Photochemistry of Naphthalene Cluster Ions $(C_{10}H_8)_n^+$, $n = 2-7$: Formation of $C_{11}H_9^+$ Ion via Intervalence Band Excitation

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Abstract: The photodissociation dynamics of naphthalene cluster ions, $(C_{10}H_8)_n^+$ with $n = 2-7$, in the visible and near-IR wavelength regions have been probed by photoionization–photofragmentation time-of-flight mass spectroscopy. An intracluster reaction leading to production of a $C_{11}H_9^+$ ion is observed when the parent cluster ions are excited with near-IR photons, while only intramolecular fragmentation pathways occur following visible band excitation. The formation of $C_{11}H_9^+$, which is assumed to possess the benzotropylium structure, is ascribed to a photochemical rearrangement of the dimer ion core produced in the parent clusters upon multiphoton excitation via the intervalence transition band. The intracluster reaction is observed only for parent cluster sizes $n \geq 4$, which suggests that the dimer ion core must be surrounded by a solvent cage involving at least two neutral molecules. We propose that the existence of a dimer core structure plays an important role in the photochemistry that occurs subsequent to excitation into the intervalence transition band.

Introduction

The observation of a chemical reaction that is specific to a cluster is one of the important topics in cluster science.[1–4] The study of such intracluster reactions is expected to provide new insights into the effects of restricted geometries and the role of solvents in reactions. Among the various types of clusters, ionic clusters afford a particularly interesting collection of systems for such study because their charge allows them to be mass-selected, thus providing unambiguous correlation of chemical reactivity with their masses.[5] Pioneering studies of chemical reactions in ionic clusters involving mass-selective spectroscopy are those of ammonia clusters,[6,7] where ion–molecule reactions take place upon multiphoton ionization to produce protonated clusters $(NH_3)_nH^+$. However, such single laser experiments suffer serious limitations, since both photoionization and chemical reactions occur simultaneously within parent clusters, and thus prevent detailed studies of chemical reactivity as a function of cluster size.

Homogeneous clusters of aromatic molecules are considered to be less reactive and thus have been chosen as representative model systems for the study of stepwise solvation and dissociation dynamics.[8–12] Interestingly, despite this apparent low reactivity, Schriver et al.[13] reported the formation of $C_7H_7^+$ cluster ions from neutral benzene clusters $(C_6H_6)_n$ following resonant two-photon ionization (R2PI) at 12.8 eV. The observation was explained in terms of an ion–molecule reaction that occurs within the clusters: $C_6H_6^+ + C_6H_6 \rightarrow C_7H_7^+ + C_5H_5^{\bullet}$. The formation probability of the $(C_7H_7)^+(C_6H_6)_{n-2}$ cluster ion, which is thought to be the tropylium ion surrounded by neutral benzene molecules, was found to increase with parent cluster size. Although they suggested that the ion–molecule reaction occurs from an excited state of the cluster ions, it was not possible to determine which excited state was involved in the reaction.

In the present study, we have utilized a photoionization–photofragmentation method combined with time-of-flight (TOF) mass spectroscopy to investigate the possibility of intracluster reactions of electronically excited naphthalene cluster ions $(C_{10}H_8)_n^+$, with $n = 2-7$. Naphthalene is highly favorable for this study, since we previously reported the electronic absorption spectra of these clusters in the wavelength range 500–1100 nm using mass-selective photodissociation spectroscopy.[14] These ions were found to exhibit two absorption features, one in the near-IR (≈1 μm) and the other in the visible (≈580 nm), nearly independent of the cluster size. The absence of any size effect on the absorption behavior led us to propose a dimer core model in which the positive charge is localized on a pair of strongly bound molecules and other neutral molecules are weakly bound to this dimer ion core, i.e., $(C_{10}H_8)_2^+(C_{10}H_8)_{n-2}$. The near-IR absorption band, which finds no match in the monomer ion spectrum, was assigned to the intervalence transition band of the dimer ion core, while the visible band was correlated to a locally excited state of the monomer cation.

