Considerably more experimental work is required to establish these trends that presently are only suggested by the data.

The idea expressed here that the relaxations are likely to occur by specific mode coupling rather than by indiscriminate decay suggests that the thermal relaxation of molecular crystals is likely to involve internal vibrational bottlenecks. We expect that the levels which are not sufficiently close to the phonon edge yet still in a region where the molecular levels are sparse will become significantly populated following the excitation of higher levels. This suggests many new experiments on vibrational dynamics in solids following optical excitation of overtones or electronically excited states.

There is a significant effect of ^{13}C impurities on the Raman line widths of a number of modes in crystalline benzene. Obviously this observation carries strong implications for the interpretations of the Raman line widths and vibrational coherence times measured in other molecular crystals with natural abundances of isotopically substituted molecules. A priori, one must suspect that the effects we have seen will also obtain in other crystals. Therefore, the coherence decay time measurements made by previous workers[16,17,19,21,23,26] can at best be regarded as lower limits to the true crystal vibrational relaxation times. Also, calculations and interpretations based on them must also be reexamined.[65] A failure to recognize this can lead to seriously incorrect conclusions about the nature of mode-to-mode vibrational energy relaxation in molecular crystals.

In certain respects, the strong impurity effects discussed here are consistent with a previous study of vibrational coherence decay in solid hydrogen.[14] While there is no evidence yet that the mechanism of impurity induced coherence decay in the para/ortho hydrogen system is identical with that of the $^{12}C/^{13}C$ benzene system, the parallel should provoke further theoretical and experimental investigation into these issues.

Future experiments might also address the relaxation functions for different levels of an exciton band. The information only exists currently for two components of the 991-cm^{-1} mode of pure and natural C_6H_6.[19,20] In that case it seems likely that scattering contributes to the measured coherence decay of level at the band center but not to the component at the band edge. The low-resolution measurements of Hess and Prasad on the 390-cm^{-1} mode of naphthalene show an intriguing qualitative difference in the line shapes of the two Davydov components.

The early work in this field has provided a most encouraging prognosis for understanding molecular crystal relaxation. While many of the concepts require further experimental investigation and the connections between theory and experiment are not yet firmly established, the new generation of laser related methods should make a significant contribution to closing these gaps.

ARTICLES

Time-Dependent Mass Spectra and Breakdown Graphs. 6. Slow Unimolecular Dissociation of Bromobenzene Ions at Near Threshold Energies

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Time-resolved photoionization mass spectrometry (TPIMS) in the millisecond range has been employed to study the reaction $C_6H_5Br^{+\cdot} \rightarrow C_6H_5^+ + Br\cdot$ in bromobenzene. Experimental photoionization efficiency curves were fitted with a QET model calculation by assuming a critical energy $E_0 = 2.76$ eV and an activation entropy $\Delta S^\ddagger = 8.07$ eu. The activation entropy corresponds to the totally loose (orbiting) transition state. Ultraslow unimolecular dissociations having microcanonical rate coefficients $k(E) \leqslant 10$ s^{-1}, at near threshold energies, can be sampled by TPIMS, in spite of competing IR-radiative decay of the parent ion.

Introduction

The bromobenzene cation undergoes a simple bond cleavage to a phenyl cation and a bromine atom

$$C_6H_5Br^{+\cdot} \rightarrow C_6H_5^+ + Br\cdot \qquad (1)$$

This reaction has been studied previously by electron-impact (EI) mass spectrometry,[1] by photoionization mass spectrometry (PIMS),[2,3] by photoelectron–photoion coincidence (PEPICO)[4,5] and by threshold ion photodissociation.[6] It demonstrates a fairly large "kinetic shift", where the "kinetic shift" is defined as the excess energy required to produce detectable dissociation of a polyatomic ion in 10^{-5} s.[7,8]

We have constructed and tested recently[8-11] a photoionization mass spectrometer which performs time-resolved experiments. It fulfills the obvious experimental approach for evaluating kinetic shifts,[12] namely measuring the shift of the ionization efficiency

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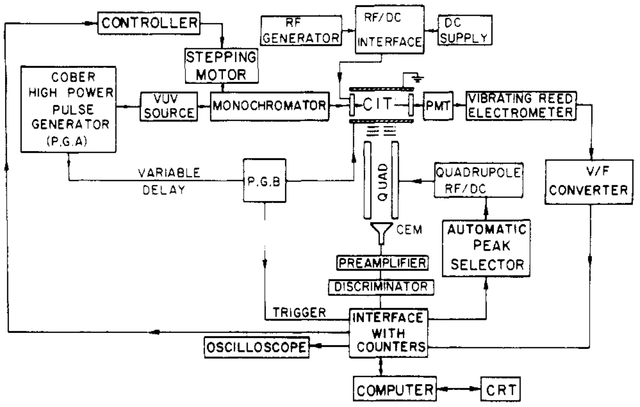

Figure 1. Time-resolved photoionization mass spectrometer (TPIMS). The vacuum UV source is a Hinteregger hydrogen discharge lamp; the monochromator is a McPherson Model 225 1-m, normal-incidence instrument, the quadrupole mass spectrometer is a EAI QUAD 1110, the computer is an Industrial Micro Systems, IMS 5000, microcomputer: PMI, photomultiplier; CEM, channeltron electron multiplier; PG, pulse generator.

curve along the energy axis as the residence time of the ion is varied. It combines the excellent energy resolution of photon impact with an extension of the time scale from microseconds to milliseconds. The central part of the instrument is a cylindrical ion trap (CIT) similar to the one employed previously[13] for electron impact.

We have applied this technique, time-resolved photoionization mass spectrometry (TPIMS), to the bromobenzene reaction. The experimental results will be presented and compared with QET calculations. The role of IR-radiative decay of the parent ion will be assessed.

Experimental Section

A block diagram of the experimental setup is shown in Figure 1. Photoionization is induced by a pulsed vacuum UV light source, a Hinteregger discharge in hydrogen producing the many-line spectrum. Photoions are trapped in a cylindrical ion trap (CIT).[13] They are ejected into the quadrupole mass filter by a drawout pulse, following a variable delay time, and counted only during the ejection pulse. Ions can be stored from microseconds to milliseconds.

The characteristic dimensions of the CIT employed are r_1 = 2 cm and z_1 = 1.5 cm. Typical operating conditions are as follows: the radio frequency of the potential applied to the cylindrical barrel electrode is 0.5 MHz ($\Omega/2\pi$) and the peak-to-peak voltage is between 300 and 1500 V (depending upon the ion masses which are trapped); no dc voltages were employed in the present experiments and the device was operated along the q axis only of the stability diagram.[13] The planar end-cap electrodes are earthed and ions are ejected after a predetermined storage time by means of a -30- to -40-V pulse applied from a pulse generator PG2 to the end cap nearest to the mass filter.

