesis.
2. A typical pulse sequence.
3. Circuit used to excite the trapped ions.
4. Circuit used to detect the cyclotron motion of the ions in trapping cell.
5. Detail of the sample and hold integration circuit portion of the detect circuit shown in figure 4.
6. Signal waveform at several points (Ia, Ib, II, III and IV) in the detect circuit of figure 4.
7. Block diagram of the instrument as it was configured for the Time Resolved experiment.
Image Currents at points Ia and Ib.

\[ I_s(t) = \frac{N q^2 r B}{m d} \sin(\omega_s t + 90) \]

\[ = \frac{N q^2 r B}{m d} \sin(\omega_s t + 90 - 180) \]

Difference Voltage at point II.

\[ V_s(t) = \frac{2 N q r}{d c} \sin \omega_s t \]

Reference Voltage at point III.

\[ V_r(t) = B \sin \omega_r t \]

Multiplied Voltage at point IV (on resonance).

\[ V_s(t) \cdot V_r(t) = \frac{N q r}{d c} \sin \omega_s t \cdot B \sin \omega_r t \]
SECTION ONE

PHOTOPHYSICS OF GAS PHASE IONS
CHAPTER THREE

RADIATIVE RELAXATION RATE OF THIOPHENOL BY THREE METHODS
INTRODUCTION:

The very slow process of vibrational energy loss from isolated gas phase molecules is well suited to study using trapped ion techniques. Alone among convenient laboratory techniques this has the possibility of holding isolated molecules under observation for a long enough time for significant energy loss to occur. The rates of such relaxations are of interest in understanding chemical and physical processes in natural molecule isolating environments such as near earth space and interstellar clouds, but their laboratory study has been slight because of lack of useful methods.

Our laboratory has developed several approaches to study of slow relaxations of isolated ions in the ion cyclotron resonance (ICR) ion trap.\textsuperscript{1-5} Among these are several techniques exploiting the characteristics of sequential two photon dissociation at appropriate photodissociating wavelengths.\textsuperscript{3-5} It is the purpose here to apply three methods based on this theme to measurement of a particularly challenging relaxation system, that of thiophenol ion. The radiative relaxation of this ion is exceptionally slow, and it is of interest to see how well the various approaches succeed in this system, and also to establish the rate of radiative relaxation of thiophenol ion with more confidence than any one measurement would provide.

The sequential two photon dissociation sequence first proposed by Freiser and Beauchamp\textsuperscript{6} in the trapped ion environment postulates the successive absorption of two photons, as in the scheme
The energy of the first photon is rapidly converted to vibrational excitation of the ion, which may then exist in its vibrationally hot state A** for a long time. The relaxation process k3, which may be collisional or IR-radiative, competes with second photon absorption to provide the ultimate removal of this A** species. The two photon nature of the dissociation is reflected in various aspects of the kinetics, including light intensity dependence and time evolution of the A+ abundance, and with suitable experiments these kinetic characteristics can be exploited to characterize the k3 relaxation process.

In relaxation experiments based on two photon dissociation an ion is considered as "relaxed" when its internal energy falls below the one photon threshold (the energy which, when added to the energy of one laser photon, is sufficient to bring about dissociation). In thiophenol ion, the thermochemistry of the dissociation reaction

\[ \text{C}_6\text{H}_5\text{SH}^+ \rightarrow \text{C}_5\text{H}_6^+ + \text{CS} \]  

is known with reasonable confidence\(^8\) (assuming the product ion to have the cyclopentadiene structure, which is the most stable known \(\text{C}_5\text{H}_6^+\) ion, and has been found in various experiments to be the product of this reaction).\(^9\) The activation energy is 3.2 eV,\(^10\) and for 514.5 nm photons, the one photon threshold lies at 0.8 eV.
Thus the relaxation process under observation in these experiments is that which takes the ions from their initial internal excitation energy to below 0.8 eV.\textsuperscript{10}

In the two pulse and chopped laser experiments, the initial excitation energy is about 2.5 eV (2.41 eV from the photon plus about 0.1 eV of average thermal energy). In the intensity dependence experiment, the initial energy is that of the electron impact produced ions. This is certainly a broad distribution, and is not known, although some speculation based on the photoelectron spectrum was given in reference 5. As a rough basis for thinking, it can be supposed that the ions initially lying between 0.8 and 3.2 eV are uniformly distributed, so that the average initial energy assignment appropriate for interpretation of the intensity dependence experiment would be approximately 2.0 eV.

As has been discussed previously, the relaxation mechanism and resulting relaxation kinetics are expected to be different for collisional relaxation and IR-radiative relaxation.\textsuperscript{11} For collisional relaxation by charge transfer with parent neutral, it is reasonable to suppose that a single charge transfer collision will result in a relaxed parent ion, and the appropriate kinetics for such a case, which lead to exponential time decay of internal energy, have been termed rate process kinetics. For IR-radiative relaxation, on the other hand, relaxation occurs through a cascade of perhaps 20 successive IR photon emissions, and the resulting energy decay, which exhibits a significant induction time followed by rapid disappearance of excited ions, has been designated cascade
kinetics.

A previous study of the two photon dissociation and relaxation of thiophenol ions by the intensity dependence approach was described.\textsuperscript{5} A collisionless relaxation rate of 3 s\(^{-1}\) was reported there. The present results are based on a more extensive and satisfactory data set, but give nearly the same result.
THE THREE METHODS:

Two-pulse Method\textsuperscript{3}. The pulse sequence for this experiment is shown in figure 1. After electron impact formation of the ions, they were allowed to thermalize for 2.5 s before the first laser pulse. The second laser pulse followed after a variable delay time $T$, and ICR detection of the extent of photodissociation was carried out 20 ms after the second laser pulse. As has been discussed in detail,\textsuperscript{3} information about energy relaxation derives from observing, as a function of the delay $T$, the amount of photodissociation which occurs in excess of that expected if the two pulses were widely separated in time. This excess arises because of the presence of not-yet-relaxed ions excited by the first pulse, at the time of arrival of the second pulse. At the limit of long delays no ions should remain above the one photon threshold, so here the dissociation should equal two times the single pulse value. The relaxation rate is most conveniently derived from the data by fitting to a computer generated simulated curve, in which the variables in the simulation are the relaxation mechanism (rate law, cascade, or other), relaxation rate, and absorption rates for the first and second photons.

See the appendix to this chapter for further discussion on this method.

Chopped-laser Method\textsuperscript{4,11}. It has been shown that instead of two light pulses, a series of repetitive pulses may be used to illuminate the ions, as diagrammed in figure 2, and relaxation rate information extracted from the dependence of dissociation on the
pulse repetition rate. This approach has the advantage of delivering more light to the ions in the course of the ion trapping period. This gives a greater extent of dissociation as compared with the two pulse method with a similar laser, and makes the measurements more precise for a given extent of signal accumulation, leading to a faster experiment.

Following electron impact formation, the ions were allowed to thermalize for 2 s. They were then illuminated with the chopped laser for 4 s, and ICR detection of the extent of dissociation followed the end of the illumination period by tens of ms. Because of concern that the charge transfer regeneration of parent ions might in some way distort the results (although the chopped laser method is not expected to be perturbed by such a regeneration), some of the experiments included continuous double resonance ejection of the m/e 66 daughter ions. In this case the ejecting rf of about 0.4 V/cm was applied at the daughter ion frequency during the entire illumination period.

Intensity-Dependence Method. This approach depends on the fact that the light intensity dependences of one photon and two photon dissociations are different, being respectively linear and approximately quadratic. The progressive relaxation of initially excited ions to an energy below the one photon threshold is monitored by an intensity dependence measurement at a variable delay T after the electron beam pulse, as shown in figure 3. The intensity dependence at a given delay T is actually measured by determining the ratio of dissociation produced by light pulses
differing in intensity by a factor of 2.
EXPERIMENTAL:

All work described here was carried out on a homebuilt ICR mass spectrometer previously described,\textsuperscript{4,12} using phase sensitive bridge detection in the 1.4 T electromagnet. Ion formation was by electron impact at a (nominal) electron energy of 12 eV. Following the appropriate thermalization and laser irradiation periods, ions were excited by the rf excite pulse of 100 $\mu$s duration, and observed during the 4 ms acquisition period. The extent of photodissociation was monitored by the laser induced decrease in parent ion intensity.

Pressure estimation in these experiments was rather uncertain. The ionization gauge used has been found in calibrations for simpler gases at high pressures to follow the literature corrections\textsuperscript{13} quite well, but this probably does not hold very well for thiophenol at the pressures used here. The best indication of the true thiophenol pressure calibration was derived from the ion molecule reaction

\[
\text{C}_6\text{H}_5\text{SH} + \text{C}_5\text{H}_5^+ \rightarrow \text{C}_6\text{H}_5\text{SH}^+ + \text{C}_5\text{H}_5
\]

which is believed to occur with near collisional efficiency. Its rate was measured at various gauge pressures in the 1-10x10\textsuperscript{-8} Torr range. Assuming a reaction rate constant of 1x10\textsuperscript{-9} cm\textsuperscript{3}·molec\textsuperscript{-1}·s\textsuperscript{-1}, the observed rates of the reaction indicated that true thiophenol pressures were of the order of .4 times the ionization gauge readings.

It was the aim of these experiments to observe collisionless
relaxation, but in fact the sample pressures used were probably not quite low enough to remove all collisional component of relaxation, since the radiative relaxation is very slow, while collisional relaxation is very efficient. As described below, this was clearly indicated by the deviation of the relaxation curve in the two pulse experiment from pure cascade kinetics. The best estimates of pressure suggest a collisional quenching rate of 0.6-0.8 s\(^{-1}\) for the two-pulse and chopper experiments, and 1 s\(^{-1}\) for the intensity dependence experiment (assuming highly efficient quenching by parent neutrals, presumably by resonant charge transfer, at a rate of 1\times10^{-9} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}). These values, while very approximate, provide the basis for a collisional correction in assigning the radiative relaxation rates.

The light source was the 514.5 nm line from the Coherent Radiation CR12 argon ion laser (upgraded to I-12 configuration). Laser pulses were produced by a mechanical shutter which was accurate and reproducible to within 2.5 ms. In the two pulse experiment the continuous laser power was about 1 W, with the beam expanded to a diameter of 3.5 cm at the vacuum window. In the chopped laser experiment the 4 s irradiation period was gated by the mechanical shutter, while the laser was chopped mechanically by a set of toothed chopper wheels with 9% duty factor. The chopper wheels were calibrated, and small corrections applied to the data assuming square law intensity dependence of photodissociation. The laser was expanded to a diameter of 2 cm. In the intensity dependence experiment the low intensity measurement was made using
a filter which attenuated the laser intensity by a factor measured as 2.08.
RESULTS:

Two-pulse method. In figure 4 is displayed a data set for the dissociation of parent ions as a function of delay time between the two pulses. About 23% of the ions were dissociated at zero delay, falling to about 13% at long delays.

In order to extract a relaxation rate constant from these data the points were fitted to a computer simulation of the two pulse kinetics. It was not possible to fit the data with a decay curve for pure cascade decay kinetics, which would be appropriate to pure IR-radiative relaxation. Such a curve is plotted as the upper dashed curve in figure 4a, and clearly has the wrong shape. However, it was found that the shape of the curve is extremely sensitive to even a small amount of collisional relaxation (assuming rate process kinetics for collisional relaxation). The solid fitted curve in figure 4a is calculated assuming a collisional relaxation rate constant (rate-process kinetics) of 0.8 s\(^{-1}\), and a radiative rate constant (cascade kinetics) of 3.3 s\(^{-1}\). (The "rate constant" for radiative relaxation is taken to be the inverse of the time required to relax 2/3 of the ions). The fit to the data appears to be satisfactory using this kinetic model and these rates. For comparison, the lower dashed curve in figure 4a is calculated from the pure rate process model, which would be appropriate for efficient collisional quenching: This model is not expected to describe the relaxation under these low pressure conditions, and indeed does not give a satisfactory fit to the data.
As an indication of the uncertainty in the radiative rate constant determination figure 4b shows the fitting curves drawn using values of 3.0, 3.3 and 3.6 s\(^{-1}\) (with a corresponding proportional variation in the contribution of 0.8 s\(^{-1}\) assigned to collisional relaxation). It appears that all of these fits are reasonable, although the preferred value of 3.3 s\(^{-1}\) is superior to the others.

**Intensity Dependence Method.** In figure 5 is displayed the change in the intensity dependence ratio as a function of time following the electron beam pulse. It is clear that right after the beam pulse the intensity dependence is near to the linear behavior of one photon dissociation, and that it changes over the course of about a second to the quadratic behavior of two photon kinetics. The solid curve on the figure shows the result of the detailed simulation, using a relaxation rate of 5 s\(^{-1}\) to characterize the decay of the electron beam generated population below the one photon threshold, and assuming that 50% of the nascent ions from electron impact ionization lie above the one photon threshold. The fit appears quite satisfactory.

At the pressure of thiophenol used in this experiment the rate of collisional relaxation is expected to be about 1 s\(^{-1}\). Accordingly, the radiative component of relaxation can be assigned as about 4 s\(^{-1}\).

These results are in reasonable accord with the previous measurement by the same technique,\(^5\) but the present more extensive data set warrants more confidence. The present experiment at 12 eV
(as opposed to 17 eV) ionizing energy might be expected to give ions of somewhat lower average initial excitation and correspondingly faster relaxation; the higher initial one photon fraction (50% vs 40%) and faster relaxation rate (4 s\(^{-1}\) vs 3 s\(^{-1}\)) found in the present experiment appear to bear this out, although the differences are marginally significant. The overall indication is that the ion population produced at 12 eV does not differ in a major way from that produced at 17 eV.

