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Elementary Photoprocesses in Benzene Clusters

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This article reports the use of the resonant two-photon ionization technique to selectively excite a molecular ion within a cluster and observe the dynamical outcome. We have excited clusters containing up to 14 benzene molecules to energies of 10.00 or 12.84 eV and measured the probability that an initially formed $C_6H_6^+$ attacks a neighboring benzene unit of the cluster according to the vapor-phase reaction $C_6H_6^+ + C_6H_6 \rightarrow C_7H_7^+ + C_5H_5$, $\Delta H = 0.63$ eV. The C_5H_5 radical is expelled from the cluster. At either energy excitation proceeds through an $X^1 1^2$ vibrational level of benzene ($X = 6$ or 8) but in the latter case the benzene cation is also produced electronically excited. Accordingly, at low-energy excitation the above pathway is entirely absent, while the 12.84-eV excitation leads to reaction with a probability increasing with cluster size, as predicted by solvation models. This result makes it appear quite likely that >12-eV excitation of condensed benzene will lead to transient tropylium ion centers for conduction electrons, accompanied by variable trapping of C_5H_5.

Introduction

When an isolated molecule is excited to a definite energy, the subsequent dynamical pathways are characterized by fixed energy thresholds. By contrast, in condensed-matter systems, thresholds for these pathways presumably still exist but the branching into each is now affected by the existence of alternative decay routes, including chemical reaction with solvent or simple dissipation (e.g. local heating).[1]

It is presumed that excitation pathways in molecular clusters must lie intermediate between these extremes, with larger clusters tending asymptotically toward condensed-matter behavior. This conjecture has not yet been established. Alternatively, advances in the production and state preparation of molecular clusters now make it possible that the study of clusters will lead to an improved understanding of transient processes in the condensed phases.[2]

Recently, a striking example of these phenomena has been much discussed, this being the case of ammonia clusters, $(NH_3)_x$.[3-6] Excitation of isolated $(NH_3)_x$ by laser photons or an electron beam has for sometime been believed to yield only the protonated cluster, $(NH_3)_yH^+$ ($y < x$). As in the case of other negative or positive ion clusters produced by excitation of neutrals,[7,8] this is explained in terms of an *ion-molecule reaction* within the cluster. One NH_3 is ionized to form an NH_3^+ center, which then attacks a neighboring NH_3 in the cluster to form the very stable NH_4^+ and expel NH_2 from the cluster. This is in accordance with the exothermic gaseous ion-molecule reactions $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ ($\Delta H = -17$ kcal/mol). This process of course has no analogue in isolated molecule excitations, but since it occurs in large clusters it follows that in condensed ammonia the transient events following ionization should include formation of solvated NH_4^+ (rather than solvated NH_3^+) ion cores.[9]

Quite recently, however, it has been shown that near-threshold one-photon ionization of $(NH_3)_x$ in the 10-12-eV range does produce $(NH_3)_y^+$, and that as x increases the abundance of the latter pathway increases to approach that of the former.[6] This shows that if the concomitant vibrational excitation of the ionized cluster is not too large and if the number of dissipative modes is sufficiently large, then even an exothermic ion-molecule reaction (with a minimal energy barrier) can be restricted indefinitely.

Although this example is the best to date at illustrating the elementary excitation dynamics of molecular clusters, the methods involved suffer some serious limitations, primarily in the distribution of energies imparted to the cluster upon ionization. In the case of single-photon ionization of ammonia clusters, the Franck-Condon principle virtually guarantees vibrational excitation of NH_3^+ up to the limit of the photon energy.[10] The technique of resonant two-photon ionization (RTPI), by contrast, has recently been shown to be capable of producing ions state selected in a very narrow energy distribution.[11]

The present paper reports the use of the RTPI technique to control the initial state of a benzene ion within a cluster, in order to study the subsequent intracluster dynamics. We have excited benzene clusters to energies of 10.00 or 12.84 eV and observed the probability that an initially formed $C_6H_6^+$ attacks a neighboring benzene according to the vapor-phase reaction[12]

$$C_6H_6^+ + C_6H_6 \rightarrow C_7H_7^+ + C_5H_5 \qquad \Delta H = 0.63 \text{ eV} \quad (1)$$

expelling the C_5H_5 radical from the cluster. At 10.00-eV photon energy, excitation is through a $6^1 1^2$ vibrational level of benzene while 12.84-eV excitation occurs primarily through an $8^1 1^2$ vibrational level. In the latter case, however, the benzene cation may also be electronically excited, allowing us to study the probability of reaction 1 following 12.84-eV excitation as a function of cluster size.