The present paper reports the occurrence of an intracluster reaction producing $C_{11}H_9^+$ from $(C_{10}H_8)_n^+$, subsequent to excitation into the intervalence transition band. The reaction

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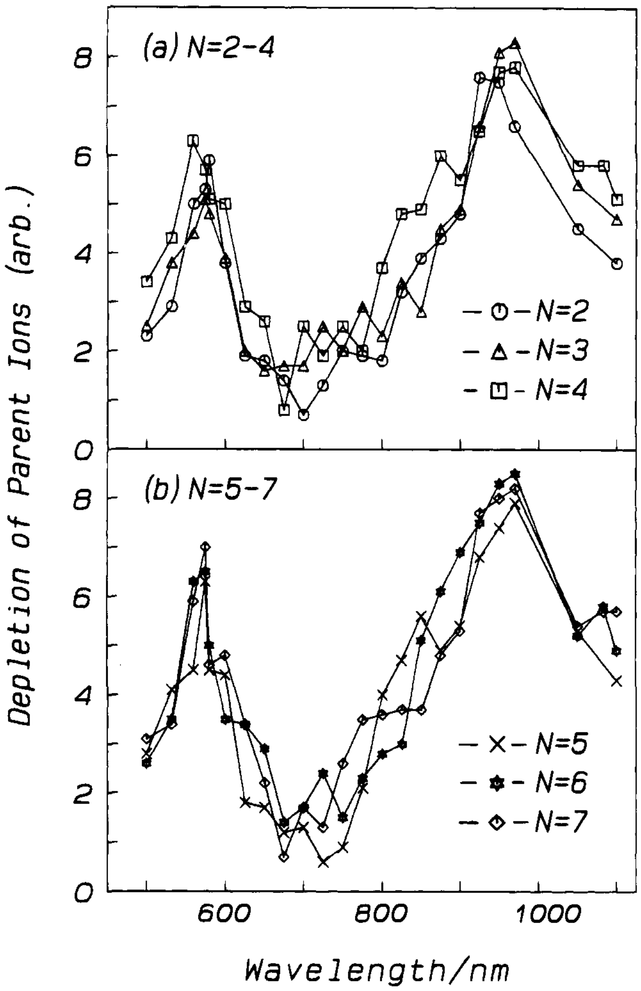

Figure 1. Photodepletion efficiency curves of $(C_{10}H_8)_n^+$, for (a) n = 2–4 and (b) n = 5–7, obtained at a pulse energy of 50 μJ. The data are reproduced from ref 14.

is found to reveal a size-dependent behavior, based on which we suggest that the process takes place only in the presence of a solvent cage.

Experimental Section

The experimental apparatus and procedure have been described in detail in our previous publication.[14] Briefly, neutral clusters of naphthalene are formed in a supersonic expansion. Each cluster is excited, using the frequency-doubled output of a Nd:YAG laser pumped dye laser, into a resonant S_1 vibronic level to produce the corresponding cluster ion via R2PI. This ionization method was found to be effective in the preferential production of a primary cluster ion of certain size, concomitant with a marked decrease in the intensities of other cluster ions. The parent cluster ions thus formed are expected to contain only small amounts of internal energy, since the ionization occurs near threshold with excess energies of <0.3 eV for all clusters. A second YAG-pumped dye laser, time-delayed by <150 ns, was used to induce photofragmentation of the primary cluster ions over the wavelength range 500–1100 nm. At low fluences (<50 μJ/pulse), most of photofragments are found to be smaller cluster ions $(C_{10}H_8)_{n-m}^+$ ($m < n$) that can be assigned as arising from a one-photon absorption. This is the condition for soft fragmentation. When the laser is employed at higher fluences, photochemical rearrangements of the primary cluster ions take place, thus producing fragment molecular ions C_xH_y in the mass spectra. This is the case of hard fragmentation. Both primary and photofragment ions were extracted by an electric field, transferred into a TOF mass analyzer, and detected by a dual microchannel plate detector. Typical mass resolution for primary ions was found to be ≈350, thus allowing ^{13}C isotope peaks to be resolved for all cluster ions studied.