**Chopper-Frequency Dependence Method.** This relaxation process is at the lower limit of feasibility for the chopped laser technique, but meaningful results were still possible. Most of the chopper rate dependence is expected to take place between 1 Hz and 2 Hz, so data were collected at 1, 2, 3 and 18 Hz. As shown in figure 6, the drop in dissociation between 1 and 2 Hz is indeed large, but there is little further change between 2 and 18 Hz. Plotted on the figure is the simulated curve assuming a relaxation rate of 2.6 s\(^{-1}\), which gives a reasonable fit to the data. Assuming a collisional relaxation component of 0.6 s\(^{-1}\), the radiative relaxation can thus be assigned as 2.0 s\(^{-1}\).
DISCUSSION:

Comparison of Methods. It is useful to compare these three methods in terms of ease and quality of data acquisition; susceptibility to artifacts; and interpretability of the results. We can first summarize our experience with the general characteristics of the three methods, and then discuss their relative performance in the study of thiophenol ion.

The two pulse method, using the gated cw laser, has been found to require extensive data collection, while still showing substantial scatter of the points, because of the difficulty in obtaining sufficient dissociation with too short, weak pulses and because the relaxation effects lead to only modest changes in the extent of dissociation. Finite pulse width limitations limit use of this approach to relaxations slower than perhaps 5 s⁻¹. (The laser intensity problem should be alleviated with the use of a pulsed laser.) It is also subject to significant artifacts due to spreading of the ion cloud between the two pulses, unless the laser beam is homogeneous over the cell volume. Interpretation is very straightforward, since the excited ion internal energy is well known after the first pulse, and the relaxation is followed directly as a function of time.

The chopped laser method can be looked at as a variation of the two pulse approach. By comparison, it alleviates the intensity problem, permits use of a cw laser to look at fast relaxation processes, and is free of cloud spreading artifacts. However, interpretation is less straightforward, and the relaxation process
is not directly displayed as a function of time.

The intensity dependence method is comparable to the two pulse method in the amount of data collection required and scatter of the data. It is free of cloud spreading artifacts. In the present implementation, where the initial ion excitation is by electron impact ionization, interpretation is not straightforward, since the initial distribution of ion internal energies is unknown. If ion excitation were carried out more cleanly, as by photoexcitation, this would be a very attractive mode of operation, since the relaxation is displayed directly versus time.

Two characteristics of thiophenol ion; its slow relaxation and its high photodissociation cross section, make the two pulse technique especially suitable in this case. As has been seen, it was possible to obtain a two pulse data set of sufficient quality to give a clear picture of the time dependence of the relaxation process, making the interpretation straightforward. The intensity dependence method gave data of similar quality and yielded similar relaxation rates, but had a less straightforward interpretation because of the unknown nature of the initial distribution of ion internal energies. The chopped laser method was, in this work, unable to exploit its advantages of high effective laser intensity, freedom from cloud spreading artifacts with a focused beam, and ability to resolve fast relaxations. Accordingly, the chopped laser results, while concordant with the other techniques, were unimpressive for this ion. (However, these assets have been invaluable in work with other ions, like benzene ion).
Thiophenol Ion Collisionless Relaxation Rate. Three separate results are reported above for the collisionless relaxation time scale of thiophenol ions, starting with an internal energy approximately in the 2-3 eV region, and relaxing to below 0.5 eV.\textsuperscript{10} If we assume as we have done in the past\textsuperscript{4} that the radiative decrease in ion internal energy can be described by an exponential decay, the first order rate constant for this cooling process is $5.2 \text{ s}^{-1}$ from the two pulse result, $5.2 \text{ s}^{-1}$ from the intensity dependence result, and $3.22 \text{ s}^{-1}$ from the chopped laser result. There is rough agreement among the three results, of which the value of $5.2 \text{ s}^{-1}$ from the two pulse experiment is most satisfactory, giving us confidence that this relaxation process has a time constant of about $1/3$ second. Of the polyatomic ions which we have studied in this regime of internal energies, this has the second slowest radiative relaxation rate constant, only iodobenzene ion ($2.9 \text{ s}^{-1}$) being slower.\textsuperscript{3,4}
CONCLUSIONS:

It is encouraging to find that all three of these methods could be applied to this relaxation problem to give concordant results. The two pulse method is the most convincing and satisfactory, and is in general the method of choice for drawing information about relaxation behavior from two photon kinetics. The power dependence and chopped laser methods can have advantages in special circumstances, and the present results verify their validity even in studying such a very slow relaxation. The radiative relaxation of this ion is slower than most previously studied benzene derivative ions; a number of such ions have been found to relax significantly faster than expected based on radiative properties of neutral molecules, but thiophenol ion has a rate close to the expectation based on similar neutrals.
APPENDIX FOR TWO PULSE METHOD:

PART I:

Although the experimental results were modeled assuming laser pulses of finite width (40 ms), it is useful to consider the simpler case of laser pulses of very narrow width, dt. In this case radiative and collisional loss of internal energy occurs only between laser pulses. Equation A1, which gives the fraction of ions remaining after two short laser pulses of width dt, is derived in part II of this appendix from the sequential two photon dissociation model of Freiser and Beauchamp (reaction scheme III in chapter 1).

\[
\frac{([A^+]+[A^{++}])}{[A^+]_0} = (1+kdt)^2 e^{-2kdt} - (kdt)^2 e^{-2kdt} \exp(-k_T t) \quad (A1)
\]

Of interest in the two pulse experiment is the fraction of ions dissociating in excess of the fraction dissociating at very long delay time \((T \to \infty)\). For the special case of short pulse width, this excess dissociation can be derived using equation A1.

\[
(FR)_T - (FR)_{T \to \infty} = (kdt)^2 e^{-2kdt} \exp(-k_T t) \quad (A2)
\]

The fraction of ions remaining after a single laser pulse is given by A3 also derived in part II of this appendix.

\[
(FR)_{\text{single pulse}} = (1+kdt) e^{-kdt} \quad (A3)
\]

Regardless of the relaxation rate, the model chosen for
relaxation or the laser pulse width the amount of dissociation at long delay time is entirely determined by the amount of dissociation at short delay times. This relationship is given by equation A4.

\[
\frac{(FR)_{T=0} - (FR)_{T=\infty}}{(FR)_{T=\infty}} = \frac{(kdt)^2}{(1+kdt)^2}
\]  \quad (A4)

Equation A4 can be used to check the data for experimental artifacts, such as those caused by parent ion regeneration, ion cloud spreading or saturation of dissociation (ion cloud hole burning) by the first laser pulse. These have been extensively discussed elsewhere.\textsuperscript{3,4}
PART II (Derivation of equation A1):

In deriving equation A1 the following assumptions were made.

1) The initial light off ion population consists entirely of ground state parent ions, denoted as $A^+_0$. The initial light off excited state parent ion abundance, $A^{**}_0$, is zero.

2) Excited parent ions, $A^{**}$, have internal energies between $E_0 - h\nu$ and $h\nu$, where $E_0$ is the fragmentation threshold. All other ions, denoted $A^+$, have internal energies below $E_0 - h\nu$.

3) Relaxation of internal energy during the short laser pulse, of width $dt$, is negligible.

4) Photon absorption is, as indicated in scheme 1, a first order process with rate $k$.

After the first laser pulse ($L_1$):

\[
\frac{dA^+}{dt} = -k A^+ \\
[A^+]_{L_1} = A^+ e^{-kdt} \tag{A5}
\]

\[
\frac{dA^{**}}{dt} = k A^+ e^{-kdt} - k A^{**} \\
[A^{**}]_{L_1} = A^{**} e^{-kdt} + A^+ kdt e^{-kdt} \tag{A6}
\]

Equation A3 can be derived using equations A5 and A6. During the dark time between laser pulses the parent ions lose internal energy with a rate $k_r$. So after the dark period:
\[ [A^{**}]_D = [A^{**}] \exp(-k_T T) \]
\[ = -A^{**} e^{-kdt} \exp(-k_T T) + A^+ kdt e^{-kdt} \exp(-k_T T) \]
\[ + A^{**} e^{-kdt} \exp(-k_T T) \]
\[ (A7) \]

\[ [A^+]_D = [A^+]_L + ([A^{**}]_L - [A^{**}]_D) \]
\[ = A^+ \left( kdt e^{-kdt} + e^{-kdt} - kdt e^{-kdt} \exp(k_T T) \right) \]
\[ + A^{**} \left( e^{-kdt} - e^{-kdt} \exp(-k_T T) \right) \]
\[ = A^+ \left( kdt e^{-kdt} + e^{-kdt} - kdt e^{-kdt} \exp(k_T T) \right) \]
\[ (A8) \]

After the second laser pulse (L2):

\[ [A^+]_L = [A^+]_D e^{-kdt} \]
\[ = A^+ \left( kdt e^{-2kdt} + e^{-2kdt} - kdt e^{-2kdt} \exp(-k_T T) \right) \]
\[ + A^{**} \left( e^{-2kdt} - e^{-2kdt} \exp(-k_T T) \right) \]
\[ = A^+ \left( kdt e^{-2kdt} + e^{-2kdt} - kdt e^{-2kdt} \exp(-k_T T) \right) \]
\[ (A9) \]

\[ [A^{**}]_L = [A^{**}]_D e^{-kdt} + [A^+]_D kdt e^{-kdt} \]
\[ = A^+ \left( kdt e^{-2kdt} \exp(-k_T T) + (kdt)^2 e^{-2kdt} + kdt e^{-2kdt} \right) \]
\[ - (kdt)^2 e^{-2kdt} \exp(-k_T T) \]
\[ + A^{**} \left( e^{-2kdt} \exp(-k_T T) + kdt e^{-2kdt} \right) \]
\[ - kdt e^{-2kdt} \exp(-k_T T) \]
\[ = A^+ \left( kdt e^{-2kdt} \exp(-k_T T) \right) \]
\[ + (kdt)^2 e^{-2kdt} + kdt e^{-2kdt} \]
\[ - (kdt)^2 e^{-2kdt} \exp(-k_T T) \]
\[ (A10) \]
Inserting A9 and A10 into

\[
\left[ \frac{[A^+]_{L2} + [A^{**}]_{L2}}{A^+_0} \right]
\]

yields equation A1:

\[
\frac{A^+ + A^{**}}{A^+_0} = (1 + kdt)^2 e^{-2kdt} - (kdt)^2 e^{-2kdt} \exp(-k_T T).
\]
REFERENCES:


10. Subsequent work on this ion (reference 14 and chapter VII) has shown that the lowest energy fragmentation channel is loss of acetylene with an activation energy of 2.9 eV. This lowers the one photon threshold to 0.5 eV.


FIGURE CAPTIONS:

1. Pulse sequence for two pulse, two photon ion trap photodissociation experiment. The cooling time \( t \) between ion formation and the first laser pulse is chosen long enough for thorough ion thermalization, and the time \( T \) between pulses is varied.

2. Pulse sequence for chopped laser two photon dissociation. The pulse widths are varied along with the pulse rate so that the average power level remains constant.

3. Pulse sequence for intensity dependence determination of dissociation. Dissociation is compared for two light intensities differing by a factor of 2.08.

4a. Results for two pulse dissociation of thiophenol ions. The upper dashed curve (-----) shows the theoretical cascade relaxation shape; the lower dashed curve (----) shows the theoretical rate process shape; and the solid curve shows the calculated shape for cascade relaxation mixed with a small component of rate process collisional relaxation, as discussed in the text.

4b. The relaxation data and fitted theoretical curve from Fig. 4a are shown, along with two additional fitted curves using relaxation rates respectively 10% lower and 10% higher than the best fit values noted in the text.

5. Intensity dependence curve showing the dissociation ratio for two light intensities as a function of cooling time between ion formation and dissociation. The solid curve is the computer modeled curve assuming exponential ion cooling with a rate of 5.0 s\(^{-1}\).

6. Chopper rate dependence of dissociation. The solid curve is the computer modeled fit assuming exponential ion cooling with relaxation rate constant 2.6 s\(^{-1}\).
SECTION TWO

SPECTROSCOPY OF GAS PHASE IONS
CHAPTER FOUR

PHOTODISSOCIATION SPECTROSCOPY OF GAS PHASE

2-METHYL-1-PENTEN-3-YNE CATION
INTRODUCTION:

An interesting feature of the electronic spectroscopy of radical cations, in contrast to the corresponding neutrals, is the prevalence of hole promotion optical transitions, so that many such ions are strongly colored in the visible wavelength region. Since photoelectron spectroscopy (PES) also views these electronic hole states, visible and near UV optical peaks of a gas phase radical cation can often be compared usefully with PES features of the corresponding neutral molecule\(^1\). When the same ion excited state is observed by the two techniques, the spectral bands are expected to be similar, with differences expected chiefly in relative vibrational peak intensities due to differing Franck-Condon factors. It should be possible to compare geometries of the neutral molecule and the ion ground state by careful analysis of these Franck-Condon factor differences. Accordingly, cations of particular interest for PDS study at high optical resolution are those whose neutrals show well resolved vibrational structure.

Photodissociation spectroscopy (PDS) is a useful approach to optical absorption spectroscopy of gas phase ions\(^2\), but relatively few of the organic ions studied by this technique have shown vibrational fine structure sufficiently well resolved to make useful comparisons with PES spectra. Broadening of peaks due to a short excited state lifetime and congestion due to molecular flexibility may both contribute to this lack of vibrational resolution. Both of these resolution degrading features are alleviated by the skeletal rigidity of triple bonded subunits in
the ion; In accord with this expectation, a number of molecules having a triple bond in a conjugated \( \pi \) system show sharply resolved vibrational structure in their PES spectra\(^3\), making them promising candidates for high resolution PDS study. As a first exploration of the high resolution PDS of the radical ions of such molecules, we describe here the photodissociation spectroscopy of the conjugated enyne radical ion I,

\[
\begin{align*}
\text{CH}_3 & \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \\
\text{CH}_3 & \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \\
\end{align*}
\]

which displays sharply resolved vibrational structure in its neutral PES spectrum\(^4\), and add this cation to the small group of medium sized organic ions showing resolved vibrational peaks in their PDS spectra\(^5\).