Experimental Section

Clusters are produced by seeding benzene in He supersonic free-jet expansions generated by a commercial pulsed gas valve (NRC-BV100, 0.5- or 1.0-mm orifice diameter). The rare gas stagnation pressure is variable in the 3-6-atm range and bubbles through ambient benzene at a rate of several milliliters per minute during operation. Experiments on toluene and perdeuteriobenzene clusters were performed in an entirely similar manner.

The pulsed gas nozzle is operated in such a way as to produce pulses shorter than 150 μs in duration,[13] as measured by the

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(11) See for example: Long, S. R.; Meek, J. T.; Reilly, J. P. *J. Chem. Phys.* **1983**, *79*, 3206.

(12) This process is readily computed by using the heats of formation of benzene, $C_7H_7^\bullet$, and $C_5H_5^\bullet$, and the IPs of benzene and C_7H_7; see ref 19 and Elder, F. A.; Parr, A. C. *J. Chem. Phys.* **1969**, *50*, 1027.

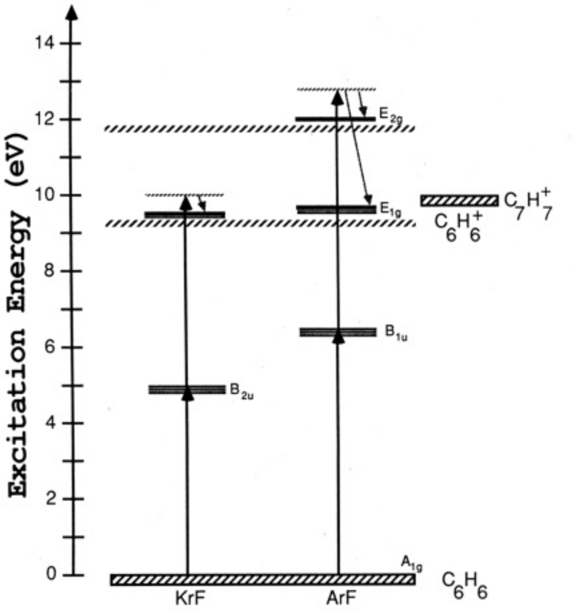

Figure 1. Relevant energy levels of benzene and the benzene cation. At left, the pathway for KrF excitation is indicated. At center and right the two paths for ArF excitation, including the threshold for $C_7H_7^+$ production via $C_6H_6^+ + C_6H_6$ reaction 1. See text for specific references.

time-of-flight profile 85 cm downstream, without diminishing cluster production. Under these conditions pumping requirements are quite modest at repetition rates up to 50 Hz. For example, under 15-Hz operation the average source chamber pressure (exhausted by a 2500 L/s unbaffled diffusion pump) is 1×10^{-5} Torr, but the pressure prior to each pulse is less than 10^{-6} Torr. The corresponding operating pressure in the ionization chamber, differentially pumped by a 4-in. diffusion pump with water baffle, is 2×10^{-8} Torr.

In these experiments the laser operates on either of two broad lines: KrF (248 nm or 5.00 eV) or ArF (193 nm or 6.41 eV), both of which have pulse widths of approximately 10^{-8} s. In contrast to other reported experiments on molecular clusters,[14,15] the laser radiation is passed through the ionizing region *entirely unfocussed*. Total pulse energies are recorded by a calibrated Lambda Physik-ILC monitor, and the pulse energy at the ionizer is measured occasionally by a Scientech power meter. The pulse energy is controlled either by varying the laser's charging voltage or by placing neutral density filters before an iris at the entrance to the ionization region.