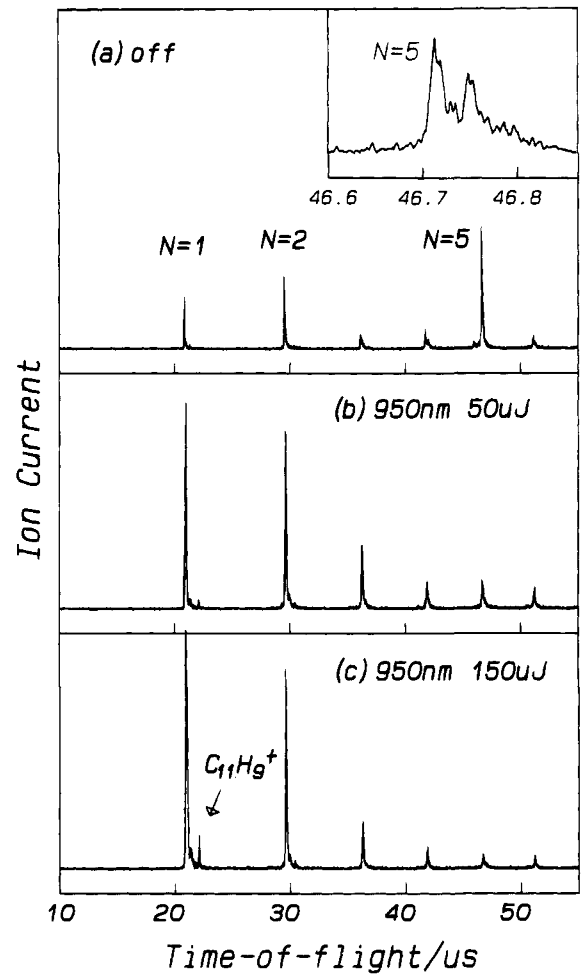

Figure 2. Comparison of parent mass spectrum obtained following R2PI of $(C_{10}H_8)_5$ at 32 215 cm^{-1} in the absence of irradiation (a) and with photofragment mass spectra obtained in the presence of 950-nm irradiation at 50 μJ/pulse (b) and at 150 μJ/pulse (c). The insert in (a) shows an expanded view for n = 5, illustrating mass resolution adequate to separation of the ^{13}C peak. Note also that a peak corresponding to $C_{11}H_9^+$ appears in (c).

Results

We previously reported the photodepletion spectra of $(C_{10}H_8)_n^+$ by collecting the intensities of a parent cluster ion before and after laser irradiation as a function of laser wavelength.[14] The results for n = 2–7 are reproduced in Figure 1. These spectra were taken under the soft fragmentation condition where no significant multiphoton effect was observed, thus presumably mimicking the electronic absorption spectra of these cluster ions. In fact, they closely resemble the absorption spectrum of the naphthalene dimer cation $(C_{10}H_8)_2^+$ directly measured in solution after γ-radiolysis.[15,16] Two broad absorption features are observed in both photodepletion and absorption spectra, one at ≈1 μm and the other at ≈580 nm, with a peak height ratio of ≈1.3. On the basis of the spectral similarity between the dimer ion and the larger cluster ions, as well as the size-independent behavior, these cluster ions can be regarded as dimer ions which are bound weakly by neutral molecules.

We assigned the near-IR absorption band to an intervalence transition of the dimer ion core produced in each cluster.[14] Thus this transition may be described as arising between the charge resonance states $\Psi_\pm = \phi^+\phi \pm \phi\phi^+$, where ϕ^+ and ϕ are the

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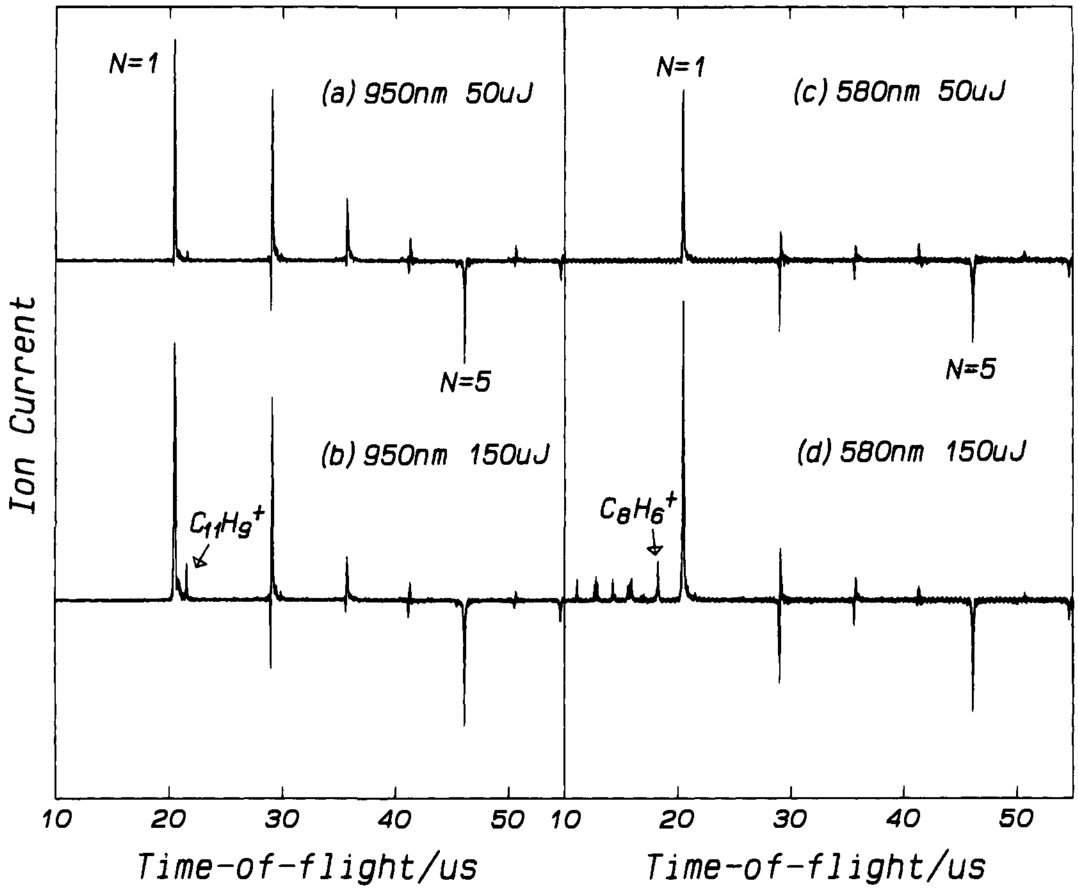