Photoelectron spectra of a number of substituted enynes have been reported\(^3\), including\(^4\) I, and they typically show strongly resolved vibrational structure in several \( \pi^{-1} \) excited states. Some substituted acetylene ions fluoresce\(^6\) but fluorescence of the enyne ions has not been reported, so that absorption spectroscopic approaches, in particular PDS, offer the only known source of optical spectroscopic information. PDS results for several enyne radical cations were described earlier\(^7\), with all of them showing usefully strong photodissociation at visible wavelengths. The cation of I, which was not included in this earlier study, is particularly favorable for high-resolution PDS because its PDS
features span the visible wavelength region.
EXPERIMENTAL:

The use of photodissociation spectroscopy in the ion cyclotron resonance (ICR) ion trap to obtain optical absorption spectroscopic information about gas phase ions has been described extensively\(^1,^2,^8\). Two ICR instruments were used in this study. The PDS spectra were taken by monitoring dissociation of parent ions on a homebuilt ICR instrument previously described\(^7,^9\), using phase sensitive bridge detection. The photoproducts were determined from mass spectra over the m/z 30 to 100 mass range taken with a second ICR instrument equipped with an IonSpec Fourier transform data system. Both instruments have 2.5 cm cubical ICR cells in a magnetic field of 1.4 T. Ions were formed by pulsed electron impact on the parent neutral, usually at a nominal electron energy of 12 eV. Following thermalization and laser irradiation periods, ions were excited by an rf excite pulse and observed during a 3 ms transient acquisition period. In work with the dye laser, a thermalization period of 450 ms was followed by a laser irradiation period of 350 ms (at 4\times10^{-8} Torr). For the argon ion laser points, a thermalization period of 120 ms was followed by a laser irradiation period of 1100 ms (at a pressure of 7\times10^{-8} Torr).

Between 458 and 515 nm (solid circles in figures 2 and 3) the ions were irradiated with five lines from the Coherent Radiation I-12 argon ion laser. Between 544 and 605 nm (squares and triangles) the Coherent Radiation Model 490 argon ion pumped dye laser was used (with Rhodamine 110 and Rhodamine 6G dyes). Point spacing was
1 nm, with a laser line width believed to be about 0.1 nm. An additional point was obtained at 538.6 nm using a Lumonics excimer pumped pulsed dye laser (open circle). Runs made with different lasers and at different times were matched by careful overlapping of points at common wavelengths. The runs were adjusted to a common intensity basis using linear scaling: Since this is a one photon dissociation with linear light intensity dependence, linear scaling is valid as long as the ion cloud was uniformly illuminated throughout all the different runs. Each individual run was made at constant laser power, to avoid the uncertainty involved in making wavelength dependent light intensity corrections to the PDS intensities.

Care was taken to illuminate the ions with homogeneous light using a standardized optical arrangement at all wavelengths. The beam was expanded by telescope to a diameter much larger than the vacuum window and restricted by a circular aperture to a diameter about 2 mm larger than the vacuum window. This ensured a reasonably homogeneous beam of standard size centered on the vacuum window. Power was measured by a Scientech Model 365 surface absorbing power meter centered in the beam.

The parent neutral of I was obtained from Parchan Laboratories, and used as received with several freeze pump thaw cycles.
RESULTS:

Dissociation Channels. Figure 1 compares the light off and light on ICR spectra with 515 nm irradiation. Loss of H• to give the m/z 79 ion is the chief photon induced process, with a small amount of product also being formed at m/z 39 (loss of propenyl radical, presumably by allylic cleavage of the C-C bond between the triple and double bonds). This photon induced fragmentation pattern is similar to the low energy electron impact pattern: For nominal electron energies in the 8.5-10 eV region, the electron impact fragments observed were also m/z 79 and 39, in a ratio of about 20:1. At slightly higher electron energies, electron impact fragments at m/z 40 and 77 became significant; at the photon energies used these were not observed as photoproducts. The small m/z 39 photoproduct was a primary photoproduct: The possibility that it came from secondary photodissociation of m/z 79 was ruled out by observing m/z 39 photoproduction in the presence of continuous double resonance ejection of m/z 79.

A precise determination of the absolute photodissociation cross section was not attempted, but a reasonable estimate (probably good to a factor of 2) gave a cross section of 1.5×10⁻¹⁷ cm² for photodissociation at 550 nm. This is a reasonable value for this fully allowed π⁻¹→π⁻¹ transition; it seems to be larger (by roughly a factor of 2) than the visible wavelength cross sections for typical diene radical cations¹⁰,¹¹.

PDS Spectrum. Figure 2 displays the low energy portion of the PES spectrum of the molecule, along with the PDS spectral data
obtained with our laser systems. The energy axis of the PES spectrum has been shifted to put the adiabatic first IP at zero energy\textsuperscript{12}. Figure 3 shows the same data on an expanded energy scale. It is seen that the PDS data fall in the region of the third IP in the PES spectrum, which is assigned as an out of plane $\pi$ orbital\textsuperscript{4}. While the dye lasers allowed the PDS spectrum to be recorded up to photon energies only slightly above the peak at 2.25 eV, still the shortest wavelength dye laser points had significantly lower intensities than the values at the peak, so that the top of the peak was definitely spanned. The PES instrumental resolution was apparently of the order of\textsuperscript{4} 10 meV, compared with the PDS resolution of about 5 meV (1 nm point spacing), so that the greater breadth of the PDS peak was certainly not an artifact of instrumental resolution.

There is an uncertainty of the order of 20 meV in the assignment of the energy of the PES first adiabatic IP (8.72 ±0.02 eV), and consequently a similar uncertainty in the absolute PES energy scale, so the precise match of the PES peak maximum with the PDS peak at 2.25 eV shown in figure 3 is uncertain to this extent. The excellent agreement actually seen in peak positions gives after the fact confirmation that the assignment of the adiabatic first IP made in figure 2 was quite accurate.

The PDS points around 2.43 eV using the argon ion laser are too sparse to show the precise shape or position of this vibrational peak, but the greater width of the PDS feature, the approximate coincidence of PDS and PES positions, and the good agreement of
relative intensities of the vibrational peaks, can be seen from the PDS data.

As discussed below, the unexpected width of the PDS spectral features could reflect a large amount of unrelaxed internal energy in the ions, and it was thus important to assess whether the spectral shape was distorted by excess ion internal energy. Accordingly, experiments were done in which, following electron impact ionization, the ions were cooled during a period of about .5 s in the presence of $2 \times 10^{-7}$ Torr of benzene or $6 \times 10^{-7}$ Torr of SF$_6$ (giving collision rates of $8 \text{ s}^{-1}$ and $20 \text{ s}^{-1}$, respectively), after which the photodissociation was carried out with a 300-350 ms pulse of laser light. While these collision conditions are not sufficient to guarantee complete collisional thermalization, experience with other ions\textsuperscript{13} indicates that either of these collisional cooling regimes would lead to major deexcitation of vibrationally hot enyne ions. In addition, the long cooling time of these experiments was probably sufficient for substantial infrared radiative cooling of any large initial excess internal energy, since radiative cooling time constants of about 0.1 to 1 s are typical of ions this size\textsuperscript{13,14}.

These experiments showed that the PDS spectral shape in the 2.05 to 2.20 eV photon energy range was independent of the extent of ion cooling using either of the collision gases. If the surprisingly gradual rise of the spectrum in this range were due to significant superthermal internal energy of the ions, these cooling experiments should certainly have shown a substantial effect on the
spectral shape, and thus we rule this out as an important factor in the broadening of the PDS peaks relative to the PES peaks.
DISCUSSION:

The wavelength coverage of the PDS spectrum is not complete enough to display an unbroken spectrum across the visible. However, a reconstruction which will be useful in the discussion can be made with fair confidence, if we assume that the spectrum consists of a progression of vibrational peaks analogous to the PES spectrum, that each of the vibrational peaks is symmetrically and inhomogeneously broadened with equal widths of all the peaks, and that the peak spacing is equal to the 180 meV (1450 cm\(^{-1}\)) vibrational interval suggested by the PES spectrum. A simple spectrum matching exercise then leads to the reconstructed spectrum shown in figure 4, in which the 0-0, 0-1 and 2-0 members of the progression have been adjusted and summed to give a good fit to the observed PDS points. The width (FWHM) of the vibrational peaks is clearly constrained at about 170 meV by the assumption that the 0-0 peak has a symmetrical peak shape, and the other features of the spectrum follow from the fitting assumptions. The fitted relative heights of the three relevant components of the progression, 0-0, 1-0 and 2-0, are 1:0.63:0.15.

Peak Heights and Franck-Condon Factors. The Franck-Condon factors in the photoelectron spectrum and the photodissociation spectrum reflect the overlap of the vibrational wave functions of the initial and final electronic states involved in each experiment. In the comparison here the photoelectron and the photodissociation experiments both access the same final state (namely the third excited \(\pi\) electronic state of the molecular ion)
having the same vibrational wave functions. However the initial states are different; in the photodissociation experiment the ground electronic state of the molecular ion and in the photoelectron experiment the ground electronic state of the neutral. Therefore any significant difference between the Franck-Condon factors of the photodissociation spectrum and those of the photoelectron spectrum must reflect differences in the overlap of the vibrational wave functions for the neutral ground electronic state and the ionic ground electronic state. These differences result from differences in the equilibrium geometries of the two states. The relative heights of the 0-0 and 1-0 peaks in the PES spectrum appear to be about 1:60, compared with 1:63 in the PDS spectrum. Thus the Franck-Condon factors for this vibrational progression are similar for the two types of spectra. This in turn suggests that the geometries of ion and neutral are similar with respect to the lengths of the bonds involved in this 1450 cm\(^{-1}\) mode.

The vibration giving rise to the observed progression has been attributed to a stretching mode involving the double bond and probably the central C-C single bond\(^4\). With this picture of the nature of the Franck-Condon excitation, a molecular orbital picture of the electronic states involved provides a satisfactory rationalization of the observations:

Figure 5 shows molecular orbital pictures\(^4\) of the excitations observed in PES and PDS. Displayed are the two out of plane and one in plane \(\pi\) orbitals lying in the energy range of interest. The
π orbital from which the electron is removed to give the excited ion electronic state common to the two techniques involves strong C-C bonding between the central carbons of the π system, so that removal of this electron would be expected to give major excitation of a carbon skeletal stretching vibration, in accord with the observations. The ion ground state differs from the neutral ground state in the removal of an electron from the highest occupied π orbital; this orbital is largely non-bonding with respect to the carbon chain, so that little geometry difference would be expected between the neutral and the ground state ion. The apparent similarity of Franck-Condon factors for the two spectra is thus reasonable in terms of this simple molecular orbital picture.

**Peak widths.** The PDS peaks are much broader than the PES peaks (170 meV versus about 50 meV). Some increase in width could be attributed to hot bands on the low energy side of the PDS peak: Such hot band tailing of the peak would be somewhat greater in the PDS case because the ICR cell temperature (around 375 K\textsuperscript{15}) is somewhat higher than the room temperature PES instrument. However, this difference should be modest, and this seems like an insufficient explanation of the substantial PDS broadening. Lifetime broadening from a short excited state lifetime does not help to explain this, since precisely the same excited electronic state of the ion is viewed in the two techniques. It seems most likely that ionization increases the flexibility of the molecule, so that the ground state of the cation samples a larger variety of geometries, and undergoes wider excursions within the local
potential minima. (While it was suggested above that the π electron removed by ionization is non-bonding with respect to the carbon chain, this is not inconsistent with lowering of angular barriers to twisting and rocking motions, which would increase the chain flexibility.) These effects would be amplified by the higher temperature of the ion sample. The ion population thus presents a wider dispersion of molecular geometries than the neutral molecule at the moment of photon impact, giving inhomogeneous broadening of the peaks.

Peak Positions. As figure 3 shows, the position of the 0-0 peak in the PDS spectrum is accurately defined as 551 nm (2.25 eV), with an uncertainty of the order of 2 nm (10 meV). Assuming that the peak is inhomogeneously broadened by conformational excursions, as discussed above, this is the 0-0 energy separation between the ion ground state and the π⁻¹ excited state for an average ion structure.

The PDS data give no direct information on the location of the 1-0 vibrational peak, or the vibrational spacing, and can thus add nothing to the conclusion from the PES spectrum that the vibration principally excited by Franck-Condon transitions is a 1450 cm⁻¹ carbon stretching mode of the ion.
CONCLUSIONS:

These results represent a successful example of our continuing effort to use the resolution of tuned laser light sources to observe vibrationally resolved PDS spectra of radical ions. It is disappointing that this ion repeats the experience of earlier cases in that spectral broadening, apparently due to inhomogeneous broadening by conformational flexibility, negates much of the potentially high optical resolution available from the laser, in spite of the anticipation of much higher resolution hoped for based on the PES spectrum. Cooling of the ICR cell and vacuum system below room temperature seems to be inescapable for achieving narrower, less congested spectral peaks through reducing conformational excursions.

This is one of the few radical cations for which we have been able to make a comparison of Franck-Condon factors between PDS and PES. The 1450 cm$^{-1}$ vibration is clearly a carbon skeletal stretch, and the similarity of Franck-Condon excitations in the PES and PDS cases is nicely rationalized by the molecular orbital picture of the expected bond length changes in the electronic transitions involved.
REFERENCES:


FIGURE CAPTIONS:

1. Mass spectra with laser off (top), and with 1.7 W irradiation at 515 nm for 120 ms. (Spectra taken with 10 shots each with laser off and laser on are shown to indicate the noise level; more extensive averaging was used to measure peak heights.)

2. PES spectrum (solid trace) and PDS spectrum (points).

3. Expanded display of the PDS spectral region of figure 2.

4. PDS spectrum shown with the reconstruction made as described in the text by superimposing 0-0, 1-0 and 2-0 vibrational components of the electronic transition.