The number of ions stored within the device, as indicated by the number collected following pulsed ejection from the trap after a given storage time, exhibits a maximum as a function of rf voltage, the position of which is mass dependent (Figure 2). The rf voltage chosen for experiments is at the crossing point of the parent–daughter stability curves (Figure 2) ensuring equal trapping efficiency.

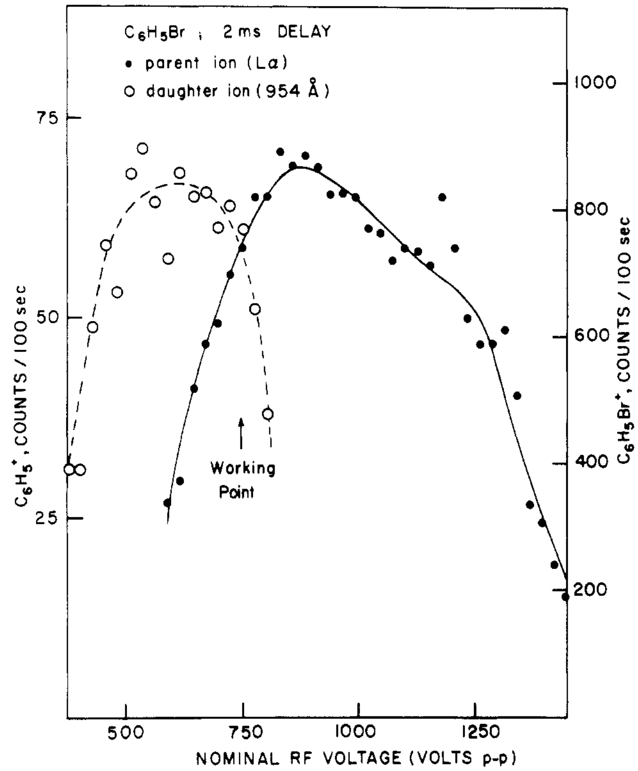

Figure 2. The number of parent ($C_6H_5Br^+$) ions and daughter ($C_6H_5^+$) ions collected, following pulsed ejection from the trap after a 2-ms storage time, as a function of the rf voltage applied to the cylindrical electrode, with zero dc bias. A mass-dependent compromise is struck between the probability of an ion when initially formed having a stable trajectory lying witin the bounds of the electrode structure, which decreases as the rf voltage increases, and the efficiency of ion trapping, which is favored at high q values (i.e., high rf voltages).[14]

Computer control of a photoionization mass spectrometer and automatic data aquisition provides a number of desirable features.[15,16] Extended signal-averaging techniques allow us to increase the sensitivity of ion detection and hence to minimize the effect of kinetic shift on fragmentation processes, even when time resolution is not available.[15] We have combined in our TPIMS extended signal-averaging techniques with time resolution. Because of the low count rates in our time-resolved experiments, a typical computer-controlled experiment which leads to a single photoionization efficiency (PIE) curve takes several days. The total number of daughter ions counted per energy point in the bromobenzene experiments was ~200. Instrumental noise is negligible and each count is a true ion count, since we are using the combination of a channeltron electron multiplier, discriminator, and counter. Thus, while ion count rates are low, the only source of error is statistical.

The microcomputer controls the wavelength setting of the monochromator via the stepping motor (Figure 1) and the mass transmitted by the quadrupole mass spectrometer through an automatic peak selector (by Vacumetrics). The light intensity emerging from the exit slit of the monochromator and entering the CIT is measured with a Pyrex window coated with sodium salicylate and a photomultiplier. A voltage-to-frequency (V/F) converter provides a digital light signal from the analog one obtained from a vibrating reed electrometer. Counters are employed to give the ion and light signals, respectively, at each wavelength setting, and these are stored in the computer. The data (ion and light intensity counts and PIE) are obtained on the computer screen in real time as is the PIE curve which is accumulated on an oscilloscope. Each computer-controlled experiment is made up of many repetitive cycles. In each cycle a series of preselected wavelengths (i.e., photon energy points) is scanned for the parent and daughter ions and the time intervals are chosen so as to obtain a nearly constant signal-to-noise ratio, at each

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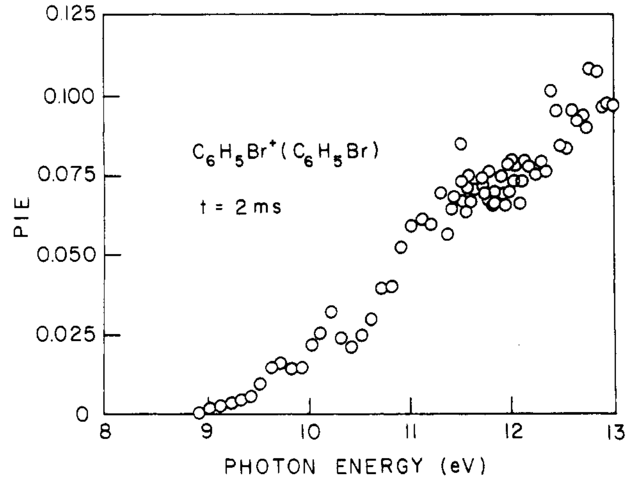

Figure 3. Photoionization efficiency (PIE) as a function of photon energy for the parent ion from bromobenzene following a storage time of 2 ms.

energy point. A typical cycle takes between 1500 and 2000 s ensuring minimal errors due to slowly varying parameters (e.g., sample pressure) during a cycle.

Long storage times are quite well defined. Thus, the 2-ms storage time was obtained as follows: A duty cycle of the lamp of 2.2 ms was employed, the lamp was pulsed on for 0.1 ms and off for 2.1 ms; the draw-out pulse was turned on for 0.05 ms at 1.95 ms following the start of the lamp-on pulse. It was noted that most of the ions were counted toward the end of the drawout pulse. The rf voltage was applied to the barrel electrode throughout the whole cycle. The shortest time of a few microseconds were run without the RF trapping voltage. A duty cycle of 50 μs was employed, the light-on pulse was 1 μs long, and the drawout pulse was applied for 5 μs following 1 μs from the start of the light-on pulse. All of the ions arrived at the end of the draw-out pulse, defining a reaction time of 6 μs with an error limit of about ±1 μs.

The entrance and exit slits of the monochromator were 500 and 600 μm, which gave an effective resolution of 5.0 Å. This corresponds to an energy resolution near the threshold for $C_6H_5^+$ formation from bromobenzene of $\simeq$0.06 eV. Typical light intensities at Lyman α (= 1216 Å) are $\sim 2.5 \times 10^7$ photons/s. Relative intensities at other wavelengths are similar to those obtained under continuous operation of the Hinteregger hydrogen discharge lamp.[17] Wavelength calibrations are achieved by using Lyman α or known H_2 emission lines.