Figure 3. Comparison of difference mass spectra for $(C_{10}H_8)_5^+$ obtained at (a) 950 nm, 50 μJ/pulse, (b) 950 nm, 150 μJ/pulse, (c) 580 nm, 50 μJ/pulse, and (d) 580 nm, 150 μJ/pulse. The spectra in parts (a) and (b) are derived from the photofragment spectra in Figures 2b and 2c, respectively, by subtracting the parent mass spectrum in Figure 2a.

ground-state wave functions of the naphthalene cation (D_0) and neutral (S_0), respectively.[17] The 580-nm band was ascribed to a local excitation corresponding to the $D_2 \leftarrow D_0$ transition of the monomer cation, which appears near 700 nm in solution.[15,18] The significant blue shift with respect to the monomer band may be taken as an indication of a stronger charge resonance interaction in the D_0 state than in the D_2 state.

In the present work, we have carried out similar photodissociation experiments at higher laser fluences than those employed previously. The results pertain to photolyses at 950 and 580 nm, corresponding to the intervalence and local excitations, respectively. Figure 2 displays representative photofragment TOF mass spectra for the parent pentamer ion $(C_{10}H_8)_5^+$ resulting from 950-nm irradiation. In this instance, the pump laser is tuned to a well-resolved $S_1 \leftarrow S_0$ vibronic transition of the neutral cluster $(C_{10}H_8)_5$ at 32 215 cm^{-1},[14] to produce the corresponding cluster ion. Therefore the parent TOF spectrum, acquired without 950-nm irradiation, features an intense peak of $(C_{10}H_8)_5^+$, as shown in Figure 2a. This demonstrates clearly that the R2PI method is capable of preferential production of a particular cluster ion. A peak corresponding to $(C_{10}H_8)_2^+$ is also observed in the spectrum, because the neutral dimer possesses a broad absorption band in the vicinity of the $(C_{10}H_8)_5$ absorption and thus can be ionized efficiently with this excitation.[14] However, this excitation energy is not sufficient to reach the monomer ionization threshold (65 666 cm^{-1})[19] via two photons, and the mass spectrum reveals only a weak feature corresponding to $(C_{10}H_8)^+$.

Figure 2b shows a spectrum obtained upon photolysis at 50 μJ/pulse with a 150-ns time delay with respect to the pump laser pulse. The spectrum shows a significant decrease in the ion intensity for the $(C_{10}H_8)_5^+$ peak, while an increase is observed for the smaller cluster ions $(C_{10}H_8)_{5-m}^+$ where $m = 1-4$. This behavior corresponds to evaporation loss of m monomers upon irradiation. Figure 2c shows a spectrum obtained at a pulse energy of 150 μJ. The intensity of the $(C_{10}H_8)_5^+$ peak is <10% of the corresponding peak in Figure 2a. Although the dominant photofragments are still $(C_{10}H_8)^+$ and $(C_{10}H_8)_2^+$, a new peak $m/e = 141$ (marked by $C_{11}H_9^+$) appears in Figure 2c. The assignment of this peak is based on its arrival time with respect to the $(C_{10}H_8)^+$ fragment (see Figure 4b).