5. MO diagrams of the three occupied π orbitals of I, showing the change in occupation for the relevant PES and PDS transitions.
Electronic transitions in the photoelectron and photodissociation experiments
CHAPTER FIVE

PHOTODISSOCIATION SPECTROSCOPY OF GAS PHASE FERROCENE CATION
INTRODUCTION:

Ferrocene is readily oxidized to give the ferricenium ion, which is stable in various solution and solid media, and whose optical absorption spectroscopy has been studied extensively. The technique of photodissociation (PD) spectroscopy in the ion cyclotron resonance (ICR) ion trap offers the possibility of studying the spectroscopy of the gas phase ion.\(^1\) The absence of solvent and matrix effects in the gas phase should make the PD spectrum interesting to compare with condensed phase spectra.

Hettich et al.\(^2\) reported PD spectra of several gas phase transition metal arene ions, but ferricenium ion was not studied. They studied highly reactive ions which have not been studied in condensed phase, and they were unable to make much progress in spectral assignment. Study of ferricenium ion offers the advantage that the electronic structure and spectroscopy of this ion are already quite well understood. We present here results from a study of the photodissociation of gas phase ferricenium ion between 570 nm and 643 nm.
**EXPERIMENTAL:**

The use of photodissociation spectroscopy in an ICR ion trap to obtain optical absorption spectroscopic information about gas phase ions has been described previously.\(^3\)\(^-\)\(^5\) The instrument used in this study had a 2.5 cm cubical ICR cell in a magnetic field of 1.4 T. Ions were produced with an electron beam pulse of 100 ms duration at an electron energy of 9-11 eV. They were trapped and irradiated with the laser for 2 s, before ICR detection of the extent of parent ion dissociation.

The 570-595 nm region was studied using Rhodamine 110 laser dye. The laser power was held constant, at a value between 60 and 100 mW, during each scan, and data from eight scans were averaged. The laser beam diameter was 1 mm. Parent neutral pressure was 2x10\(^{-8}\) Torr.

Rhodamine 6G was used to scan the region from 580 nm to 625 nm. Seven separate scans were averaged. The laser power was held constant at a value between 100 and 180 mW during each scan. The beam diameter was held constant at a value between 1 and 4 mm during each scan. Parent neutral pressure was 6x10\(^{-8}\) Torr.

The lowest energy region from 620 to 643 nm was scanned using Rhodamine B laser dye. The laser power was 60 mW, with a beam diameter of 1 mm. The parent neutral pressure was 5x10\(^{-8}\) Torr.

The extent of photodissociation was followed by monitoring the decrease in parent ion intensity when the laser was turned on. The short wavelength (Rhodamine 110) and long wavelength (Rhodamine B) segments were each scaled by a multiplying factor to match the
Rhodamine 6G points in the regions of overlap. A 5\% variation in the values of the multiplying factors used in matching up the data shown in figure 1 still gave reasonable match-ups between the three sections of the spectrum.

**Effects of Position of Laser Beam.** If tuning the dye laser across the wavelength range of the dye resulted in changes in alignment of the laser beam, the spectrum could be distorted by the changing overlap of laser beam and ion cloud. To insure that the wavelength dependence of photodissociation between 615 and 603 nm was not due to this effect, the effect of beam position on the extent of photodissociation was examined at 615 and 603 nm. It was found that optimizing the beam alignment at either of these wavelengths gave the best dissociation at both wavelengths, ruling out the possibility of a beam wandering artifact at least over this range.

**The Possibility of Excess Internal Energy.** Electron impact ionization probably produces ions initially containing some excess vibrational energy. To eliminate the possibility that the observed photodissociation wavelength dependence was distorted by such excess internal energy, photodissociation spectra of thoroughly thermalized ions were compared with ions which were not carefully thermalized.

Vibrational internal energy in excess of thermal can be removed efficiently by collisions with thermal parent neutral\(^6\). This process is commonly observed to remove a large fraction of excess internal energy on each collision, presumably by resonant charge
transfer and/or resonant vibrational energy transfer.

By allowing up to 50 such collisions during a 4.5 second light off period after ion formation at a neutral pressure of 3.5x10^-7 Torr, the ions were cooled to thermal energies before being irradiated. The ratio of extent of dissociation at 603 nm to that at 615 nm provides a measure of the size of the peak at 603 nm. This ratio was compared for non thermalized ions and for ions that were collisionally thermalized as described above, using the same irradiation time and conditions in both cases. The ratio was found to be the same, indicating that the spectral structure at 603 nm was not distorted by superthermal ion internal excitation.

**UV Experiments.** The intensity dependence measurements at 308 nm used pulsed irradiation from a Lumonics excimer laser model TE-860-3 with XeCl lasing gas. At 266 nm, similar measurements used quadrupled pulses from a Lumonics HY 1200 Nd:YAG laser. Both lasers gave approximately 10 ns pulses, with a beam diameter of the order of 1 cm.

The time resolved photodissociation experiment has been described.\(^7\) Light pulses at 240 nm were obtained using doubled (532 nm) output from the Lumonics HY 1200 Nd:YAG laser to pump the Lumonics Hyperdye 300 dye laser at 480 nm (Coumarin 480 dye). The dye laser output was doubled with the Lumonics Hypertrak 1000 doubling accessory using a beta-barium-borate doubling crystal. Output at 240 nm was about 1 mJ/pulse with a beam diameter of about 2 mm.
RESULTS AND DISCUSSION:

The only dissociation channel observed at any of the wave lengths used (240, 266, 308, and ~600 nm) was the ring loss process

\[ \text{Fe(C}_5\text{H}_5\text{)}_2^+ \rightarrow \text{Fe(C}_5\text{H}_5\text{)}^+ + \text{C}_5\text{H}_5. \]

As will be clear from the discussion below, this dissociation requires at least three photons in the wavelength region around 600 nm (2 eV). It is commonly assumed that such a multiphoton dissociation with a cw light source in the ICR ion trap occurs by sequential absorption of the photons, with the energy of each successive photon being rapidly converted to vibrational internal energy of the ion. The optical absorption intensities and selection rules are thus those corresponding to one photon absorption by electronic ground state ions.

The Photodissociation Spectrum:

The photodissociation spectrum is shown in figure 1. Photodissociation is observed over the entire wavelength range studied, with the highest level at 603 nm. The spectrum shows substantial variations with wavelength, and over this wavelength range, appears to have three clear maxima at roughly 580 nm, 603 nm and 625 nm.

In the condensed phase ferricenium cation has D_{5d} symmetry.\(^8\) Figure 2 shows the MO energy level diagram. The relative ordering of the e\(_2\)g and a\(_1\)g orbitals is still a matter of some dispute. The order we have chosen, putting the e\(_2\)g orbital higher in energy than the a\(_1\)g orbital, is consistent with photoelectron spectroscopic (PES) assignments.\(^9b\)
Ionization of neutral ferrocene occurs by removal of an electron from the predominantly metal derived $e_{2g}$ orbital to give the odd electron cation $\text{Fe}(\text{Cp})_2^+$. The electronic ground state of ferricenium has been established by magnetic susceptibility and low temperature EPR studies as $^2E_{2g}$ with the electron configuration $(a_{1g})^2(e_{2g})^3.10,11$

The electronic transition responsible for the absorption around 16000 cm$^{-1}$ (625 nm, 1.98 eV) is a $^2E_{2u} \rightarrow ^2E_{1g}$ ligand to metal charge transfer (a $e_{1u} \rightarrow e_{2g}$ electron promotion).10b The photodissociation in this region for the gas phase ferricenium ion reflected in figure 1 must be due, at least in part, to this same electronic transition.

**Spectral Structure:**

The series of three photodissociation maxima seen in figure 1 with a spacing of about 23 nm (600 cm$^{-1}$) appears at first glance to be a vibrational progression. However, the peak spacing is substantially different from that expected from condensed phase absorption spectra, casting some doubt on an interpretation in terms of vibrational fine structure, and in addition to discussing the possibility of assigning this structure to vibrational states, we will also indicate a possible alternative interpretation in terms of multiple electronic transitions.

**Vibrational Fine Structure Assignment.** In the condensed phase at cryogenic temperatures, the absorption spectrum is dominated by a prominent vibrational progression with a spacing of 305 cm$^{-1}$ (~12 nm). This has been assigned by several authors$^8,10a$ to the
totally symmetric metal ligand stretching mode, \( v_4 \), of \( a_{1g} \) symmetry which occurs in the neutral at a frequency of 305 cm\(^{-1}\). This structure broadens considerably with increasing temperature, and the room temperature solution phase spectrum has a broad, nearly structureless absorption in the 600 nm region.\textsuperscript{10b} In addition Hendrickson et al.\textsuperscript{12} observed excitation of two less intense modes in the condensed phase low temperature spectrum: (i) the symmetric ring tilt \( v_{16} \) (\( e_{1g} \)) and (ii) the perpendicular ring distortion, \( v_{28} \) (\( e_{2g} \)). These occur in the neutral vibrational spectrum at 390 cm\(^{-1}\) (\(-15\) nm) and 600 cm\(^{-1}\) (\(-23\) nm) respectively. Table I compares the frequency of these three modes in the neutral (\( ^1A_{1g} \)), the excited ion (\( ^2E_{2u} \)) and the ground state ion (\( ^2E_{2g} \)).

Although the 600 cm\(^{-1}\) (23 nm) peak spacing in the photodissociation spectrum is close to the frequency of the \( v_{28} \) vibrational mode, it would be surprising for excitation of this non-totally symmetric vibration to give such a prominent progression. (Such excitations could be vibronically allowed in this ion through the Jahn Teller effect, so this assignment is not completely ruled out.) Nor does it seem likely that the \( v_4 \) mode has its frequency raised in the gas phase up to around 600 cm\(^{-1}\) to give a progression corresponding to the peaks in the PD spectrum. Thus the structure in the PD spectrum does not correspond well to our expectations for vibrational structure, and we will suggest a possible alternative assignment of the three peaks as separate electronic transitions instead of a vibrational progression.

**Electronic Transitions.** The presence of several low lying
excited states of the ion raises the alternative possibility that the three apparent maxima in the spectrum in figure 1 correspond to distinct electronic transitions. Optical spectroscopy and theory suggest three low energy electronic states as suggested in figure 3. The three states of symmetries $^2E_2g$, $^2A_{1g}$, and $^2E_{1u}$, have the electron configurations $(e_{1u})^4(a_{1g})^2(e_{2g})^3$, $(e_{1u})^4(a_{1g})^1(e_{2g})^4$ and $(e_{1u})^3(a_{1g})^2(e_{2g})^4$ respectively. The orbitally degenerate $^2E_2g$ is split by spin orbit coupling and a low symmetry distortion into a doublet, and the $^2E_{1u}$ state is similarly split into two components by spin orbit interaction. The splitting of the $^2E_{1u}$ state has been placed around 200 cm$^{-1}$ by optical spectroscopy.

The literature concerning the ordering and spacing of the low lying electronic states is so varied and contradictory that little can be concluded with even qualitative confidence. For instance, the $^2E_2g$-$^2A_{1g}$ separation has been assigned values in the 200 - 500 cm$^{-1}$ range from magnetic susceptibility, inelastic neutron scattering and Raman studies, but has been given a completely contradictory assignment around 2800 cm$^{-1}$ from gas phase PES studies. The $^2E_2g$ doublet splitting has been assigned inconsistently as 900 cm$^{-1}$ from EPR and susceptibility measurements and 515 cm$^{-1}$ from neutron scattering measurements. All sources agree on the $E'$ component of $^2E_2g$ as the ground state, but beyond that it seems justified only to say that there are several low lying states which have symmetry allowed optical transitions to the upper $^2E_{1u}$ state. Figure 3 thus
represents no more than a guess as to a possible ordering of the states.

As suggested by the speculative scheme in figure 3, this array of electronic states could give three distinct electronic transitions and hence three distinct peaks, each an unresolved doublet in the photodissociation spectrum of figure 1. Only the shortest wavelength of these transitions, \( ^2E_{2g}(E') \rightarrow ^2E_{1u} \), would be seen in the low temperature or room temperature optical spectrum, since only the \( ^2E_{2g}(E') \) state would be thermally populated to a significant extent. However, in the multiphoton photodissociation spectrum, absorption of the first photon gives the ion sufficient internal energy for extensive thermal population of all of these low lying electronic states. The second and third photons could then induce all of the transitions indicated in figure 3, giving corresponding maxima in the multiphoton PD spectrum at 580 nm, 603 nm and 625 nm.

**UV Measurements and the Dissociation Threshold:**

Electron impact appearance potential measurements give a threshold for ferricenium ion dissociation around 6 eV.\(^{17}\) This value is probably higher than the true thermochemical endothermicity of ferricenium ion dissociation, since there are bonds (such as the C-H bonds) which can certainly be broken with less than 6 eV of energy. These conventional threshold measurements are not definitive, not only because of the well known unreliability of electron impact appearance potentials, but also since a kinetic shift of as much as one or two eV would not be
surprising for an ion of this size.

Dissociation in the ICR ion trap alleviates kinetic shift problems by allowing longer for the ion to dissociate, and the accurately known photoexcitation energy removes uncertainty about the energy deposited in the dissociating ion. In cases like the present one where efficient two photon dissociation occurs at wavelengths below the one photon threshold, identification of the one photon threshold depends on identifying the wavelength of transition from two photon to one photon characteristics. This was successfully carried out in the case of halobenzene ion dissociations to yield very precise thermochemistry. In the present case, it was not possible to achieve a wavelength short enough to give one photon behavior, but by characterizing the dissociation behavior at the shortest available wavelengths it was possible to set a confident lower limit on the one photon threshold energy. We approached this using two of the trapped ion photodissociation techniques available to us: the light intensity dependence of the extent of photofragmentation, and the time dependence of photofragment appearance after a 10 ns laser pulse.

**Light Intensity Dependence.** A light intensity dependence measurement can provide an indication of the number of photons required for dissociation at each wavelength. Dissociations requiring only one photon always exhibit a linear dependence on light intensity, while those requiring 2 or more photons usually exhibit a nonlinear dependence. A nonlinear light intensity dependence always implies a multiphoton process, but a linear light
intensity dependence is uninformative: it may correspond to a one photon process, or it may correspond to a multiphoton process with one of the photon absorption steps being rate limiting.