Sample pressures in the CIT were kept as low as possible in order to avoid bimolecular processes. They were adjusted such that collision-induced dissociation at energies below the expected unimolecular dissociation threshold was minimal and are estimated to be $\leq 10^{-6}$ torr (not measured directly). The constancy of the pressure during runs was judged by the constancy of the parent ion count rates at Lyman α. Sample temperatures are estimated to be room temperature (~30 °C). The sample was introduced through a Granville-Phillips variable-leak valve, which had to be heated to 60 °C to prevent clogging of the leak. While the leak valve is situated at a fair distance from the CIT, it is possible that the temperature of the ionized sample is slightly higher than 30 °C.

Kinetic energy release distributions (KERDs) were obtained as previously described.[18] A MAT 311 reverse Nier-Johnson mass spectrometer was employed with electron impact ionzation at 70 eV. The fragmentation of the bromobenzene cation occurring in the second field-free region was obtained by scanning the electrostatic sector at a constant acceleration potential (MIKE scan). The width of the β (energy-defining) slit of the instrument is fixed at 0.4 mm. The time window sampled is 18–22.2 μs. The KERD, $P(E_t)$, was derived from the measured peak by using the expression[19,20]

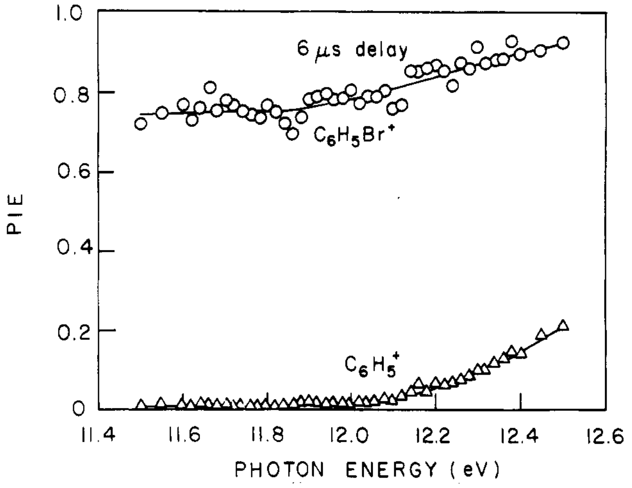

Figure 4. Parent ($C_6H_5Br^+$) and daughter ($C_6H_5^+$) PIE curves (to scale) at a short storage time of 6 μs, near the energy threshold for dissociation.

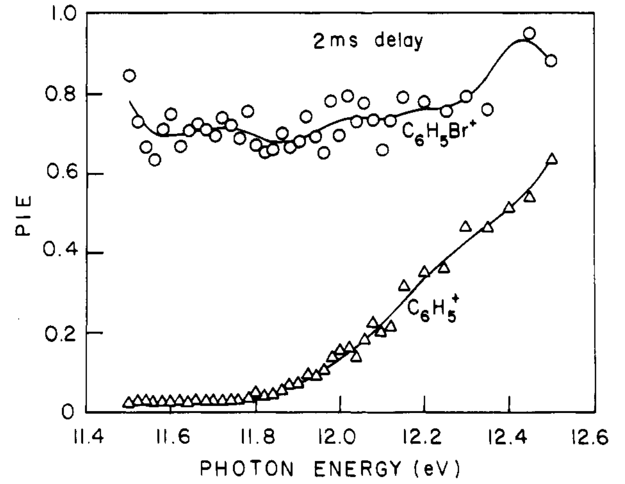

Figure 5. Parent ($C_6H_5Br^+$) and daughter ($C_6H_5^+$) PIE curves (to scale) at a long storage time of 2 ms, near the energy threshold for dissociation.

$$P(E_t) = \mathrm{d}I(E)/\mathrm{d}E \qquad (2)$$

where $I(E)$ is the peak intensity at energy E.

Chemicals were commercially available and employed without further purification. Their purity was checked by EI mass spectrometry. C_6D_5Br was from MSD Isotopes Canada with a stated isotopic purity of 99.5 atom % D.

Results and Discussion

Figure 3 represents the PIE curve for the bromobenzene ion at a storage time of 2 ms. The data are in fair agreement with previous continuous (not time-resolved) PI data.[2] The PIE curves for the daughter ion (Figures 4 and 5) are clearly time dependent both in terms of the onset energy and in terms of the intensity relative to the parent.

Time-resolved daugher ($C_6H_5^+$) PIE curves were calculated on the basis of the QET model due to Rosenstock et al.[5] This was done in the following way: The microcanonical rate coefficient $k(E)$ was calculated as a function of energy by an RRKM program.[21] The activated complex frequencies were taken the same as for the reactant ion (and neutral molecule[22]) except for the six halogen-dependent normal modes. One of these (670 cm^{-1}) was taken as the reaction coordinate[4,5] and the other five were set equal

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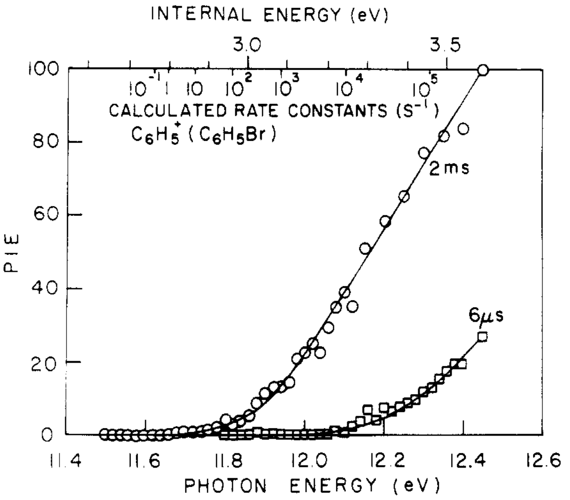

Figure 6. Time-resovled experimental (circles and squares) and calculated (smooth lines) daughter ($C_6H_5^+$) PIE curves. The maximum possible internal energy in the ion (upper scale) for a zero kinetic energy electron was calculated from the photon energy, $h\nu$ (lower scale) and from the known ionization energy of bromobenzene,[5] $IE(C_6H_5Br) = 8.97$ eV as follows: internal energy (eV) $= h\nu - 8.97 + 0.12$, where the 0.12-eV correction stands for the average thermal energy of neutral bromobenzene at the temperature of the experiment (303 K). The calculated bromobenzene ion dissociation rates at these internal energies are also shown on the upper scale. The PIE curves were exactly calculated from the QET model; see text for further details.

to 130 cm^{-1}. Time-resolved daughter-ion breakdown curves were calculated from the rate-energy dependence ($k(E)$) at 0 K; these give the internal energy dependence of the fractional abundance of the daughter ion. The threshold photoelectron spectrum (TPES)[4] was adopted as the energy deposition function for our photoionization experiments. The 0 K breakdown curves were convoluted with the instrumental slit function, with the calculated thermal energy distribution at the temperature of the experiment and with the TPES. The resultant curves represent the calculated first derivatives of the PIE curves of the daughter ion, provided the threshold law for photoionization is a step function.[23] These curves were integrated to compare them with the time-resolved experimental PIE curves.