The photofragmentation behaviors are more clearly seen in the difference mass spectra shown in Figure 3. The spectra in parts (a) and (b) are obtained by subtracting the parent mass spectrum in Figure 2a from the photofragment spectra in Figures 2b and 2c, respectively. The negative peaks demonstrate the depletion of parent cluster ions, mainly $(C_{10}H_8)_2^+$ and $(C_{10}H_8)_5^+$, due to 950-nm irradiation, to produce the positive peaks for photofragments. Comparison of the difference mass spectra obtained at two laser fluences reveals that fragmentation pattern is affected by the laser fluence. As described below, a linear relationship between laser power and logarithm of depletion efficiency of the parent cluster ions is maintained at pulse energies below 50 μJ. This suggests that photofragments produced at 150 μJ/pulse (Figure 3b) arise partly from multiphoton effects.

Also shown in Figure 3 are typical difference mass spectra resulting from 580-nm irradiation. It is evident that the visible

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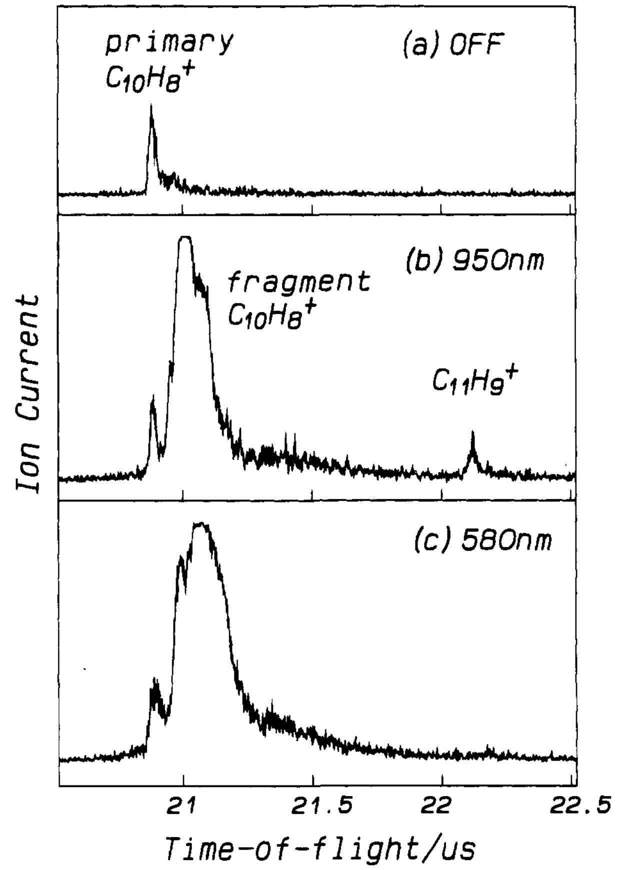

Figure 4. Expanded traces of the TOF mass spectra in the monomer cation region resulting from R2PI of $(C_{10}H_8)_5$ (a) without irradiation, (b) with irradiation at 950 nm, 150 μJ/pulse, and (c) with irradiation at 580 nm, 150 μJ/pulse.

excitation produces mostly monomer fragments even under the soft fragmentation condition (50 μJ/pulse). An analogous photodissociation propensity was reported for benzene cluster ions[10,11] and explained by a statistical dissociation model.[12] Compared to the 950-nm photodissociation results, photofragmentation of the monomer itself takes place upon irradiation at higher laser power. Thus numerous peaks corresponding smaller fragments than the monomer cation (e.g., $C_8H_6^+$) are present in the spectrum depicted in Figure 3d.

Figure 4 shows a portion of TOF mass spectra showing the monomer cation region on an expanded scale. The spectrum in Figure 4a obtained without irradiation shows a primary monomer ion, while those in Figures 4b and 4c are resulting from irradiation of $(C_{10}H_8)_5^+$ at 950 and 580 nm, respectively. The spectrum in Figure 4b reveals monomer fragments, which arrive ≈150 ns after the primary ion peak, and a $C_{11}H_9^+$ peak. No feature attributable to $C_{11}H_9^+$ is observed in Figure 4c. It is also noted that the primary monomer ion shows no detectable depletion at either wavelength, which indicates that the observed photofragments arise from dissociation of the cluster ions.