The light intensity dependence was found to be nonlinear at 308 nm and 266 nm, indicating multiphoton thermochemistry at these wavelengths. Two photon dissociation at 266 nm puts a lower limit of about 4.7 eV on the dissociation threshold.

**Time Resolved Photodissociation.** ICR observation of the time dependence of photofragment appearance is able to time resolve photofragmentations with rate constants between $5 \times 10^2$ s$^{-1}$ and $5 \times 10^5$ s$^{-1}$. For ions like ferricenium ion having 30 or more internal degrees of freedom, there is almost always a wavelength region of at least several tenths of an eV just above the one photon fragmentation threshold where the dissociation is slower than $5 \times 10^5$ s$^{-1}$, so that a time dependence is observed in the time resolved photodissociation experiment.

Time resolved data at 308 nm (4.02 eV), 266 nm (4.66 eV) and 240 nm (5.17 eV) showed that all the FeCp$^+$ product ions were formed by fast photofragmentation ($k > 5 \times 10^5$ s$^{-1}$) at these wavelengths. We interpret this to mean that all of these photon energies are below the one photon fragmentation threshold. Thus the FeCp$^+$ photofragment observed at 308, 266 and 240 nm is formed through a two photon process, with the energy deposited by the two photons being large enough to give rapid dissociation. Thus we conclude from these results that at 8.04 eV (the energy of two 308 nm photons) the two photon fragmentation rate is faster than $5 \times 10^5$
s⁻¹, while at 5.17 eV (the energy of one 240 nm photon) the one photon fragmentation rate is slower than 5x10² s⁻¹. From the failure to observe any one photon dissociation at 240 nm we can accordingly set a lower limit of 5.4 eV (including an allowance for 0.25 eV of ion thermal energy) on the dissociation threshold.

**Dissociation Energy.** A careful distinction should be drawn between the dissociation threshold considered above, and the thermochemical activation energy E₀ for the dissociation reaction. The threshold is the lowest excitation energy at which dissociation can be observed, while E₀ is the excitation energy at which the dissociation rate goes to zero. These thus differ by the energy of the kinetic shift. It has been stressed²¹ that even in ion trapping experiments where there is unlimited time for dissociation to occur, there is still an **intrinsic** kinetic shift because the excited ions deactivate by infrared radiative emission at rates of the order of 10² s⁻¹, and dissociation must be at least this fast to compete successfully. In the ferrocene ion case, RRKM modeling indicates that, even for a very loose transition state (∆S° = +20 cal K⁻¹), the internal energy of the parent ion must be at least 0.5 eV above the value chosen for E₀ before the FeCp⁺ fragment is produced rapidly enough to compete with radiative relaxation. Thus the lower limit of 5.4 eV on the dissociation threshold obtained above is consistent with an E₀ for the dissociation of about 4.9 eV, or even somewhat lower. No data so far reported give a precise measurement of the Fe-ring bond strength in ferrocene ion, but from the present results and discussion it is evidently
quite high, probably in the 4.5-5 eV range.
CONCLUSION:

The gas phase ferricenium ion shows the expected multiphoton photodissociation in the region around 600 nm where the ion is known to absorb light in condensed phase. We cannot give a definitive assignment of the three distinct maxima observed in the gas phase spectrum, but it seems most attractive to attribute them to three separate electronic transitions.

Neither the intensity dependence result at 266 nm, nor the time resolved photodissociation result at 240 nm, show any indication of one photon dissociation at these wavelengths. This indicates that the threshold energy for observable dissociation of this ion is higher than about 5.4 eV.
REFERENCES:


5. A survey can be found in: Dunbar, R.C. in Photofragmentation of Molecular Ions; T.A. Miller; V.E. Bondybey, eds.; North Holland, 1983.


TABLE I

Vibrational frequencies (in cm\(^{-1}\)) for 3 electronic states of Fe(C\(_5\)H\(_5\))\(_2\) and Fe(C\(_5\)H\(_5\))\(_2^+\).

<table>
<thead>
<tr>
<th>Electronic States</th>
<th>(v_4(a_{1g}))</th>
<th>(v_{16}(e_{1g}))</th>
<th>(v_{28}(e_{1u}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1_{A1g}(a))</td>
<td>305</td>
<td>390</td>
<td>600</td>
</tr>
<tr>
<td>(2_{E1u}(b))</td>
<td>305</td>
<td>403</td>
<td>470</td>
</tr>
<tr>
<td>(2_{E2g}(c))</td>
<td>305</td>
<td>427</td>
<td>591</td>
</tr>
</tbody>
</table>

a) Ground state neutral. Frequencies are from ref. 12.
b) Excited ion. Frequencies are from ref. 12.
c) Ground state ion. Frequencies are from ref. 13.
FIGURE CAPTIONS:

1. Photodissociation spectrum of ferricinium ion.

2. Molecular orbital energy level diagram for ferricinium ion. 
   (From reference 8.)

3. Low energy electronic states and electronic transitions to the
   \( {^2}E_{lu} \) excited state, based on a speculative assignment of the
   energies of the low lying electronic states, as discussed in
   the text.
SECTION THREE

PHOTOCHEMISTRY OF GAS PHASE IONS
CHAPTER SIX

TIME RESOLVED STUDY OF THE FRAGMENTATION OF TRI-T-BUTYLBENZENE CATION
INTRODUCTION:

With 138 internal degrees of freedom tri-t-butylbenzene ion is the largest ion studied so far in this laboratory. Fragmentation kinetics of such large ions are of interest to us for several reasons.

First, much of the thermochemistry of gas phase ions is derived from fragmentation thresholds that are usually derived from appearance potential measurements using techniques such as electron impact, threshold photodissociation and Photoelectron-Photoion-Coincidence (PEPICO). However, such measurements are subject to a phenomenon called kinetic shift which causes the measured appearance potential to be anywhere from zero to several electron volts above the actual threshold value. This problem becomes more severe as the number of internal degrees of freedom increases. It is important to increase our understanding of these effects in large ions, for which appearance energy measurements are often the only source of thermochemical information. The Time Resolved Photodissociation, TRPD, experiment is not affected by kinetic shift because of the instruments ability to trap ions for extended periods. We have therefore applied this method to the fragmentation of tri-t-butylbenzene where kinetic shift is expected to be a problem simply because of the ion's large size.

Second, the quasiequilibrium theory of unimolecular decomposition has been widely and successfully applied to the fragmentation kinetics of medium sized ions and is now the usual approach to such kinetics. However, since it assumes complete
energy randomization throughout the energized ion, this theory is expected to break down for molecules so large that energy dispersal cannot compete with localized bond breaking.

Several studies have shown that the technique of time resolved photodissociation of gas phase ions in the ion cyclotron resonance ion trap mass spectrometer to be a powerful approach to observing fragmentation kinetics of ions with well controlled internal energy.\textsuperscript{2-5} Presented in this chapter is a TRPD study of the fragmentation kinetics of three substituted benzenes: \textit{t}-butylbenzene (TBB), 1,4-di-\textit{t}-butylbenzene (DTBB) and 1,3,5-tri-\textit{t}-butylbenzene (TTBB). In particular, the TTBB ion is the largest ion we have studied and probably the largest ion for which fragmentation kinetic measurements have been obtained.
EXPERIMENTAL:

The ICR-TRPD experiments were carried out as has been described in detail in previous publications,\textsuperscript{4,5} using the phase-sensitive-detection ICR spectrophotometer. Parent ions were produced by electron impact at a nominal electron energy of 10 eV. The electron impact produced methyl loss fragments were completely ejected using a 900 ms double resonance Rf pulse before parent ion irradiation. The parent ions were irradiated after being thermalized by colliding with parent neutral at a neutral pressure of 1-7x10^{-7} Torr for approximately 2 seconds. These conditions were determined to be thermalizing as described below. Following the laser pulse and the variable delay an rf excite pulse of 20 us duration and 50 V p-p was applied at the daughter ion frequency followed by a 3 ms transient acquisition. The variable delay between laser and excite pulse was typically swept over 20 values and 100-200 such sweeps were accumulated to give the TRPD daughter ion appearance curve. The pulse sequence for the TRPD experiment is shown in figure 1.

All of the wavelengths used in this study were generated by a Lumonics pulsed laser system operating in the externally triggered mode. The doubled output of a Lumonics HY-1200 Nd:YAG laser (in addition to providing the 532 nm light at an energy of 23 mJ) was used to pump a Lumonics Hyperdye 300 dye laser to generate the red wavelengths with an energy of 4 mJ. Rhodamine 590 laser dye was used for 568 nm, rhodamine 610 laser dye was used for 583.5 nm and rhodamine 640 laser dye was used for 615 nm. The beam diameter was
about 5 mm at all wavelengths.

It is convenient at this point to discuss the instrument response function that must be used in the time resolved experiment here and in chapter 6. This is discussed also in reference 5.

ICR Signal Equation for the Time Resolved Experiment: The abundance of fragment ions from unimolecular photofragmentation of a population of parent ions, with a uniform internal energy, grows with time, t, according to \( B^+ = B_0^+ (1 - e^{-kt}) \) where k is the first order rate constant. However, because of the type of ion detection used in an ICR spectrometer, additional considerations must be made in order to arrive at the ion signal equation.

First, for fragmentations that occur with a time constant on the order of the Rf excite pulse width, \( \Delta \), consideration must be given to the effect of this finite width. When this is done the resulting ICR signal equation is

\[
S = C \left( 1 - \frac{(1 - e^{-k\Delta})}{k\Delta} \right) e^{-kt}
\]

(1)

where C is a constant independent of t, k and \( \Delta \).

Second, if the dephasing rate \( \delta = (\omega_d - \omega_p) \) is not fast compared to the fragmentation rate this simple expression breaks down. This problem arises because the daughter ion and parent ion frequencies are sufficiently alike that when the ICR excite pulse at the daughter ion frequency, \( \omega_d \), is turned on parent ions are also accelerated, initially in phase with the daughter ions. If these parent ions dissociate before they become dephased with the daughter ions their in-phase cyclotron velocity is added to the acquired velocity of the corresponding daughter ions and increases
the daughter ion signal above the level expected from equation 1. The necessary correction term has been derived in reference 5 and when added to the simple expression 1, gives the ICR signal equation 2:

\[
S = C \left\{ \Delta + \frac{1}{k} e^{-kt} (e^{-k\Delta} - 1) \right.

+ \frac{1}{k} \frac{\omega \pi}{\omega} \frac{e^{-kt}}{1 + (\delta/k)^2} \left[ 1 - \frac{k}{\delta} \exp(-k\Delta) \sin \delta \Delta \right.

- e^{-k\Delta} \cos \delta \Delta \left. \right\} \right.

\tag{2}
\]

This is the ICR signal equation used in all the time resolved work presented here and in chapter VII.
RESULTS:

**Fragmentation Pathways.** The three parent ions were observed to lose only methyl at all wavelengths studied. For TBB this is known to be the only photodissociation pathway at visible wavelengths.\(^6\) For TTBB we have assigned a benzyl like structure to the product based on its favorable appearance and the analogy to the known product ion structure from the photodissociation of TBB.\(^6\)

\[
(C_4H_9)C_6H_3^+ \rightarrow (C_4H_9)_2C_6H_3C(CH_3)_2^+ + CH_3.
\]

\[m/z \ 246 \quad m/z \ 231\]

Although the t-butyl cation is prominent in the electron impact mass spectra of these ions,\(^7\) we were unable to detect its formation by one photon photodissociation at visible wavelengths.

**Cross Section and Light Intensity Dependence Measurements.** A light intensity dependence was measured for all three ions after being collisionally thermalized with parent neutral for more than a second before irradiation. For TBB and DTBB this required a pressure of 1.25x10\(^{-7}\) Torr for two seconds and for TTBB it required a pressure of 5x10\(^{-7}\) Torr for 1.5 seconds. Photofragments were detected 20 \(\mu\)s after irradiation for TBB and DTBB and 55 \(\mu\)s after irradiation for TTBB. A linear light intensity dependence was found for each of these ions at the wavelengths studied: 532 nm and 572 nm for TBB and DTBB and 573 nm for TTBB.

In addition the one photon photodissociation cross section at 532 nm was estimated as 1.85x10\(^{-18}\) cm\(^2\)/photon for TBB and as 4.66x10\(^{-18}\) cm\(^2\)/photon for DTBB.
Cooling Study. In order to model a near threshold fragmentation process for an ion of this size the initial distribution of the internal energy before photon absorption must be characterized and included in the model.\(^2,5,8\) A population of thermalized ions contains a canonical distribution of internal energies that is accurately represented by a Boltzmann distribution taken over all internal degrees of freedom. An ion population formed by electron impact initially has some superthermal (excess) internal energy\(^9\) which is not easily characterized. Such an ion population must be thermalized by collisions with parent neutral before irradiation. To determine the conditions necessary to thermalize TTBB ions, parent ions were allowed to undergo a number of collisions with parent neutral at a variety of neutral pressures and light-off periods, followed by irradiation at 572 nm and time-resolved detection of photofragments. Conditions were considered thermalizing if the resulting fragmentation rate could not be decreased further by increasing the amount of cooling. Under these conditions the ion population was considered thermal. For TTBB ions this was about two seconds at a neutral pressure of approximately \(2\times10^{-7}\) Torr giving around 10 parent ion neutral collisions.

Branching Ratio Between Photo-Products from Methyl Loss and T-Butyl Loss. The \(M^+\)-methyl photofragment ions in this study were detected 200 us after irradiation of TTBB parent ions that had been thermalized at \(7\times10^{-7}\) Torr for two seconds. The ratio of the abundance of the methyl loss fragment (m/z 231) to the abundance of
the t-butyl loss fragment (m/z 57) is the branching ratio. At both
of the wavelengths considered (532 and 576 nm) there was
insufficient production of mass 57 to be detected.