The relative intensities of the experimental PIE curves of the parent (Figures 4 and 5) served to scale the experimental daughter PIE's at different storage times, following background subtraction. The daughter PIE curves were reproduced very well by the QET calculation. Figure 6 represents two such curves where the open circles and squares are experimental and the curves are calculated. From the rate constant calculations, it is estimated that rate coefficients $k \leq 10$ s^{-1} are observable for ion storage times of several milliseconds.

Figure 6 demonstrates for the first time convincingly the existing kinetic shift on the PIE curve for a daughter ion resulting from a unimolecular dissociation of statistical origin.

The statistical nature of the reaction at near threshold energies has been further verified by a theoretically calculable, experimentally observable secondary deuterium isotope effect (Figures 7 and 8). These experiments were run on a 1:1 mixture of C_6H_5Br and C_6D_5Br to ensure equal number densities of the isotopic species. Secondary isotope effects have been studied previously in this system in the microsecond time range, both by EI[24] and by PEPICO.[25] It was concluded[25] that the CH and CD vibrational modes participate fully in the energy flow of the isolated molecular ions, even though the CH and CD bonds are not involved in the formation of product $C_6H_5^+$ and $C_6D_5^+$ fragment ions. It was noted[25] that "it would be most interesting to determine

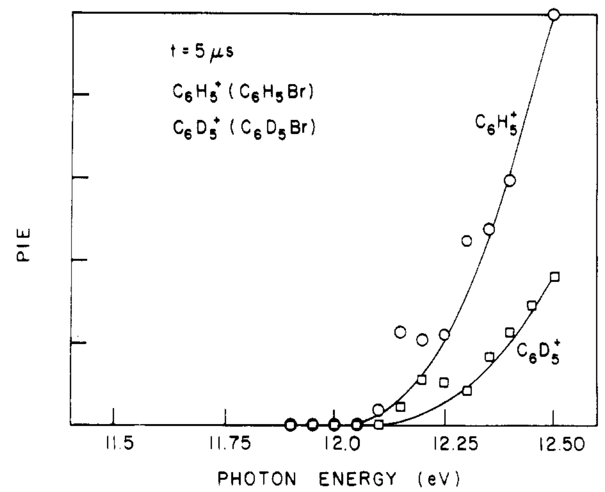

Figure 7. Experimental (open circles and squares) and calculated (smooth lines) PIE curves at a short storage time of 5 μs for $C_6H_5^+$ and $C_6D_5^+$ from a 1:1 mixture of C_6H_5Br and C_6D_5Br. The scatter near threshold is due to poor statistics and/or incomplete correction for the light intensity near Lyman β. In the QET calculation the model is due to Rosenstock et al.[5] as in Figure 6, with the changes made in the frequencies for the deuterated molecule, introduced by Baer and Kury.[25]

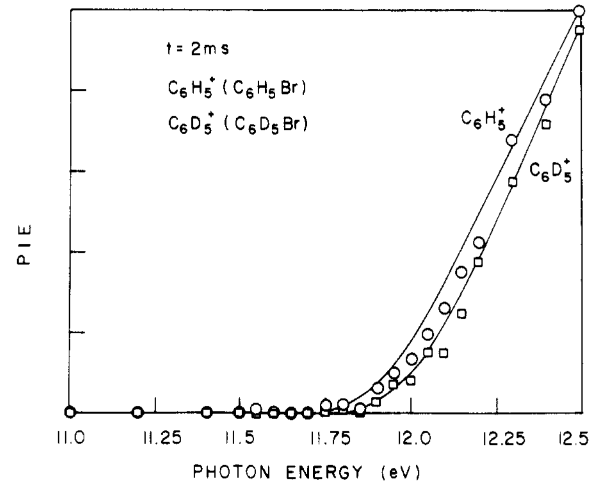

Figure 8. Experimental (open circles and squares) and calculated (smooth lines) PIE curves at a long storage time of 2 ms for $C_6H_5^+$ and $C_6D_5^+$ from a 1:1 mixture of C_6H_5Br and C_6D_5Br.

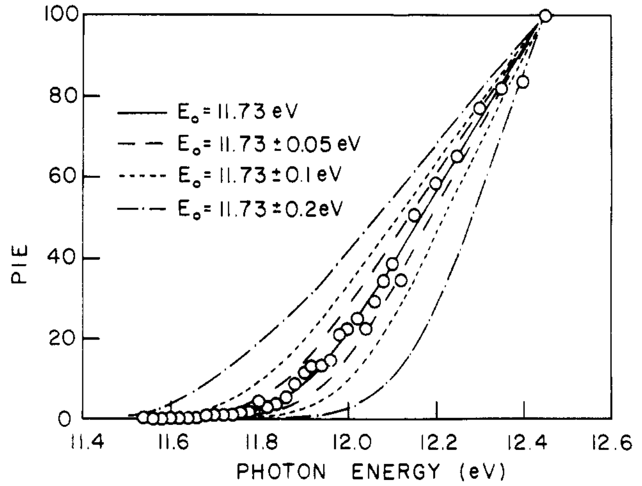

Figure 9. Experimental (open circles) and calculated (see legend) PIE curves for $C_6H_5^+$ from C_6H_5Br at $t = 2$ ms. All the curves are normalized to the highest energy experimental point. Different normalizations gave very similar results in spite of some scatter in the experimental curve. See text for further details.

whether energy flow continues to be random at the very low energies" above the dissociation threshold (<0.5 eV). Our results

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indicate that this is indeed the case, although we have not determined the rate constants at threshold directly.

Figure 9 represents a sensitivity analysis for the threshold energy. The experimental PIE curve for $C_6H_5^+$ at 2 ms is compared with calculated curves at different threshold energies. In these calculations the vibrational frequencies of the activated complex were kept constant and equal to the ones employed by Rosenstock et al.[5] Excellent agreement is obtained for a 0 K photon threshold energy of 11.73 ± 0.05 eV. This is the value obtained by Rosenstock et al.[5] from PEPICO data in the microsecond range. This establishes the critical energy (or "activation energy") for reaction 1 at $E_0 = 2.76 \pm 0.05$ eV and the value for the heat of formation of the phenyl cation at $\Delta H_f{}^\circ{}_0(C_6H_5^+) = 270$ kcal/mol.