Ions are created within Extranuclear's axial-beam ionizer, which has been user modified to obtain large photoionization volumes and high collection efficiencies. By varying the iris diameter, we have estimated that the useful ionization volume is no less than 0.5 cm^3. Negative or positive ions of up to 1100 amu are quadrupole mass filtered before striking a conversion dynode (CD) at ±4 kV. Secondary particles from the CD strike a channeltron electron multiplier at variable voltage from −900 to −1500 V. This method of detection has the advantages that heavy ions are detected with an efficiency closer to that of light ions and that negative ions can be detected nearly as efficiently as positive ions.

In preliminary tests of this apparatus we have studied abundances of Ar clusters by electron impact to reproduce literature pressure-dependence results[16] and have detected efficient formation of I^- from the two-photon ionization of CH_3I. The negative ion collection efficiency is demonstrated by our ability to detect molecular oxygen clusters $(O_2)_x^-$ from low-energy electron impact and reproduce the results of Märk et al.[17]

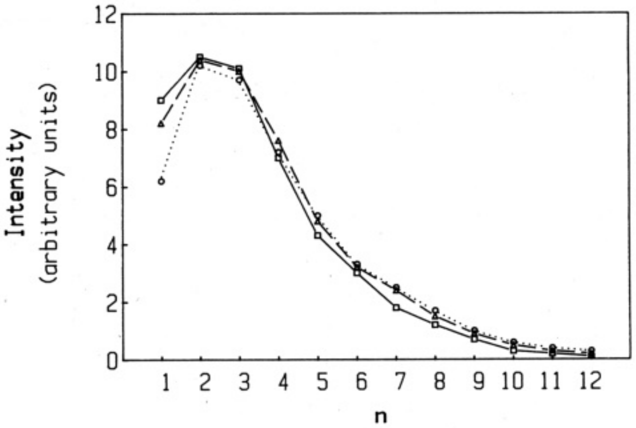

Figure 2. Photoionization of benzene clusters, $(C_6H_6)_n$, with unfocussed ArF radiation at fluences of 2 (○), 3 (△), and 4 mJ/cm^2 (□), indicating excess cluster evaporation at higher fluences. Mass units along the abscissa represent the number of benzene molecules in a cluster.

Energetics of Relevant Processes

The states of the benzene molecule are probably the best known of any polyatomic molecule,[18,19] and transient photoprocesses in solvated benzene have been the subject of at least ten experimental studies in the past decade.[20] These factors make benzene an ideal choice for molecular cluster experiments. Most remarkable for our experiments is a coincidence (Figure 1) which places the KrF laser line accidentally resonant with the 1^26^1 level of benzene's B_{2u} state and the ArF line resonant with the 1^28^1 level of its B_{1u} state.[21] (The latter fact has apparently not been recognized despite the availability of an excellent synchrotron absorption spectrum by Koch and Otto.[22]) While the effect of clustering or solvation is known to shift these levels to lower energy (by up to 2800 cm^{-1} in the case of the B_{1u} state in cryogenic benzene films[23]), it is clear that one-photon absorption in these spectral ranges produces only lightly vibrationally excited benzene.

It follows that resonant two-photon ionization of a benzene molecule in clusters will prepare benzene cluster ions in which the benzene ion is prepared in a very narrow Franck–Condon distribution of vibrational states.[11] This is illustrated in Figure 1, where KrF excitation places the benzene cation in its lowest electronic state, tending toward 1^26^1 excitation (0.29 eV above threshold). ArF-laser excitation, however, produces benzene ions in both ground and excited electronic states, each with its own narrow Franck–Condon distribution tending toward 0.29–0.40-eV vibrational excitation. These levels are indicated in Figure 1.