At 532 nm the scatter in the laser on signal at the ICR
frequency where we expected to see the m/z 57 fragment (~375.200
kHz) was about 1/6 of the m/z 231 signal. At 576 nm the scatter
was about 1/4 of the m/z 231 signal. This gives us a lower limit
on the branching ratio (231:57) of 6:1 at 532 nm and 4:1 at 576 nm.
We assume that in the range of energies discussed in this chapter
the only photoproduct is M+-methyl.

**Time Resolved Study.** A time resolved study was done on the
appearance of the M+-methyl photoproduct at several wavelengths for
TBB, DTBB and TTBB cations.

In the case of TBB and DTBB the ion populations were
thermalized prior to irradiation at a parent neutral pressure of
6x10^-7 Torr for 2 seconds. Both of these ions fragmented much too
fast to be time resolved with our instrument. Several wavelengths
were tried: 532 and 572 nm with TBB and 532, 572 and 614 nm with
DTBB. It was not possible to try redder wavelengths with these two
ions (thus slowing the fragmentation to a time resolvable rate)
because the optical absorption cross section fell off too rapidly
to the red.6,10

Using TTBB ions that had been thermalized at 4x10^-7 Torr for 2
seconds, time resolved appearance curves of methyl loss fragment
ions were collected at four wavelengths, and are shown in figure 2.
Dissociation is seen to be slow on a time scale of tens to hundreds
of $\mu$s, and shows the expected slowing as the photon energy decreases.
MODELING OF APPEARANCE CURVES:

Generating the Appearance Curves. The solid curves in figure 2, which were fitted by eye to the experimental data points, were generated by convoluting the instrument response function with a distribution of fragmentation rates, \( P(k(E)) \). This distribution corresponded to the internal energy distribution, \( P(E_{th} + h\nu) \), that a population of TTBB ions, originally thermalized at 375 K, would have immediately after absorbing a photon of energy \( h\nu \) as shown in figure 3 for a photon energy of 615 nm. To produce the corresponding distribution of rates, \( k(E_{th} + h\nu) \), the distribution of internal energies was combined with one of four rate-energy curves. The rate-energy curves were each generated by an RRKM type rate calculation which used the steepest descents state counting procedure on one of four different reaction models, the rate being given by equation 9 in the introduction. The thermally corrected fragment ion signal was then given by equation 3

\[
\text{Sig} = \int P(k(E)) \cdot S(k(E_{th} + h\nu)) \cdot dk(E)
\]  

(3)

where \( S(k(E_{th} + h\nu)) \), calculated from the instrument response function (equation 2 in this chapter), is the signal magnitude due to daughter ions formed with the fragmentation rate constant \( k(E_{th} + h\nu) \) and \( P(k(E)) \) is the probability that an ion will fragment with a rate constant \( k(E) \). The integration is over the distribution of rates. This convolution procedure has been described in detail.\(^{11}\)

Reaction Models. The four reaction models each used a 650 cm\(^{-1}\)
vibration as the reaction coordinate. In reaction models 1 and 2 the methyl and t-butyl rotations were considered as low frequency torsions in both the energized parent ion and the transition state. The transition state of reaction model 1 was tightened and that of model 2 was loosened.

Reaction models 3 and 4 were used to investigate the effect of internal rotations on the model. Both included nine methyl and three t-butyl internal rotations with $\beta$ values of 45 and 2 cm$^{-1}$ respectively, each of which included a symmetry factor of 3.12 One of the 2 cm$^{-1}$ t-butyl rotations was frozen into a 400 cm$^{-1}$ torsion in the transition state of reaction model 4.

Table I lists the parent ion an transition state frequencies for each of these reaction models.

**Effect of Thermal Distribution on Appearance Curve Shape.** If, after photon absorption, the ion internal energy in excess of the fragmentation threshold is comparable to the spread of ion thermal energies, then the distribution of thermal energies must be included to adequately model an energy dependent process. Under such conditions the energy content of the ion population is not adequately described by a single energy value (i.e.; photon energy + $<\text{thermal energy}>$), nor is a single value for the rate constant an adequate description of the fragmentation process since the fragmentation rate is a function of the internal energy in excess of threshold.

To adequately model the experimental appearance curves for TTBB ion fragmentation it was clearly necessary to convolute in the
thermal distribution of fragmentation rates. Figure 4 compares the fit of single exponential (dashed line) and thermal distribution (solid line) appearance curves with the experimental appearance curve at 615 nm. Only the curve that includes a thermal distribution of fragmentation rates adequately fits the experimental data.

Results from Modeling. For each of the four wavelengths studied Table II lists the rates predicted from reaction models 1, 3 and 4 along with the activation parameters used. These rates were taken from the corresponding rate energy curve at an energy equal to the photon energy plus the average thermal energy of the parent ion population. The average thermal energy is 5595 cm\(^{-1}\) (0.69 eV) for reaction models 1 and 2 and 5093 cm\(^{-1}\) (0.63 eV) for reaction models 3 and 4. The best values for \(\Delta S^+\) and \(E_o\), for a particular reaction model, were chosen from the rate energy curve that when convoluted through equation 3 produced appearance curves that best fit the experimental appearance curves.
DISCUSSION:

TBB and DTBB Ions:

Loss of methyl from a t-butyl group attached to the benzene ring involves no obvious rearrangement and is therefore expected to be a simple bond cleavage proceeding through a loose transition state. This indeed is what Brand and Baer found for TBB.\(^8\) They were able to fit their PEPICO data over the range of internal energies from about 1.3 to 1.6 eV using a transition state with activation parameters \(E_0 = 1.22 \text{ eV}\) and \(\Delta S^\# = +5.0 \text{ cal/K}\). (We calculated this value of \(\Delta S^\#\) from the list of frequencies in reference 8). This loose transition state is reasonable for simple cleavage of the methyl C-C bond. For TBB these values indicate that fragmentation is too fast to be time resolved on our instrument (which cannot time resolve fragmentation rates faster than \(5 \times 10^5 \text{ s}^{-1}\)) even at the lowest photon energies for which the ion had sufficient absorption cross section. Increasing the number of internal degrees of freedom to a value appropriate to DTBB and using the same activation parameters as Brand and Baer we calculated the fragmentation of DTBB to be faster than \(5 \times 10^5 \text{ s}^{-1}\) at the longest wavelengths available in the TRPD study. This is consistent with the complete lack of time dependence we observed for both of these ions.

TTBB Ion:

Adding further internal degrees of freedom appropriate to the TTBB ion and using Brand and Baer's activation parameters brings the predicted fragmentation rate into the regime accessible to the
TRPD experiment. In addition adding the third t-butyl group to the benzene ring in TTBB has the effect of shifting the optical absorption spectrum to the red, enhancing the optical absorption cross section for redder photons. Therefore, unlike TBB and DTBB, TTBB ions underwent photoinduced loss of methyl at a rate slow enough to be time resolvable at four wavelengths between 615 and 532 nm. The four experimental appearance curves, shown in figure 2, were fitted as described in the section on modeling.

**RRKM Best Fit Model.** Although from analogy with TBB this fragmentation is expected to involve a simple methyl C-C bond cleavage, one should not necessarily expect that in TTBB it will proceed through a loose transition state since there may be steric crowding of the region in the plane of the aromatic ring by the two additional meta oriented t-butyl groups. If this crowding is extensive enough it will force the methyl group to leave along a trajectory perpendicular to the plane of the ring giving restricted freedom in the transition state of TTBB compared to that of TBB.

The best fit was in fact obtained using a rather tight transition state with the activation parameters $\Delta S^\# = -7$ cal/deg and $E_0 = 1.2$ eV (solid line in figure 2). This tight transition state is designated Model 1, and is displayed in Table 1. The reaction coordinate was considered to be a $650 \text{ cm}^{-1}$ vibration and several vibrational frequencies were increased in the transition state.

We also tried to fit the data using the loose transition state of Brand and Baer, $\Delta S^\# = +5.5$ cal/deg, with a greater number of
internal degrees of freedom appropriate to TTBB. In this case the best fit was obtained using a value of 1.35 eV for $E_0$. This loose transition state is Model 2 and is also displayed in Table 1. The fits obtained with the loose transition state were noticeably inferior to those obtained with the tight transition state.

The best fit RRKM rate-energy curve is plotted in figure 5. The four points designated on the curve correspond to the average internal energies of the ion population at the four wavelengths. The solid lines on the plots of figure 2 are the predicted daughter ion curves from the convolution of this rate-energy curve with a thermal distribution according to equations 3 and 4.

It is worth noting that $E_0$ for the tight transition state is the same as the value used by Brand and Baer for TBB. This is expected, since the thermochemistry of the methyl C-C bond breaking should be little influenced by addition of one or two extra t-butyl groups to the benzene ring. In contrast the $E_0$ required for the best fit with the loose transition state is higher than the TBB value by 0.15 eV.

We conclude from modeling of this fragmentation that a tighter transition state is preferred for methyl loss from TTBB ion because of steric interaction between adjacent t-butyl groups.

**Internal Rotations.** TTBB has a number of degrees of freedom which may be either torsions or internal rotors (9 methyl groups and 3 t-butyl groups). We examined what the affect of including and hindering these internal rotations would be on the shape of the rate-energy curve and on the values for the best fit parameters
using the reaction models 1, 3 and 4. Each model is discussed in
the section "Modeling of Appearance Curves" and each is listed in
table 1. In model 4 one of the three t-butyl rotations was frozen
into a torsion of 400 cm\(^{-1}\), the rationale being that as the C-CH\(_3\)
bond stretches toward cleavage, the free rotation of the reactive
t-butyl group would be restricted by steric interaction of the
adjacent t-butyl groups.

Table 2 lists the relevant points on the rate-energy curves of
the three models, as well as the RRKM parameters. The values of \(E_o\)
vary by less than 0.05 eV between the three models, and values of
\(\Delta S^\#\) vary within a range of 1.6 cal/K. These variations are not
important in comparison with other uncertainties in the RRKM
fitting procedure. In addition all three models, when convoluted
with the appropriate thermal distribution according to equations 1
and 2, generated thermally corrected appearance curves that fit the
experimental curves equally well. We conclude that the approach
chosen for modeling the internal rotational degrees of freedom is
not a significant question in the RRKM modeling of these results.

**Kinetic Shift.** The conventional kinetic shift is the internal
energy in excess of the fragmentation threshold that must be
deposited in the parent ion to produce a detectable amount of
photoproduct, about 1% fragmentation, between the time of parent
irradiation and the time of photofragment ion detection, usually\(^{13}\)
about 10\(^{-5}\) s (which translates into a minimum fragmentation rate of
10\(^3\) s\(^{-1}\)). The intrinsic kinetic shift is the excess energy needed
to give a fragmentation rate of about 10 s\(^{-1}\) (fast enough to
compete with energy relaxation by ir photon emission occurring with a rate of around 100 s$^{-1}$).\textsuperscript{13,14}

Using the rate-energy curve in figure 5 the conventional kinetic shift of the methyl loss fragmentation threshold derived from standard appearance potential measurements can be easily predicted for ions with no thermal internal energy (the zero K case) as well as for thermal ions. Thus while the wavelength corresponding to $E_0$ is 1000 nm (1.2 eV), the zero K standard appearance energy would correspond to about 500 nm (2.4 eV), a conventional kinetic shift of 1.2 eV. The standard appearance energy for thermal ions (375 K), where the fragmentation is aided by the thermal internal energy of the ions (an average value of about 0.69 eV in the case of TTBB), is 1.71 eV (730 nm), which is a conventional kinetic shift of about 0.5 eV.

The internal energy at which the fragmentation is fast enough to compete with radiative relaxation (10 s$^{-1}$ or faster) is 1.9 eV, about 0.7 eV above the threshold. For parent ions at 0 K the intrinsic kinetic shift is therefore 0.7 eV. For thermal parent ions with about 0.70 eV of thermal internal energy the intrinsic kinetic shift is essentially zero.
CONCLUSIONS:

The dissociation kinetics of TTBB ion are well described by RRKM modeling, giving strong support to the validity of the QET picture of dissociation of ions of this size. It is worth noting that the dissociation was found to be slower than predicted from the loose transition state that was analogous to the one for the TBB ion dissociation. If localized bond breaking were to take place prior to complete equilibration of internal energy the dissociation would be expected to be faster than the predicted RRKM rate.

The zero Kelvin kinetic shift is large, as expected, giving approximately a doubling of the threshold. The intrinsic kinetic shift is less but still a large fraction of $E_0$. The present results reinforce the point that for larger ions the effects of kinetic shift and thermal energy content on the observed threshold are so large that the appearance energy of daughters has essentially no relation to the true dissociation thermochemistry. Only by measuring the dissociation rate as a function of energy, deconvoluting the contribution of thermal internal energy and extrapolating to zero rate, can the true dissociation activation energy be determined from measurements of daughter ion intensities.
<table>
<thead>
<tr>
<th>Parent Ion Frequencies&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Transition State Frequencies&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No rotations</strong></td>
<td><strong>Reaction model 1</strong></td>
</tr>
<tr>
<td>3000, 30</td>
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</tr>
<tr>
<td>1500, 24</td>
<td>1500, 23</td>
</tr>
<tr>
<td>1250, 10</td>
<td>1250, 13</td>
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<td>1000, 34</td>
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<td>400, 10</td>
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<td>275, 8</td>
<td>275, 11</td>
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<tr>
<td>190, 10</td>
<td>190, 7</td>
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<tr>
<td><strong>12 rotations</strong></td>
<td><strong>Reaction model 3</strong></td>
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<td>275, 6</td>
</tr>
<tr>
<td>45, 9 (R)</td>
<td>45, 9 (R)</td>
</tr>
<tr>
<td>2, 3 (R)</td>
<td>2, 3 (R)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Oscillator frequency in cm<sup>-1</sup>, mode degeneracy.
Table II

Fragmentation rates calculated from the three Reaction Models. (s⁻¹)

<table>
<thead>
<tr>
<th>Ion internal energy in cm⁻¹</th>
<th>Model 1ᵃ</th>
<th>Model 3ᵇ</th>
<th>Model 4ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>24391 (532 nm)</td>
<td>2.65x10⁴</td>
<td>2.53x10⁴</td>
<td>2.60x10⁴</td>
</tr>
<tr>
<td>23200 (568 nm)</td>
<td>1.35x10⁴</td>
<td>1.30x10⁴</td>
<td>1.32x10⁴</td>
</tr>
<tr>
<td>22732 (583.5 nm)</td>
<td>1.01x10⁴</td>
<td>9847</td>
<td>9962</td>
</tr>
<tr>
<td>21855 (615 nm)</td>
<td>5776</td>
<td>5653</td>
<td>5677</td>
</tr>
</tbody>
</table>

a. E₀=9840 cm⁻¹, ΔS#=-7.44 eu, <Eₜₜ>=5595 cm⁻¹
b. E₀=10020 cm⁻¹, ΔS#=-8.60 eu, <Eₜₜ>=5093 cm⁻¹
c. E₀=9550 cm⁻¹, ΔS#=-6.07 eu, <Eₜₜ>=5093 cm⁻¹
d. Ion internal energy is equal to the photon energy at the indicated wavelength plus the ion thermal energy predicted from model 1.
e. The ΔS# for model 2, not listed here, was +5.55 cal/K.
REFERENCES:


12. The B value for the internal rotation of the t-butyl group was calculated from the expression for internal rotation, \( B = h^2\sigma^2/(2I) \). The value for the moment of inertia \( "I" \) along the \((\text{CH}_3)_3\text{C}-\text{C} \) bond axis was obtained from the overall rotational constant \( "A" \) for t-butyl cyanide (4600 MHz from reference 16) according to the expression for overall rotation along the C-CN bond axis, \( A = h/(8\pi^2I) \). A similar calculation was carried out for methyl rotation using \( I = 5.3 \times 10^{-47} \) kg m\(^2\) from reference 16.