A few words are in order concerning the activation parameters. Rosenstock has demonstrated the usefulness of calculating equivalent activation entropies, $\Delta S^\ddagger$, and preexponential factors, A_∞, in spite of the fact that these pertain to the canonical system and measurements are made in a nonthermal system. This was commented upon by one of us previously.[26] Rosenstock et al.[5] have calculated an equivalent 1000 K entropy of activation for their model $\Delta S^\ddagger = 8.6$ eu and a hypothetical unimolecular thermal A factor at 1000 K of 9.4×10^{14} s^{-1}. These values were criticized by Pratt and Chupka.[3] We have recalculated these values, employing the same set of activated complex vibrational frequencies as Rosenstock et al.[5] and found the original ones to be in error and obtain instead $\Delta S^\ddagger = 8.07$ eu and $A_\infty(1000\text{ K}) = 3.29 \times 10^{15}$ s^{-1}. These values are very close to those for the Klots–Langevin phase-space type model[27] employed by Pratt and Chupka[3] in their calculations.

Because the values are very close to those obtained for the Klots model it is concluded that the present model corresponds to the totally loose complex. Furthermore, an exact phase space calculation with angular momentum conservation gave us $k(E)$ dependences, breakdown curves, and PIE's which were indistinguishable from the Rosenstock model calculation, provided the same critical energy, E_0, was employed. These calculations followed prescriptions which appear in the literature for solving the Langevin-phase space theory exactly.[28,29] These involve an exact counting of rotational states and averaging over the initial rotational distribution of the dissociating ion. The following parameters were employed in the phase space calculations: rotational constant of the bromobenzene cation, $B_0 = 4.1 \times 10^{-2}$ cm^{-1}; rotational constant of the $C_6H_5^+$cation[27b], $B = 0.15168$ cm^{-1}, polarizability of the Br· atom, $\alpha(\text{Br}\cdot) = 3.5 \times 10^{-24}$ cm^3. Vibrational frequencies of $C_6H_5^+$ were obtained[3] by removing three vibrations corresponding most closely to the carbon–halogen local modes from the vibrational frequencies of neutral chlorobenzene.[22] An alternative set of $C_6H_5^+$ vibrational frequencies[27b] gave similar results. Clearly, the model which gives us agreement with our experimental data, for $E_0 = 2.76$ eV, is the totally loose orbiting transition-state model.

Pratt and Chupka[3] carried out PI experiments on metastable ions sampling a lifetime range 10^{-4}–10^{-5} s. They suggest a heat of formation $\Delta H_f{}^\circ{}_0(C_6H_5^+) = 274 \pm 1$ kcal/mol on the basis of the orbiting complex model which corresponds to a critical energy $E_0 = 2.98$ eV for reaction 1. Figure 10 shows a comparison of our experimental PIE curve with the calculation based on the Pratt and Chupka model; there is clearly no agreement.

The availability of experimental results at several reaction times allows one to perform a sensitivity analysis.[5,8] In such an analysis, the activation parameters, E_0 and $\Delta S^\ddagger$, which affect the PIE curves, are varied until a unique pair gives agreement with the experimental data. Since the orbiting transition state gives an upper limit for rate constants based on RRKM tight transition states, $\Delta S^\ddagger$ has to be less than or equal to 8.07 eu. For $E_0 > 2.76$ eV, $\Delta S^\ddagger$ has to be greater than 8.07 eu to fit the data and this is impossible. On the other hand, it is possible to fit the experimental data at a storage time of 2 ms by a concomittant reduction of E_0 and $\Delta S^\ddagger$. If E_0 is reduced by 0.1 eV to 2.66 eV, $\Delta S^\ddagger$ has to be reduced to 2.87 eu to obtain a good fit of the PIE curve at 2 ms (Figure 11). These parameters ($E_0 = 2.66$ eV and $\Delta S^\ddagger = 2.87$ eu) do not fit, however, the 6-μs data (Figure 11). Our data thus agree best with the original model by Rosenstock et al.[5]

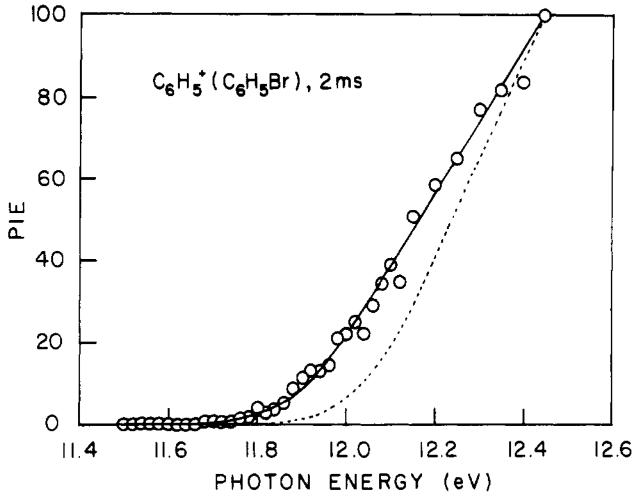

Figure 10. Comparison of the experimental (open circles) and calculated PIE curves for $C_6H_5^+$ at 2 ms. The smooth line represents the calculation according to the model of Rosenstock et al.[5] with $E_0 = 2.76$ eV (= 63.65 kcal/mol) and $\Delta S^\ddagger = 8.07$ eu; the dotted curve is calculated according to the model of Pratt and Chupka[3] with $E_0 = 2.89$ eV and $\Delta S^\ddagger = 7.86$ eu. Both of the calculated curves were normalized to the highest energy experimental point.

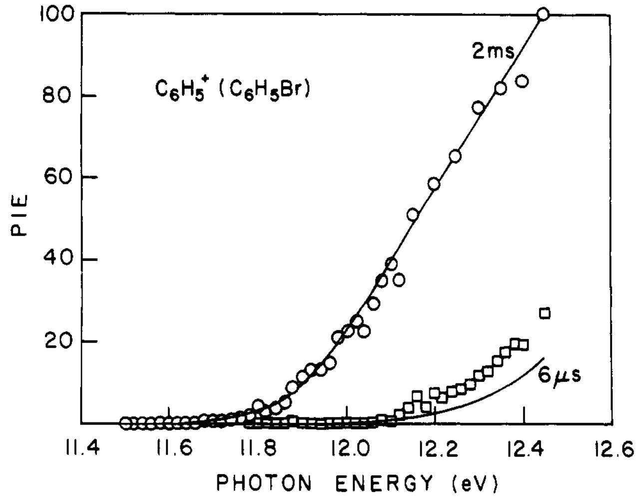

Figure 11. Comparison of the experimental (open circles and squares) time-resolved PIE curves with QET calculations assuming $E_0 = 2.66$ eV (= 61.35 kcal/mol) and $\Delta S^\ddagger = 2.87$ eu.