Also indicated is the threshold for production of $C_7H_7^+$ and C_5H_5, the process in which an isolated benzene molecule is ionized and reacts with another isolated C_6H_6, reaction 1. This is an endoergic process made possible largely by the notable stability of the tropylium ion (symmetrical $C_7H_7^+$).[12] By contrast, the lowest intramolecular fragmentation pathways lie near 13 (loss of H or H_2) and 14 eV (loss of C_2H_2 or C_3H_3) and therefore require multiphoton processes.[24]

Not shown in Figure 1 are the shifts in levels caused by partial solvation in a cluster, since these remain largely unknown. Hopkins et al.[25] suggest −40, −115, and −149 cm^{-1} as $A_{1g} \rightarrow B_{2u}$ origin band

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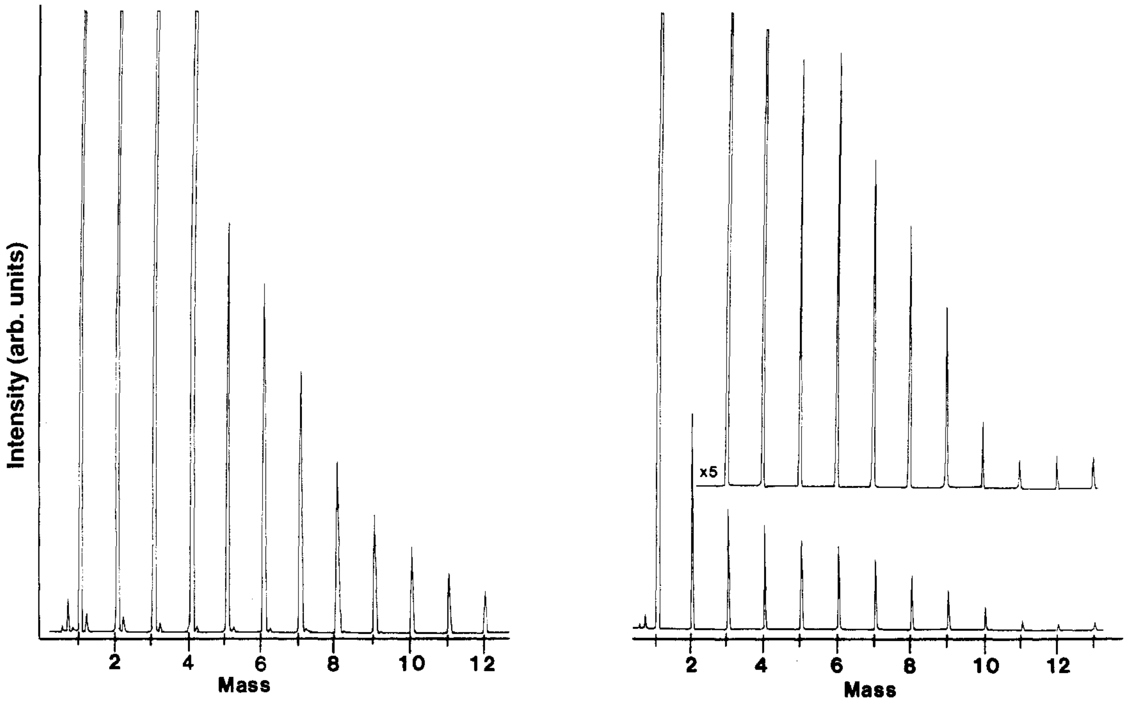

Figure 3. Comparison of benzene cluster distributions with 10.00- and 12.82-eV excitation under otherwise identical conditions. (a) Distribution with ArF (12.82 eV) excitation. (b) Distribution with KrF (10.00 eV) excitation. Note the flat base line for the low-energy distribution, even with increased multiplier potential. Mass units same as in Figure 2.