In order to probe the photochemistry of $(C_{10}H_8)_n^+$ in the near-IR region in greater detail, we have measured the intensity of the $C_{11}H_9^+$ fragment as a function of photolysis laser power. The results obtained for $(C_{10}H_8)_5^+$ are plotted on a double logarithmic scale and shown in part (a) of Figure 5. The saturation of the $C_{11}H_9^+$ fragment formation is evident at higher fluences. Since the neutral cluster $(C_{10}H_8)_5$ is predominantly ionized by R2PI through its resonance intermediate, the $(C_{10}H_8)_5^+$ ion is expected to be the most abundant ion (see Figure 2a). Therefore, a substantial portion of the $C_{11}H_9^+$ intensity may be ascribed to dissociation of the $(C_{10}H_8)_5^+$ parent, with minor contributions from the other parent ion. In order to confirm this behavior, we have also measured the laser power dependence of the depletion yield for $(C_{10}H_8)_5^+$. The result is shown in Figure 5b. It is seen that the logarithmic plots of the photodepletion efficiency I_0/I, where I_0 and I are the $(C_{10}H_8)_5^+$ ion intensities before and after photolysis, respectively, reveal a linear relationship with pulse energy up to 50 μJ. This finding indicates that the $C_{11}H_9^+$ fragment which appears at the expense of the $(C_{10}H_8)_5^+$ parent is due to multiphoton effects. This is also suggested by the power dependence of the $C_{11}H_9^+$ fragment formation in Figure 5a, which reveals a slope of approximately 2 in the lower fluence region.

The dependence of the $C_{11}H_9^+$ fragment formation yield has been studied as a function of cluster size using 950-nm irradiation. Figure 6 compares difference mass spectra obtained subsequent to photolysis of the parent cluster ions $(C_{10}H_8)_n^+$ ($n = 3-6$) with a pulse energy of 150 μJ. In each case, the R2PI method was used to ionize the corresponding neutral cluster through an appropriate resonance intermediate. These spectra are normalized to produce the same peak intensity for the monomer fragment ion $C_{10}H_8^+$. Interestingly, no detectable trace of $C_{11}H_9^+$ is observed upon photolysis of $(C_{10}H_8)_2^+$ and of $(C_{10}H_8)_3^+$ (see Figure 6a), while this fragment ion is seen in the experiments with larger cluster ions of size $n \geq 4$. The failure to observe the $C_{11}H_9^+$ fragment for $n \leq 3$ is not due to falsification in the mass analysis, since the spectrum in Figure 6a exhibits significant amounts of the monomer fragment intensity. As shown in Figure 6c, the relative intensity of $C_{11}H_9^+$ with respect to the monomer fragment appears to be largest for the photodissociation of $(C_{10}H_8)_5^+$. One might therefore expect that, among the parent cluster ions studied, the $(C_{10}H_8)_5^+$ ion is most favorable for the production of $C_{11}H_9^+$. However, as described below, larger cluster ions of size $n \geq 6$ could be more favorable for the intervalence photochemistry. Although the $(C_{10}H_8)_2^+$ parent also exhibits a strong depletion signal, this species has a negligible contribution to the appearance of $C_{11}H_9^+$, as demonstrated in Figure 6a.

For larger cluster ions of size $n \geq 6$, the application of the R2PI method is hampered because of the difficulty in selecting intermediate transitions that favor production of a particular cluster ion. This results in the lack of size selectivity in photolysis. This situation is apparent in Figure 6d, where the pump laser is tuned to an intense transition of the neutral cluster $(C_{10}H_8)_6$.[14] Despite this preferential excitation, the $(C_{10}H_8)_6^+$ peak appears weakly in the parent mass spectrum (not shown) and the $(C_{10}H_8)_2^+$ ion becomes a predominant parent ion. This relative abundance in the parent ions accounts for the fact that the $(C_{10}H_8)_2^+$ parent reveals the largest signal loss in Figure 6d. Based on the observation in Figure 6a that the $(C_{10}H_8)_2^+$ ion does not produce the $C_{11}H_9^+$ fragment, we conclude that most of the monomer fragments appearing in Figure 6d arise from the photodissociation of $(C_{10}H_8)_2^+$, while the $(C_{10}H_8)_6^+$ parent ion is responsible for the formation of $C_{11}H_9^+$. Thus, one could expect that photodissociation of $(C_{10}H_8)_6^+$ or larger cluster ions might produce more of the $C_{11}H_9^+$ fragment than that of $(C_{10}H_8)_5^+$.

Discussion

Based on the above findings, we propose a mechanism which explains qualitatively the formation of $C_{11}H_9^+$ from $(C_{10}H_8)_n^+$ ($n \geq 4$) upon irradiation in the intervalence transition region. The $C_{11}H_9^+$ ion is known to be formed from various neutral