Reaction 1 possesses no barrier along the reaction coordinate as is clearly evident from the kinetic energy release, which is of statistical origin.[3,30] We have carried out experiments of our own, with electron impact ionization, to determine kinetic energy releases for reaction 1. The experimental KERD, at a most probable excess energy of 0.64 eV, is best represented by a phase space calculation (Figure 12) assuming an orbiting transition state. The average kinetic energy according to the phase space calculation is $\bar{E}_t = 72$ meV. The experimental average KER we have obtained is 70 ± 9 meV.

One of us has suggested[32] that a variational criterion for the location of the transition state may be particularly well suited for

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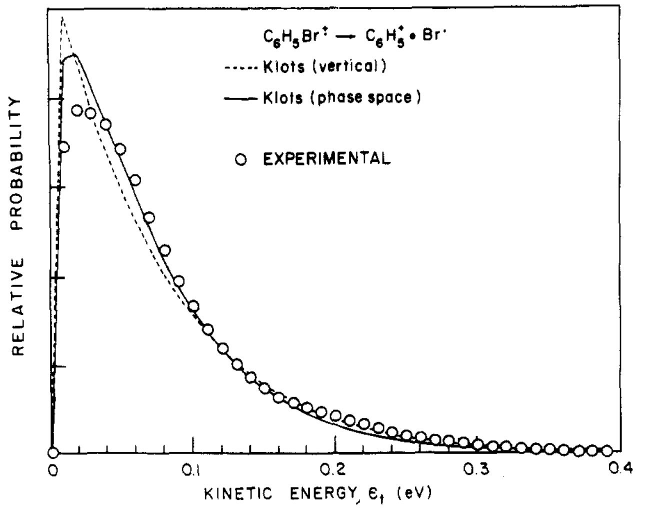

Figure 12. Kinetic energy release distributions for metastable $C_6H_5Br^{+\cdot}$ ions undergoing reaction 1 in the second field-free region of a MAT 311 mass spectrometer. Open circles are experimentally obtained from the first derivative of the metastable ion peak shape.[18-20] The curves are calculated as follows: --- is the "vertical" approximation by Klots;[31] — is the exact Langevin model phase-space calculation with thermal-averaged angular momentum of the reactant.[28,29,31] The following parameters were employed in the phase space calculations: Rotational constant of the bromobenzene cation, $B_0 = 4.1 \times 10^{-2}$ cm^{-1}; Rotational constant of the $C_6H_5^+$ cation,[27b] $B = 0.15168$ cm^{-1}, polarizability of the Br· atom $\alpha(\text{Br}\cdot) = 3.5 \times 10^{-24}$ cm^3 and vibrational frequencies of the phenyl cation (in cm^{-1}):[27b] 3082 (5)8 1598 (6), 1089 (9), 842 (2), 508 (5). The internal energy distribution of metstable ions was calculated according to $P(E) = e^{-k(E)t_1} - e^{-k(E)t_2}$ with $t_1 = 18$ μs and $t_2 = 22.2$ μs taking the $k(E)$ from the orbiting transition-state model with $E_0 = 2.76$ eV. The single energy-valued KERDs were folded with the $P(E)$ distribution to give the final KERD.

ionic systems since many ionic dissociations have a negligible reverse activation energy. Bowers and co-workers have successfully employed[20,33,34] a transition-state switching model for unimolecular and bimolecular reactions in the $C_4H_6^{+\cdot}$, $C_4H_8^{+\cdot}$, and $C_6H_6^{+\cdot}$ systems. According to this model, in the case of no barrier along the reaction coordinate, at low values of internal energy $E \approx E_0$ the orbiting transition state has the minimum flux F, since the number of states is very small and the microcanonical rate coefficient k is given by F^{ORB}/ρ_A where ρ_A is the density of states of the reactant. At $E > E_0$ the tight transition state takes over, because of the rapid increase in F^{ORB} with E. The rate coefficient is then given by $F^{\ddagger}/\rho_A$, where $F^{\ddagger}$ is the flux (sum of states divided by Planck's constant) for the tight transition state.

In view of the recent literature on the topic of transition-state switching,[20,33-35] it is of great interest to find out whether unimolecular reactions in ionic systems, which proceed via a single potential well from reactants to products, such as reaction 1, undergo transition-state switching. The ion–molecule reaction system $C_6H_5^+/Br\cdot$ (the reverse of reaction 1) has not yet been studied. The present time-resolved PIE data on the unimolecular reaction combined with the KER data and the previous PEPICO[5] and PI[3] data indicate, however, that an orbiting transition state adequately describes the experiments over the whole energy range of interest, up to about 1 eV above threshold and there is no need to invoke a tight transition state at higher internal energies. We are currently involved in more calculations and experiments to clarify this point.

Several problems are encountered when long-lived ions are being studied by trapping methods. These are (a) collision-induced dissociation, (b) collisional relaxation, and (c) radiative relaxation.

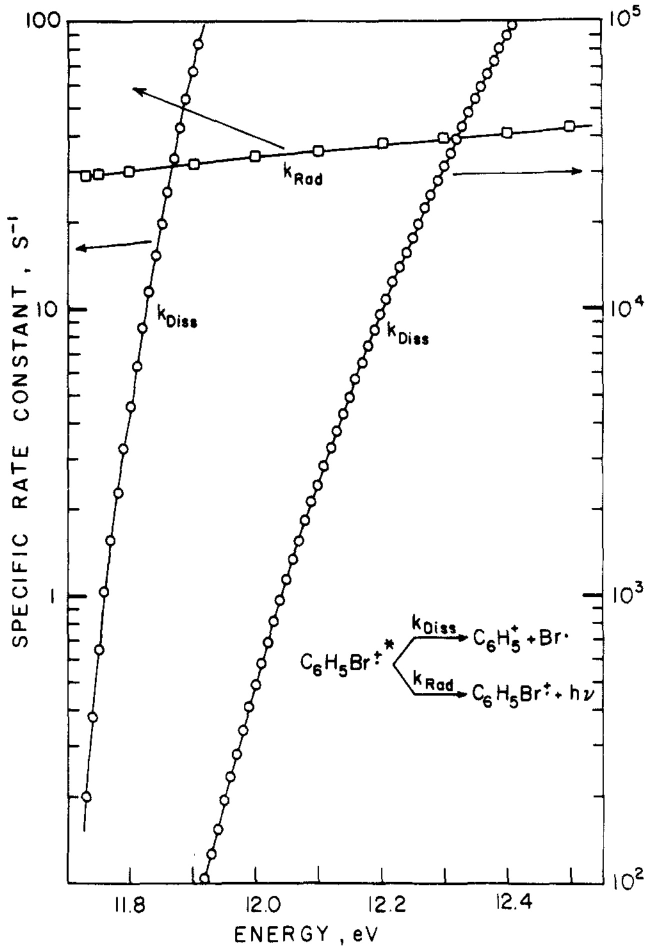

Figure 13. Calculation microcanonical rate coefficients as a function of energy (ionization energy = 8.97 eV plus internal energy in the ion). The dissociative rate constant has been calculated as before by assuming $E_0 = 2.76$ eV. The radiative rate constants have been calculated according to Dunbar[38] (see text).