FIGURE CAPTIONS:

1. Pulse sequence for the Time Resolved Photodissociation experiment. See text for details.

2. Methyl loss fragment ion appearance curves for thermalized tri-t-butylbenzene cations at photon energies of 615, 583.5, 568, and 532 nm. The solid curves were generated from the tight transition state with $\Delta S^* = -7.4$ cal K$^{-1}$ and $E_0 = 9840$ cm$^{-1}$.

3. Internal energy distribution of the parent ion population before and after absorption of a 615 nm photon.

4. Fits to the 615 nm experimental appearance curve with a single exponential (dashed line) and a thermal distribution (solid line). The two modeled curves differed only in the treatment of thermal energy.

5. Rate-Energy curve for the transition state, $\Delta S^* = -7.44$ cal/K and $E_0 = 1.2$ eV (9840 cm$^{-1}$), that best fit the experimental appearance curves.
CHAPTER SEVEN

TIME RESOLVED STUDY OF THE FRAGMENTATION OF THIOPHENOL CATION
INTRODUCTION:

Because charged molecules are easy to manipulate and detect, the study of unimolecular dissociation kinetics has received much impetus from ion dissociations studied in various kinds of mass spectrometers. The most clear-cut and satisfactory experiments of this kind have taken advantage of the ability of photons to deposit precisely known increments of energy, affording to various photoionization and photodissociation experiments the advantage of excellent knowledge of the internal energy of the fragmenting molecule.

Recent advances in studying dissociation kinetics by both photoionization and photodissociation have opened up ways of observing unimolecular dissociations with very low rates, having dissociation time constants of several milliseconds or longer. The time resolved photodissociation (TRPD) experiment in the ion cyclotron resonance (ICR) ion trap,\(^1\) is such a technique which is finding application to a variety of slow dissociation systems.

The dissociation of thiophenol ion in the region of 3.5-4.5 eV internal energy is a slow dissociation about which little quantitative kinetic information has been available, and the application of these two techniques has provided the first rate values for this system.

In the internal energy regime of interest here, the ion dissociates competitively to two products according to
Initial TRPD observations\textsuperscript{2} of the rate of m/z 66 production from thiophenol ion photodissociation at 308 nm indicated a unimolecular rate constant near $10^5$ s\textsuperscript{-1}. This rate was strikingly faster than the approximately $1\times10^3$ s\textsuperscript{-1} predicted from reasonable RRKM modeling of the process. A tight transition state was assumed in this initial modeling of this system, considered to be almost surely involved in such a rearrangement fragmentation.

This unexpected result inspired a more extensive examination of the system, to investigate whether (a) the initial TRPD observations were flawed, (b) the thermochemically derived activation energy of 3.2 eV used in the modeling was too high, (c) the assumption of a tight transition state should be reconsidered, or (d) RRKM theory (which involves statistical or quasiequilibrium theory assumptions) is violated in this case. Experiments with the TRPD technique, along with auxiliary work using Fourier transform mass spectrometry and two photon photodissociation have been used to characterize the dissociation channels yielding both m/z 66 and m/z 84, leading finally to a satisfactory picture of this system in the slow dissociation regime.
EXPERIMENTAL:

The ICR-TRPD experiments were carried out as has been described in detail in previous publications,\(^1\) using the phase sensitive detection ICR spectrometer. Electron impact ionization at a nominal electron energy of 12 eV was used to produce parent ions. A thermalization time of 1-2 s was used between the ionization pulse and the laser pulse; as discussed below in the thermalization studies, pressures of neutral thiophenol varied from 5x10^{-8} Torr to 1x10^{-6} Torr. Following the laser pulse, and following the variable delay, an rf excite pulse of 12 \(\mu\)s duration and 50 V p-p was applied at the daughter ion frequency, followed by transient acquisition for 2 ms. In a typical experiment, the delay time between laser and detection was swept over about 40 values, and 50-100 such sweeps were accumulated and averaged to give the TRPD spectrum.

A Lumenics excimer laser was used at 308 nm, giving a pulse of a few mJ energy, which was focused to a spot diameter of a few mm at the ICR cell. A similar spot at 355 nm was produced by a Lumenics HY-1200 Nd/YAG laser with frequency tripler. Pulses from both lasers have a duration of about 10 ns, which is very short compared with the dissociation and detection time scales.

The Fourier transform photodissociation mass spectrum was taken using an FT ICR spectrometer with an IonSpec Fourier transform data system. The ions were not thoroughly thermalized, with a pulse of light at 308 nm being delivered 100 ms after the electron beam pulse at a pressure of 1.5x10^{-7} Torr.
RESULTS:

The principal results are the dissociation rates into each of the two principal products as a function of internal energy of the parent.

Time-Resolved Photodissociation:

In the ICR-TRPD experiment, parent ions are formed by electron impact, thermalized, and photoexcited by a monochromatic pulsed laser. The appearance of daughter ions is plotted as a function of delay after the laser pulse, using the fast ICR detection capabilities of the ICR instrument. Since absorption of a photon gives a parent ion of precisely known internal energy (within the spread of initial thermal energies), each TRPD curve gives a single, well-defined point on the rate-energy curve.

There is an important point to remember when dissociation branches into two or more significant competing product channels, as is the case for thiophenol ion photodissociation at 308 nm. At first glance one would expect the shapes of the appearance curves for the two product ions to reflect the unimolecular rate constants of the dissociations leading to each, but this is actually not the case. Assuming that the photoexcited parent ion branches competitively to the two products, the shapes of the appearance curves for both product ions are identical, and both are the same as the parent-ion disappearance curve. So the rate constant derived from the shape of either of the daughter appearance curves is the parent-ion disappearance rate constant, that is to say, the sum of the two rate constants for the competing channels. The rate
constant for each individual channel is obtained by multiplying this number by the branching fraction for the channel in question.

Figure 1 shows the ICR photodissociation mass spectrum (light-on and light-off) at 308 nm, taken on the Fourier-transform ICR spectrometer. It is seen that m/z 84 and 66 are the only major photodissociation products, and are produced in comparable abundance, although the branching ratio is unreliable here since the parent ions were not thoroughly thermalized in this spectrum. Using thermalized parent ions TRPD curves were obtained for both m/z 84 and m/z 66 ions at 308 nm, as shown in figure 2, and for m/z 84 at 355 nm, as shown in figure 3. There was insufficient photoproduction of m/z 66 for measurement at 355 nm, and it was estimated that m/z 66 production was less than 25% of m/z 84 production.

Dissociation Rate Constants. Analysis of the 308 nm TRPD curves requires care, since the dissociation rate is near the limit of time resolution of the technique. The basic signal equation is

\[ S^0(\tau) = C(\Delta + (1/k) e^{-kr}(e^{-k\Delta} - 1)) \]  

where \( S(\tau) \) is the daughter ion signal as a function of the delay \( \tau \) between the laser pulse and the beginning of the ICR excite pulse, \( \Delta \) is the length of the excite pulse, and \( k \) is the dissociation rate constant. However, as discussed in chapter 6, a correction is needed in case the dissociation is fast and the ratio of parent to daughter masses is not sufficiently large, as was particularly true for m/z 84 production at 308 nm. With the correction term, which
was derived in reference 1c, the signal equation takes the form

$$S_{corr} = S^0 + \frac{e^{-k\tau}}{1 + (\delta/k)^2} \left[ 1 - \frac{e^{-k\Delta} \sin(\delta \Delta)}{(k/\delta)} \right]$$

where $\omega_d$ and $\omega_p$ are the cyclotron angular frequencies of the daughter and parent ions, respectively, $\delta = \omega_d - \omega_p$, and $\omega = (\omega_d + \omega_p)/2$.

Finally, if the thermal spread of internal energies is significant, the thermal distribution of rate constants k(E) must be folded into equation (2) as discussed in reference 1a and chapter 6:

$$S_{thermal} = \int P(k(E)) \cdot S_{corr}(k(E_{th} + E_{photon})) \, dE_{th}$$

where $P(k(E))$ is the probability that an ion will fragment with a rate constant $k(E)$. This was done using a cell temperature of 375 K at which thiophenol ions have an average thermal energy of 0.16 eV.

As expected, the photoproduction curves for m/z 66 and 84 at 308 nm had similar shapes (figure 2), supporting the assumption that these ions are produced competitively. Equation (3) gave good fits to the curves, from which rate constants of 2.0x10^5 s^-1 (m/z 84) and 2.2x10^5 s^-1 (m/z 66, average of 7 values) were derived at 4.20 eV internal energy. The best overall rate constant value was considered to be 2.2x10^5 s^-1. A branching ratio of 1.4:1 was measured for the m/z 84:66 ratio. This implies unimolecular
dissociation rate constants of $1.3 \times 10^5$ s$^{-1}$ for the m/z 84 reaction, and $9 \times 10^4$ s$^{-1}$ for the m/z 66 reaction. Equation (3) gave an excellent fit to the 355 nm data (Figure 3) using a rate constant of $2.8 \times 10^3$ s$^{-1}$ at 3.66 eV. Assuming a negligible m/z 66 contribution to dissociation at this energy, this value may be taken as the unimolecular dissociation rate for the dissociation of parent ion to m/z 84. (It was estimated that m/z 84 production was at least 4 times greater than m/z 66 production at 355 nm, which sets a lower limit of $2.2 \times 10^3$ s$^{-1}$ for the 84 production rate constant, and an upper limit of $5 \times 10^2$ s$^{-1}$ on the 66 production rate constant.) These rate values can be combined with RRKM modeling to draw rate-energy curves for the m/z 66 and 84 dissociation reactions, as described below.

**Collisional Cooling and Ion Thermalization.** Because the rate of photodissociation yielding m/z 66 was so much faster than initially expected, pains were taken to assure thermalization of the parent ions, and to exclude the possibility of a large rate acceleration due to unrelaxed excess internal energy. As illustrated in figure 4, electron-impact-produced ions were indeed superthermal: the figure compares TRPD curves with and without thorough thermalization. The upper set of data points were taken with the laser pulse 1 s after ionization, at a pressure of $5 \times 10^{-8}$ Torr, giving one to two collisions before the laser pulse, while the lower set of points used a delay of 2 s and a pressure of $6 \times 10^{-7}$ Torr, giving approximately 25 collisions. The photoappearance rate is almost 3 times faster under the low-pressure conditions ($6 \times 10^5$
s\(^{-1}\)) than under the high-pressure conditions (2.2\times10^5 \text{ s}^{-1}). As shown below, 25 collisions is in fact more than ample for thorough thermalization of the ions.

The use of TRPD in this way as an ion thermometric technique for observing ion cooling has been described several times for other ions,\(^{1a,1b}\) a recent study of styrene ion being particularly comprehensive.\(^{1c}\) Since this approach to measuring small amounts of unrelaxed excess internal energy was both convenient and successful for thiophenol ion, a more extensive set of data was taken from which the collisional cooling rate could be estimated. The radiative cooling properties of thiophenol ion were studied in previous studies using two photon photodissociation methods,\(^{3,4}\) but the collisional cooling rate was not very well determined. Dissociation rate constants were measured as a function of the number of thermalizing collisions from 0.7 to 40. Using the rate energy curve (shown below as figure 6) to convert the dissociation rate constants into excess internal energy values, a curve of energy versus collision number was constructed as shown in figure 5. While the scatter of this plot is substantial, one should note that the sensitivity of the measurement to excess internal energy is very high, with a precision of the order of .02 eV.

Assuming as a reasonable approximation that the initial internal energy of the ions decreases exponentially due to both collisional and infrared radiative relaxation processes,\(^{5}\) the excess ion internal energy \(E\) is expected to follow the function

\[
E(t) = E_0 \cdot \exp\left[\cdot\left(k_R + k_c P\right)t\right]
\]  

(4)
where $E_0$ is the initial internal energy, $k_r$ and $k_c$ are the radiative and collisional relaxation rate constants, and $P$ is the pressure of neutrals. Since $t$ was constant at 1 s in this series of experiments, the radiative contribution was constant, giving

$$E(t) = \text{const} \cdot \exp(-k_cPt)$$

(5)

The exponential curve drawn through the points on figure 5 provides an acceptable fit to this expected exponential decay. The decay constant is 3 collisions, corresponding to a collisional cooling rate constant of $4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which indicates that two collisions remove half the excess energy in the parent ion, even when the excess energy is in the very low regime between thermal and 0.1 eV. Collisional cooling is thus quite efficient.