shifts for benzene dimer, trimer, and tetramer, but excitation energy shifts for ionization are likely to be larger.[26] In what follows we implicitly assume that these shifts are likely to be negligible on the scale of Figure 1. Also not shown are thresholds for evaporation of benzene molecules from a cluster ion, but estimates of these energies show that this is a likely process even for the small excess energies shown in Figure 1. In particular, simple models[27] predict a stepwise evaporation energy for small neutral benzene clusters of 0.2–0.3 eV, while the bulk benzene heat of vaporization is 0.44 eV per molecule. The binding around a solvated ion is to be expected to be somewhat larger, but Hopkins et al.[25] demonstrated that, of the dimer ions detected from two-photon excitation 0.2 eV above benzene's ionization potential, more than 50% came from the trimer. Thus it is reasonable to expect from 10.0-eV excitation a distribution of losses peaking at one benzene loss. In the case of production of electronically excited benzene cation, the intracluster chemical reaction channel competes with multiple losses or evaporation, corresponding most nearly to the dissipation process mentioned above.

Results

The above energetic analysis generates expections and questions to which at present only direct experiments can yield a definitive answer. Specifically, one wants to know for state-prepared molecular cluster ions whether excess energy is dissipated to cluster evaporation or stored for intracluster chemical reaction, as in eq 1. Our experiments seek to answer these questions for small benzene clusters, $(C_6H_6)_n$ ($n = 2$–14).

A preliminary concern is whether one can eliminate subsequent absorption by the cluster ion. Fragmentation of benzene in intense laser fields has been intensively studied,[28,29] and by focussing the laser we reproduce essential features of this work and further find that all clusters are destroyed. We therefore have operated completely unfocussed at fluences of 2–10 mJ/cm^2, or more than an order of magnitude lower than that quoted by Hopkins et al.[25] Still, at the high end of this range we find (1) a relative depletion of larger clusters, and (2) fragmentation to produce $C_4H_4^+$, $C_3H_3^+$, and their clustered analogues. These are characteristic of the absorption of additional photons by the cluster ion.

Figure 2 shows the effect of ArF-laser fluence on the observed distribution of benzene cluster ions. Evident is the tendency to deplete larger clusters at higher fluences, with a corresponding increase in the abundance of smaller cluster ions. A decrease in the intramolecular fragmentation pathways was observed at lower fluences as well. At 2 mJ/cm^2 and lower the remaining major peaks scale together with laser fluence and are therefore the products of fixed energy excitations. It is under these conditions that we can expect to see results indicative of the essential processes.

Figure 3 shows low-fluence mass spectra obtained by using 10.00- and 12.82-eV resonant two-photon excitation under otherwise identical conditions. The essential results are immediately clear:

(1) At 10.00 eV no intramolecular fragmentation or intracluster ion-molecule reaction occurs.

(2) At 12.82 eV, peaks corresponding to $(C_6H_6)_nC_7H_7^+$ (solvated tropylium ions) also appear with an abundance relative to the next higher $(C_6H_6)^+_{n+2}$ which increases slowly with increasing cluster size.

Various checks have been performed to test the correctness of this explanation. The C_7H_7 ion is also produced with high efficiency from toluene,[15] and toluene is a potential contaminant in benzene, so that mixed benzene–toluene clusters might produce such a peak. But ionization of toluene under the same conditions (12.82 eV) always produced a larger $C_7H_8^+$ peak and greater intrinsic fragmentation. Other experiments with 99.9% C_6D_6 clusters showed the expected mass 98 peak and others corresponding to $(C_6D_6)_nC_7D_7^+$ for $n = 1$–11.

Finally, a pathway producing solvated $C_7H_7^+$ which does not involve an ion–molecule reaction is that of ion-pair formation:

$$(C_6H_6)_2 \xrightarrow{h\nu} (C_6H_6)_2^* \xrightarrow{h\nu} C_7H_7^+ + C_5H_5^- \qquad (2)$$

This process always has a lower threshold energy because of the electron affinity of C_5H_5.[30] But under no conditions were we able

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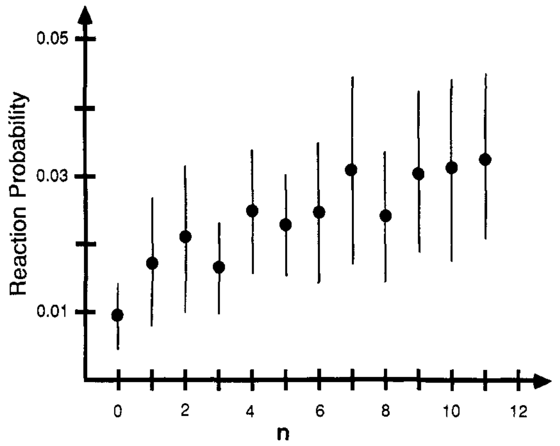