We have addressed each of these problems in the case of bromobenzene. We find that our largest error comes from factor (a) since the ions gain kinetic energy from the rf field and the pressure in the CIT is not low enough to completely rule out this contribution. We are currently designing a more intense light source which should enable work at lower sample pressures without sacrificing sensitivity. Collisional and radiative relaxation have previously been studied for bromobenzene by Dunbar and coworkers.[36] According to Dunbar[37] an upper limit on the lifetime of a metastable-ion decomposition is imposed by the competing relaxation of internal excitation by IR radiative cooling. This upper limit lies in the range of ~15–60 s^{-1}. Collisional relaxation in bromobenzene is very fast,[36] since it occurs via charge exchange between a vibrationally excited bromobenzene cation and a neutral bromobenzene with a bimolecular rate constant[6] $k_b = 1.1 \times 10^{-9}$ cm^3/(molecule·s).

We have calculated the energy dependence of the rate coefficient for radiative decay k_{Rad} in bromobenzene following Dunbar's outline.[38] Infrared absorption intensities of bromobenzene were taken from Goplen et al.[39] An equivalent internal "temperature" T of the molecule was calculated for a given internal energy by approximating the microcanonical distribution as a canonical distribution. At the threshold energy for reaction 1 of 2.76 eV the temperature is ~1750 K. The radiative contribution of each active normal-mode quantum state is calculated by

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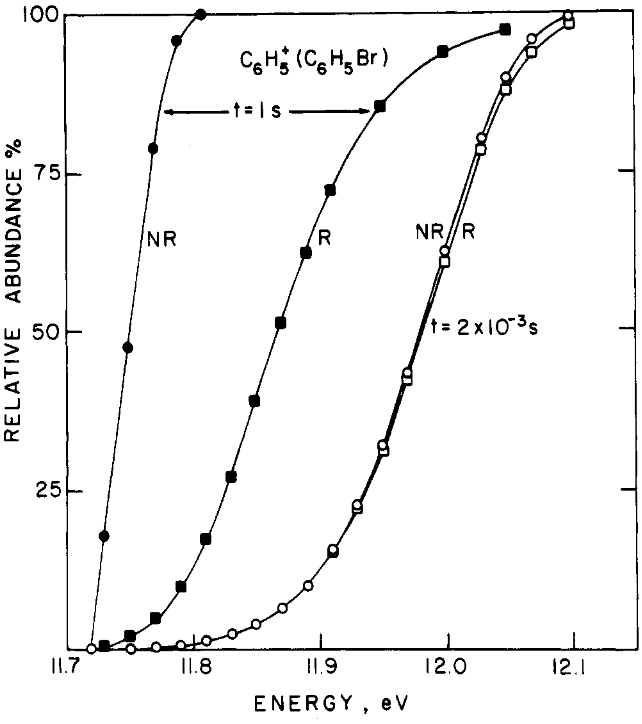

Figure 14. Calculated 0 K time-resolved breakdown curves for the phenyl cation with and without inclusion of the radiative decay term (R and NR, respectively).

weighting its intrinsic oscillator strength (derived from absorption measurements) by the probability that the excited level will be occupied at temperature T, with a final sum over all modes and all states. k_{Rad} is calculated from the energy lost per second from the excited bromobenzene cation by division by 700 cm^{-1}, since bromobenzene is a "cool" radiator in Dunbar's terminology[37] and the emission of a single photon of 700 cm^{-1} leads to a drastic slowing of RRKM dissociation. While this type of calculation is not quite realistic, it is the best one currently available.

Figure 13 represents the calculated energy dependences for the radiative and dissociative decays of the bromobenzene cation. At the lowest photon energies right above threshold k_{Rad} is clearly higher than the dissociative rate constant k_{Diss}. This is in agreement with the calculations by Dunbar and Honovich.[6] We investigated next whether this causes an intrinsic kinetic shift in the observation of product ions. The rate energy dependences of Figure 13 were employed to calculate time-resolved breakdown curves for the daughter ion with (R) and without (NR) radiative decay (Figure 14). Clearly, radiative decay has a minimal effect on the curves at $t = 2 \times 10^{-3}$ s but has a marked effect at a storage time of 1 s. The longest ion storage time employed by us to date was 2×10^{-3} s (Figure 6) and agreement with theory is excellent. IR-radiative limiting decay does not cause a kinetic shift in our present experiments.

Slow fragmentations are observable and are unperturbed by radiative decay if only low extents of overall (radiative and dissociative) decay of the metastable ion are allowed. The breakdown curve for $C_6H_5^+$ at $t = 2$ ms remains almost unchanged with or without radiative decay since the fractional abundance is given by

$$\mathrm{Fr}(C_6H_5^+) = \frac{k_{Diss}}{k_{Diss} + k_{Rad}}[1 - e^{-(k_{Diss}+k_{Rad})t}] \simeq$$

$$\frac{k_{Diss}}{k_{Diss} + k_{Rad}}(k_{Diss} + k_{Rad})t = k_{Diss}t \simeq 1 - e^{-k_{Diss}t}$$

For small $(k_{Rad} + d_{Diss})t$, $\mathrm{Fr}(C_6H_5^+) = k_{Diss}t$; k_{Rad} has no effect on this result even if $k_{Rad} >> k_{Diss}$. On the other hand, the fractional abundance of the excited parent ion is $\mathrm{Fr}(C_6H_5Br^{+*}) = e^{-(k_{Diss}+k_{Rad})t} \simeq d^{-k_{Rad}t}$. If $k_{Rad} > k_{Diss}$ the lifetime of the parent ion is dictated by the radiative decay and the slow dissociative decay will not be observed. In this respect there is no conflict with the idea of an intrinsic kinetic shift.[6]

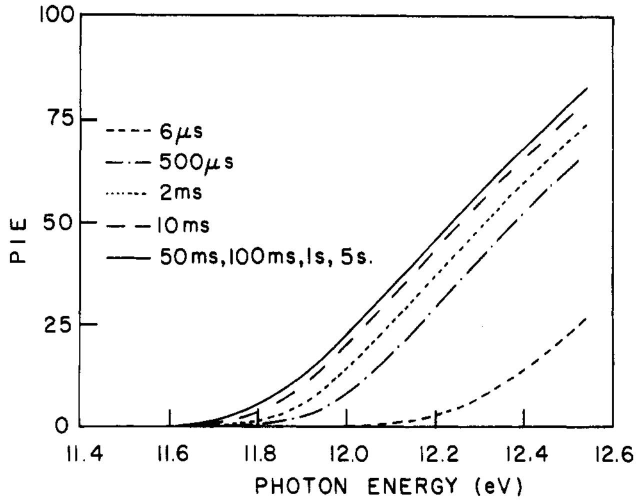

Figure 15. Calculated time-resolved PIE curves for the phenyl cation for 303 K; these calculations take into account a radiative decay term.