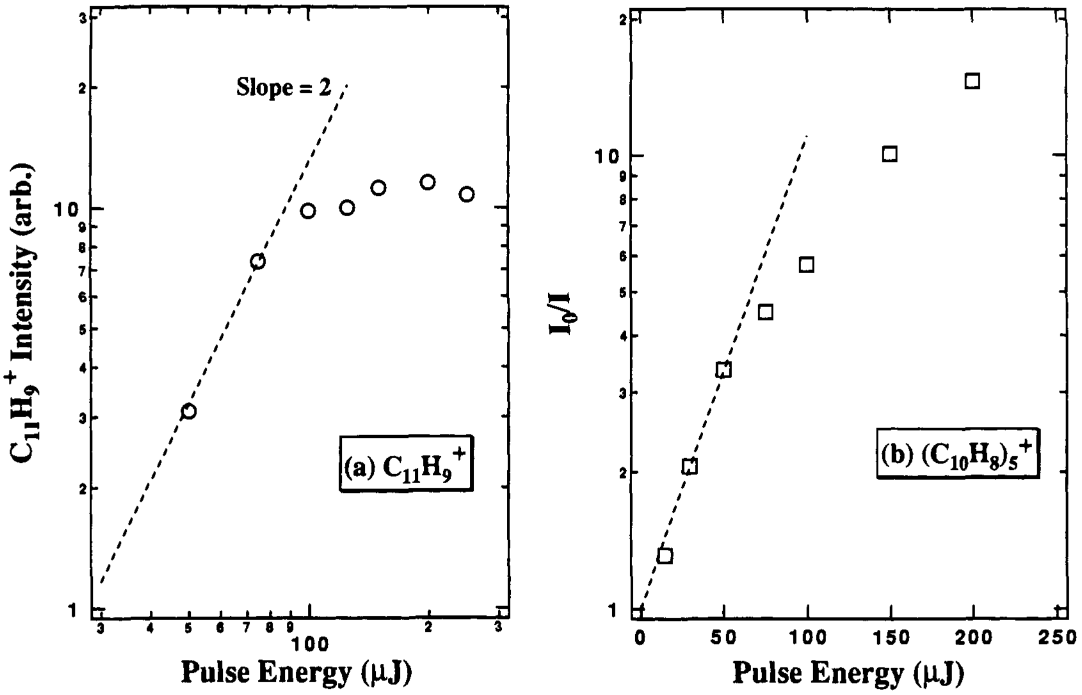

Figure 5. Laser power dependences of (a) $C_{11}H_9^+$ ion intensity and (b) photodepletion of parent $(C_{10}H_8)_5^+$ ion intensity, resulting from 950-nm irradiation.