Figure 4. Probability of intracluster chemical reaction as a function of cluster size for 12.82-eV excitation. Each point represents the ratio of the signal intensity of the clustered tropylium ion, $(C_6H_6)_nC_7H_7^+$, to the signal intensity of the parent cluster, $(C_6H_6)_{n+2}$. The probability is <0.001 for all clusters following 10.00-eV excitation.

to detect $(C_6H_6)_nC_5H_5^-$ or any other negative ions.

Discussion and Conclusions

We have identified that when clusters of benzene are photoionized at definite energies (and in narrow Franck–Condon determined energy distributions) an intracluster ion–molecule reaction takes place with a probability depending critically on excitation energy and weakly on cluster size. By taking the ratio of the intensities of the $(C_6H_6)_n(C_7H_7)^+$ peak to the $(C_6H_6)^+{}_{n+2}$ peak we obtain a crude measure of this probability, which is shown in Figure 4. The result obtained does not depend strongly on how this ratio is taken and shows a result which we believe is likely to survive any more refined analyses: The probability of $C_7H_7^+$ formation (with C_5H_5 expelled) increases slowly with cluster size in clusters of two to 13 benzene molecules.

Because the vibrational energy distributions produced via ArF and KrF excitation are expected to be nearly the same (Figure 1), it is therefore likely that this reaction is made possible by *trapping of the excitation energy in the first excited state of the benzene cation.* The dynamical fate of this $^2E_{2g}$ electronic excitation is well-known for the isolated benzene cation: internal conversion occurs within 1 ps (Rydberg state line width estimates[19] indicate ~400 fs).[31] The trapped 2.5 eV is then evidently sufficient to overcome the barrier to reaction 1.

The leveling off of this process for small benzene clusters suggests that this process is intrinsic to condensed benzene systems. Nonetheless, it is clear that, for sufficiently large clusters, the endoergicity of reaction 1 implies escape of $C_5H_5^\bullet$ from the cluster will be negligible, and the reverse reaction will occur, freeing ~0.6 eV (neglecting differences in solvation of $C_6H_6^+$ and $C_7H_7^+$) to evaporate one or two additional benzene molecules from the cluster.

The steady increase in reaction probability, followed by size independence in the n = 7–11 region, is consistent with the general idea that this quantity should depend on the number of nearest neighbors of the initial ion. Once a solvation shell is completed it should remain unchanged.

In condensed matter, however, C_5H_5 once created must diffuse back to the $C_7H_7^+$ ion, and it is not clear whether this will occur on the same time scale as geminate pair recombination. Thus it would be of interest in condensed-phase photoconductivity studies to monitor transient $C_5H_5^\bullet$ absorption, as well as photocurrents and solvated-electron absorbances.[32]

In conclusion, using well-defined excitation of molecular clusters we have demonstrated that intracluster ion–molecule reactions take place even if the process is endoergic, providing that the initial electronic excitation can be trapped. This result has significant implications for transient photoprocesses in liquid benzene.

Note Added in Proof. Since this work was completed, a photoelectron spectrum of benzene with 6.41-eV radiation has appeared.[33] The results are interpreted to show that *all* benzene ions are produced in the ground electronic state, but in a bimodal distribution, the first part sharp at up to 0.5 eV above the ^2E_g origin and the second peaked near 2.0-eV internal energy. This differs from our proposed mechanism but does not alter our conclusions in any significant manner and does demonstrate a source of hot ionic benzene for the ion–molecule reaction.

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Registry No. C_6H_6, 71-43-2; $C_6H_6^+$, 34504-50-2; $C_5H_5^\bullet$, 62744-94-9.

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