Efficient collisional cooling of an ion by its parent neutral molecule is common in the somewhat higher internal energy regime (0.5-3 eV) for which most experimental information is available, and was also found for styrene ion in the low-energy regime. Resonant charge transfer is generally accepted as accounting for the high collisional cooling efficiency, and this mechanism would be expected to remain highly efficient even under the present conditions of small excess energy above thermal.

**Two Photon Photodissociation.** At visible wavelengths, the photodissociation of thiophenol ion is energetically inaccessible with one photon, and dissociation occurs by sequential absorption of two photons. This two-photon process was extensively characterized and exploited using several techniques in the ICR ion
trap with the aim of measuring ion energy relaxation rates.\textsuperscript{3,4} For the purposes of the present discussion, the important point is that as the photon energy approaches the one photon dissociation threshold, a transition from two photon kinetics is expected, signaled by changes in the pressure dependence, laser chopping rate dependence and light intensity dependence of the extent of dissociation.

As an approach to fixing the dissociation threshold energy for thiophenol ion, the dissociation kinetics were characterized using 458 nm (2.71 eV) photons from the argon ion laser. The kinetics showed unquestionable two photon behavior at this wavelength. It is expected that one photon characteristics of the kinetics would be observed if the one photon threshold were less than 2.9-3.0 eV (allowing for the thermal energy content of the ions). Accordingly, this result was taken as a further confirmation that the dissociation threshold for thiophenol ion is not as low as 2.9 eV.
DISCUSSION:

The initial motivation for the careful study of thiophenol ion rate-energy curves reported here was the surprising observation that the m/z 66 photodissociation was much faster than expected based on the expected tight transition state and using the accepted threshold of 3.2 eV\(^2\). It has become clear that this observation is correct, and that a loose transition state is inescapably necessary for RRKM modeling of this reaction. To clarify this question, calculations were done using a reasonably tight transition state having a calculated \(\Delta S^\#\) (1000 K) of -1.4 eu. Using a critical energy of 3.2 eV, this leads to a calculated dissociation rate of \(6 \times 10^2\) s\(^{-1}\) at 4.22 eV internal energy (corresponding to photodissociation at 308 nm), nearly 100 times slower than the observed rate at 308 nm. Thus such a model is completely unsuccessful.

A more serious possibility is that the transition state is tight, but the activation energy for this dissociation is lower than 3.2 eV. Using the same tight transition state and a critical energy of 2.9 eV, a rate-energy curve can be calculated which gives a roughly correct rate of \(5 \times 10^4\) s\(^{-1}\) at 4.2 eV. There are, however, a number of reasons to reject this model for the dissociation. The first difficulty with this model is its divergence from experiment at lower internal energies. At 3.66 eV, corresponding to 355 nm photodissociation, the rate is predicted to be \(2 \times 10^3\) s\(^{-1}\) while, as seen above, the TRPD results at 355 nm put an upper limit of \(5 \times 10^2\) s\(^{-1}\) for the dissociation to m/z 66. Along
the same lines, this model clearly predicts that m/z 66 will be comparable to m/z 84 at low internal energies, while the result at 355 nm clearly shows that m/z 84 is the dominant dissociation product at low internal energies. Moreover, an activation energy of 2.9 eV for m/z 66 production is hard to reconcile with the convincing threshold observed near 3.2 eV by Lifshitz et al.\(^8\). And finally, the dissociation endothermicity of 3.2 eV which is calculated from rather good thermochemical values\(^7\) is probably near the activation energy for dissociation, since the kinetic energy release was observed to be low\(^8\) suggesting little or no reverse activation energy for this process. Accordingly, such a tight transition state may be totally ruled out for this dissociation within the assumption of the applicability of RRKM theory. Since we would assume RRKM theory to be valid unless forced to abandon it, we will discuss this reaction further on the assumption that the rate limiting transition state is indeed fairly loose, with \(\Delta S^\#(1000 \text{ K})\) of +14 eu.

Using this loose transition state with a critical energy of 3.2 eV the rate energy curve shown in figure 6 was calculated and used as the basis for the satisfactory modeling of results from a time-resolved photoionization study of m/z 66 formation.\(^8\) As noted on the plot this curve also passes through the TRPD point determined at 308 nm (4.20 eV).

The rate-energy curve for m/z 84 formation shown in figure 6 is obtained using a somewhat tight transition state, with \(\Delta S^\#(1000 \text{ K}) = 2.74\) eu and critical energy of 2.82 eV. As shown, it passes
through the two experimental points. This transition state, which is much tighter than an orbiting transition state, does not seem unreasonable for a rearrangement dissociation. The endothermicity of the m/z 84 dissociation, assuming a product ion of the thiophene structure, is calculated from thermochemical values\textsuperscript{7} as 2.91 eV. Thus the critical energy (2.82 eV) derived from the RRKM fit is slightly lower than the endothermicity, which is not unreasonable for a tight transition state (although this energy difference may not be experimentally significant).

**Potential Surface Model.** The potential surface proposed to account for the loose transition state in the rate-limiting step of the m/z 66 reaction is sketched in figure 7. It is suggested that the tight transition state corresponding to the molecular rearrangement, designated "A" on the figure, has negative activation entropy, but has an energy below 2.9 eV, so that passage through this transition state is not rate limiting in the internal energy regime of interest here. The rate limiting loose transition state, designated "B", has an energy of 3.2 eV and a $\Delta S^\#$ of +14 eu, which are the kinetic parameters indicated by the data for the rate limiting step.

The nature and structures of these transition states can only be pure speculation, but to clarify thinking about them, we can speculate that the dissociation mechanism might look like the following, assuming a 1,3-hydrogen shift rearrangement route for the sake of argument:
Scheme 1.

Speculative structures along the reaction coordinate for m/z 66 formation.

The breaking of the C-C bond in transition state "B" is suggested as the high energy process on the potential surface, so that even though its entropy is high, approaching the looseness of an orbiting transition state, nevertheless it constitutes the kinetic bottleneck in the dissociation.

It should be emphasized that the two transition state picture of this dissociation is proposed as being strongly implied by the experiments, but without any serious advocacy of the particular speculative transition state structures drawn in Scheme 1. One possibly testable prediction of this model is that the m/z 66 dissociation process should exhibit transition state switching at some internal energy above 4.2 eV, as the tight transition state becomes rate limiting and slows the dissociation below the rate
suggested by extrapolating the rate-energy curve of figure 6 to higher energies.\textsuperscript{9,10,11}

\textbf{Comparison with Phenol.} An interesting comparison and contrast with the corresponding dissociation of phenol ion can be made.\textsuperscript{12}

The activation energy for CO loss from phenol ion is about 2.9 eV\textsuperscript{13,14}, which is notably in the same vicinity as suggested for the rearrangement transition state in the thiophenol case. However, phenol is very different in that the dissociation endothermicity (about 1.3 eV) is much less than the activation energy, so that phenol ion exhibits a large reverse activation energy for this process, accompanied by a large kinetic energy release. Thus we might draw a corresponding potential surface for phenol ion dissociation as in figure 8.

For neutral systems, the special stability of CO is such that extracting CO from an alcohol is of the order of 2 eV less endothermic than extracting CS from the corresponding thiol. In the case of phenol and thiophenol ions, it is similarly true that the loss of CO from phenol ion is about 2 eV less endothermic than loss of CS from thiophenol ion (1.3 vs. 3.2 eV). Assuming that this added product stabilization in the alcohol case develops as the carbon rehybridizes to form the triple bond of CO, it is entirely reasonable that the rearrangement transition state "A" in figure 7 would have similar energies in the phenol and thiophenol cases; but in the phenol case the dissociation would be strongly downhill from this point, while in the thiophenol case it would be uphill, with the second transition state "B" turning out to be rate
determining. These contrasting pictures are clearly seen in the comparison of figures 7 and 8. Thus, as we view it, for phenol ion the rearrangement transition state is rate limiting, while for thiophenol ion the orbiting transition state corresponding to separation of the products is rate limiting, with the prior rearrangement being kinetically insignificant.
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5. The expectation of exponential radiative cooling was discussed in R. C. Dunbar, J. Chem. Phys. 90, 7369 (1989). While exponential collisional cooling seems to be a reasonable first approximation, there is little theory or data bearing on this question.


11. C. Lifshitz, Advances in Mass Spectrometry ...


FIGURE CAPTIONS:

1. Photodissociation mass spectrum for thiophenol ion photodissociation at 308 nm in the FTMS ion trap.

2. TRPD curve for m/z 66 and m/z 84 photoproduction at 308 nm.

3. TRPD curve for m/z 84 photoproduction at 355 nm.

4. Comparison of TRPD curves for m/z 66 photoproduction at 308 nm with thermalized (O) and unthermalized (Δ) parent ions, showing the markedly faster dissociation for the ions containing excess internal energy.

5. Internal energy of thiophenol ions as a function of pressure of neutral gas, measured 1 s after the electron beam pulse. The internal energies were measured by quantitative analysis of TRPD curves like those shown in figure 4.

6. Rate-energy curves calculated by RRKM modeling for the two thiophenol ion dissociation channels using the transition states and parameters described in the text. Also shown are the points for m/z 84 ([I]) and the point for m/z 66 (O) obtained from the TRPD results.

7. Proposed potential energy surface for the two dissociation channels for thiophenol ion.

8. Proposed potential energy surface for dissociation of phenol ion by loss of CO.
Laser on

Laser off
Fragment (relative abundance)

m/z 84
355 nm

Delay Time (us)
Future Work:

During the course of this work several areas have opened themselves for further investigation. Two areas in particular where investigations could be conveniently expanded using the available experimental tools involve the photo-induced unimolecular fragmentations of ferrocene and thiophenol cations. Outlined below are some thoughts for future experiments with these two ions.

Ferrocene: Further TRPD investigations of the photo-induced ring loss of ferrocene cation are warranted. In chapter V the energy requirement for this fragmentation was not fully determined because of a large kinetic shift; only a lower limit of 5.4 eV was set for the fragmentation threshold. It is therefore of interest to apply the TRPD experiment to study this reaction further. By measuring the fragmentation rate at several ion internal energies a rate-energy curve can be constructed. RRKM modeling of this curve will give a value of the activation energy that is free from kinetic shift effects. In addition this fragmentation was found to require the energy content of two photons in the UV energy range available from our lasers. This makes it an attractive prospect for a two-color-two-pulse TRPD experiment in which the first photon is supplied by the first laser pulse and the second photon (of different energy) is supplied by the second laser pulse. Using this approach the ion internal energy is not limited to twice the photon energy. Instead the energy of the first photon can be varied independently of the second allowing a finer control over the energy deposited in the ion.
Thiophenol: The photofragmentation of thiophenol cation could be investigated further. Starting with parent ion labeled in the anomeric position with $^{13}\text{C}$ and looking at the fraction of label remaining in the 66 m/z photofragment ion it may be possible to determine the origin of the carbon in the CS neutral fragment. Such a study has been carried out with ions that were formed from the labeled neutral by impact with 70 eV electrons, but has not been done in the lower energy regime of interest to us.

**Comments on the TRPD method:**

The TRPD method has been used in this work to determine (i) the rate of internal energy loss and (ii) the activation energy for unimolecular fragmentation of vibrationally excited ions. The following discussion concerns the merits and suitability of applying the TRPD method to these measurements.

In chapter III the rate of internal energy loss was determined by following the ion's internal energy over time using methods based on the kinetic differences between one and two photon dissociations. With these methods it was not possible to monitor the ion's internal energy below the one photon threshold; the internal energy below which one photon is insufficient to bring about fragmentation. Since this threshold is usually greater than the average thermal energy of the ion, it was not possible, using these methods, to measure the relaxation rate down to thermal energies.

To follow the loss of internal energy below the one-photon threshold it was necessary to use the TRPD method, as in chapter
VII for thiophenol ion. Since the fragmentation rate provides a
direct measure of the internal energy, it is possible, using the
TRPD method, to monitor the ion's internal energy all the way down
to thermal energies. At higher internal energies the TRPD
experiment becomes less useful in measuring relaxation rates,
because the fragmentation is too fast to time resolve on our
instrument.

The TRPD experiment also avoids the problem of kinetic shift in
determining the activation energy, $E_0$, for a photofragmentation.
In the TRPD experiment the value of $E_0$ is obtained from RRKM
modeling of several rate energy points that are measured without
requiring that the internal energy of the ions (photon plus
thermal) be near threshold, where kinetic shift is a problem.
BIBLIOGRAPHY

Chapter I


Chapter II


Chapter III


10. Subsequent work on this ion (reference 14 and chapter VII) has shown that the lowest energy fragmentation channel is loss of acetylene with an activation energy of 2.9 eV. This lowers the one photon threshold to 0.5 eV.


Chapter IV


Chapter V

   (b) Faulk, J.D.; Dunbar, R.C. J. Phys. Chem. 1990, 94(6), 2324. 


5. A survey can be found in: Dunbar, R.C. in Photofragmentation of Molecular Ions; T.A. Miller; V.E. Bondybey, eds.; North Holland, 1983.


Chapter VI


12. The B value for the internal rotation of the t-butyl group was calculated from the expression for internal rotation, \( B = \frac{h^2 \eta^2}{2I} \). The value for the moment of inertia "I" along the \((\text{CH}_3)_3\text{C} - \text{C}\) bond axis was obtained from the overall rotational constant "A" for t-butyl cyanide (4600 MHz from reference 16) according to the expression for overall rotation along the C-CN bond axis, \( A = \frac{h}{(8\pi^2 I)} \). A similar calculation was carried out for methyl rotation using \( I = 5.3 \times 10^{-47} \text{ kg m}^2 \) from reference 16.


Chapter VII


5. The expectation of exponential radiative cooling was discussed in R. C. Dunbar, J. Chem. Phys. 90, 7369 (1989). While exponential collisional cooling seems to be a reasonable first approximation, there is little theory or data bearing on this question.


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