PIE curves were next calculated for $C_6H_5^+$ at several storage times (Figure 15). In spite of radiative decay, improvement in lowering the onset energy is foreseen by extending the storage time. The PIE curve remains unchanged at storage times greater than 50 ms (Figure 15). Dunar and Honovich[6] claim that the intrinsic kinetic shift due to IR radiative decay cannot be overcome experimentally by allowing the ions more time to dissociate, although it can be counteracted by using higher product-ion detection sensitivity. Our data indicate that allowing the ions more time to dissociate and using higher product-ion detection sensitivity allows one to overcome the kinetic shift in mass spectrometer appearance energy measurements as well as the intrinsic kinetic shift due to IR radiative decay. The 0 K threshold energy we obtain ($E_0 = 2.76 \pm 0.05$ eV) is within the error limits of the one by Dunbar and Honovich, $E_0 = 2.81 \pm 0.07$ eV.[6] It is of interest to compare our time-resolved appearance energies with previous literature values. Our value at 6 μs is $\mathrm{AE}(C_6H_5^+)_{6\ \mu s} = 12.05 \pm 0.05$ eV and is in excellent agreement with the value for energy-selected electrons;[30] at 500 μs we obtain $\mathrm{AE}(C_6H_5^+)_{500\ \mu s} = 11.8 \pm 0.05$ eV and at 2 ms, $\mathrm{AE}(C_6H_5^+)_{2\ ms} = 11.7 \pm 0.05$ eV. These appearance energies are so-called "vanishing current" values, which we adopt consistently in our measurements.[11] They contain contributions from the ionization and subsequent fragmentation of thermally excited precursor molecules. It is interesting to notice that our AE value at 2 ms is in very good agreement with the old PI value by the Russian group of Sergeev et al.[2] who have not used time resolution.

We find that a relaxation term as fast as $k \simeq 100$ s^{-1} changes the $C_6H_5^+$ curve at 2 ms to a minimal extent. This means that as long as our sample densities are less than 9×10^{10} molecules/cm^3, the PIE curve will not be perturbed by a collisional relaxation rate constant[36] of 1.1×10^{-9} cm^3·molecule^{-1} s^{-1}. The pressure of the sample in the CIT has to be less than 2.8×10^{-6} torr. If longer storage times are to be employed, the sample densities will have to be reduced further. In previous work that we did on cyclooctatetraene[40] (COT) we reduced the sample density to a value such that the charge transfer reaction[41] between the product $C_6H_6^+$ ion and neutral C_8H_8 was completely avoided. Under these conditions, collisional relaxation and collision-induced dissociation of $C_8H_8^+$ ions are negligible. In bromobenzene, charge transfer between the product $C_6H_5^+$ and neutral C_6H_5Br is endothermic and we could not gauge the bromobenzene density in a similar way. The C_6H_5Br densities employed were, however, considerably lower than the COT densities employed previously, as judged by readings of the ionization gauge which is situated directly outside the CIT.

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Conclusion

A kinetic shift on the PIE curve of $C_6H_5^+$ from bromobenzene was observed directly for the first time by employing time-resolved photoionization mass spectrometry. The appearance energy following 2-ms storage time is $AE(C_6H_5^+) = 11.7 \pm 0.05$ eV. The experimental results are reproduced by QET calculations assuming a loose, orbiting transition state with $E_0 = 2.76$ eV and $\Delta S^\ddagger = 8.07$ eu. There is no evidence for a transition-state switching at increased internal energies up to ~1 eV above threshold, although this point is currently under further investigation. IR radiative decay of the $C_6H_5Br^+$ parent ion has no effect on the PIE curve of $C_6H_5^+$ at 2 ms, even though the radiative rate at the threshold for dissociation is more than two orders of magnitude faster than the dissociative rate. Within the uncertainties concerning the possible contributions of collisional relaxation and collisional dissociation discussed above, our results support the phenyl ion heat of formation, $\Delta H_f{}^\circ{}_0(C_6H_5^{+}\cdot) = 270$ kcal/mol deduced by Rosenstock et al.[5] This value is consistent with the most recent heat of formation of the phenyl radical obtained from neutral kinetics[42] combined with the ionization energy of the phenyl radical.[43]

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Registry No. C_6H_5Br, 108-86-1; $C_6H_5Br^{+}\cdot$, 55450-33-4.

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Identification of Ammonia Clusters in Low-Temperature Matrices Using the FTIR Short-Pulsed Matrix Isolation Technique

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The clustering of ammonia in rare gas matrices at 15 K has been studied by Fourier-transform infrared (FTIR) matrix isolation spectroscopy. The experimental technique is based on trapping of short-pulsed (~1.4 ms) supersonic beam molecules into the matrices where the trapped ammonia molecules are allowed to self-associate. The method is shown to be a sensitive technique for quantitative identification of the hydrogen-bonded clusters. Detailed studies of the concentration and nozzle stagnation dependences enable us to identify the bands due to dimer, trimer, and higher clusters. Considerations in terms of an extended quenched reaction model reveal strong evidence for stepwise association of NH_3 to give $(NH_3)_2$, $(NH_3)_3$, and a number of different $(NH_3)_n$ species. It is shown that these matrix infrared studies are complementary to the gas-phase infrared studies of the ammonia clusters.

Introduction

Investigation of molecular clusters is an area of current active research and a number of different experimental methods are being employed to elucidate the structures and dynamic properties of these species. In the present work we have examined the use of a new technique of short-pulsed matrix isolation by investigating the formation of ammonia clusters under various experimental conditions.

Ammonia clusters are subjects of both experimental and theoretical interest because ammonia is a simple molecule that undergoes extensive self-association in the gas phase.[1-6] A number of experimental methods have been employed to study ammonia clusters. The molecular beam electric resonance technique has been used to obtain structural parameters, which revealed that the gas-phase ammonia dimer has a linear hydrogen bond while the trimer exhibits a cyclic structure.[2] Vibrational predissociation and infrared photodissociation spectra have been obtained for the $(NH_3)_2$ species prepared by a pulsed supersonic expansion.[7] The spectrum obtained with an IR laser corresponds to the dimer absorption spectrum of ammonia. Two-photon-ionization mass spectroscopic studies of the ammonia clusters provide information on the electronic excited states of the clusters as well as on the distribution of the clusters in a supersonic molecular beam.[5,6]

The matrix isolation technique has proven to be an excellent method for the study of relatively weakly bound complexes.[8,9] Matrix isolation studies of the NH_3 monomer have been reported for over two decades,[10-19] but those of the NH_3 clusters are very

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