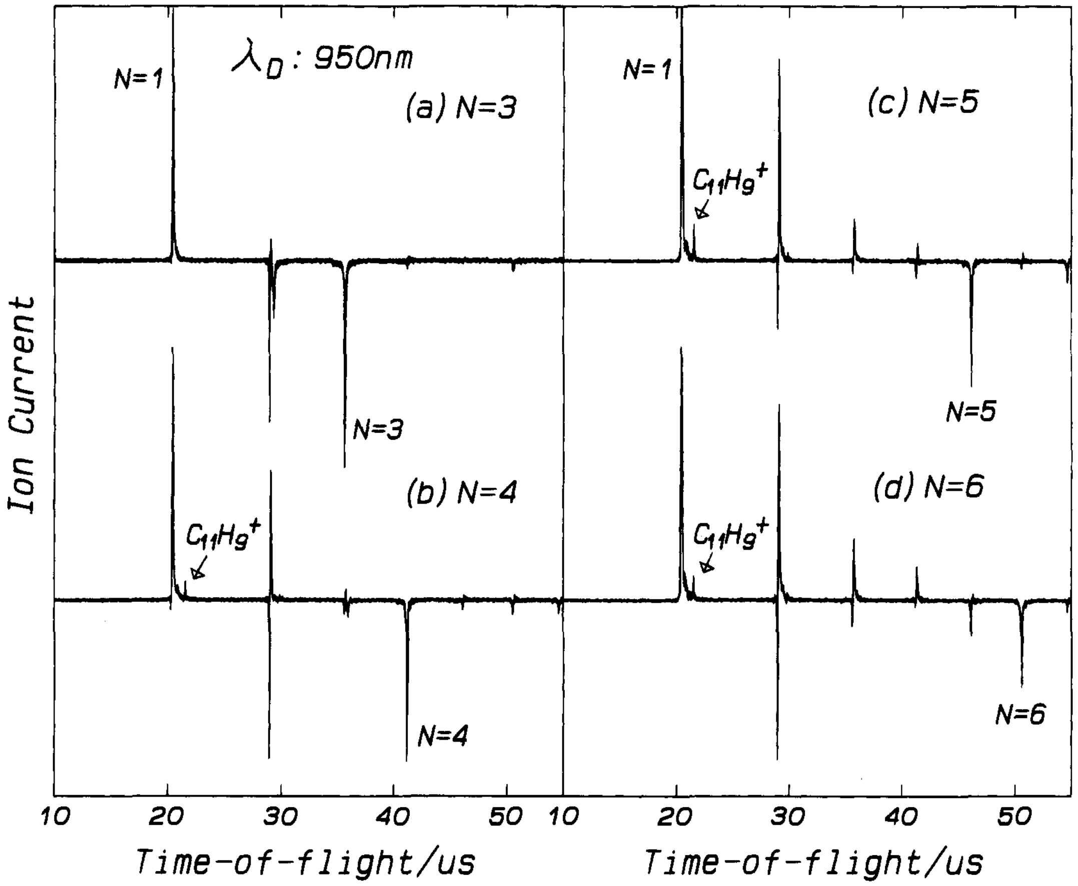

Figure 6. Difference mass spectra for (a) $(C_{10}H_8)_3^+$, (b) $(C_{10}H_8)_4^+$, (c) $(C_{10}H_8)_5^+$, and (d) $(C_{10}H_8)_6^+$, measured at 950 nm, 150 μJ/pulse.

precursors (e.g., 1- and 2-(chloromethyl)naphthalene) by electron impact ionization,[20-22] or from ionic precursors (e.g., 1- and 2-methylnaphthalene cations) following photodissociation.[23-25] The species produced by the former method has been identified

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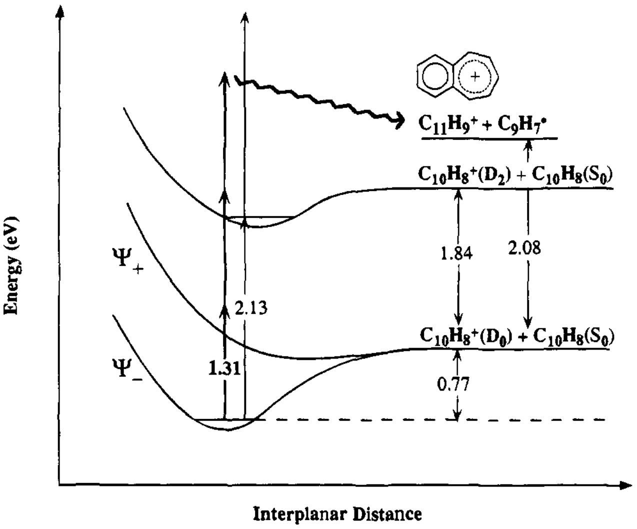

Figure 7. A schematic representation of the potential energy diagram showing the formation of $C_{11}H_9^+$ from the naphthalene dimer ion.

as a benzotropylium ion based on collisional activation studies.[26] The heat of formation has been estimated to be ≈250 kcal/mol,[21] although the methylnaphthalenium structure could give rise to a similar value. This value, together with the heats of formation reported for $C_{10}H_8^+$, $C_{10}H_8$, and $C_9H_7^+$,[21,27] gives a ΔH of ≈2.1 eV for the gaseous ion−molecule reaction: $C_{10}H_8^+ + C_{10}H_8 \rightarrow C_{11}H_9^+ + C_9H_7^•$. This process thus requires at least two photons at 950 nm (1.31 eV).

Since near threshold ionization is employed in the present experiment, the resulting parent cluster ions are expected to be in the ground electronic state with small amounts of internal energy (<0.3 eV).[28] Another important energetical consideration is the stability of the parent cluster ions. Previous photodissociation results[14] indicate that these species are described essentially as a strongly bound dimer, in which the positive charge is localized, surrounded by other neutral molecules, i.e., $(C_{10}H_8)_2^+(C_{10}H_8)_{n-2}$. The stability of this core, which is explained by the charge resonance interaction between the two molecules, is responsible for the occurrence of the intervalence transition band in the near-IR region. The fact that the intervalence transition energy of $(C_{10}H_8)_2^+$ is not affected by further clustering, at least up to $n = 7$, confirms that these cluster ions are likely to possess such a core structure. The dissociation energy of the naphthalene dimer cation has been derived from a thermochemical measurement to be 0.77 eV,[29] which is roughly in accord with half the intervalence transition energy (≈0.6 eV). If we take the thermochemical value for the stabilization of the dimer core produced in the cluster ions, a ΔH of 2.85 eV will be required for the conversion of the dimer ion into $C_{11}H_9^+$ and $C_9H_7^•$. This predicts that the dimer ion must absorb at least three 950-nm photons to reach the product energy level. The sharp increase in the $C_{11}H_9^+$ intensity shown in Figure 6a, revealing a two-photon behavior, could be an indication that the $C_{11}H_9^+$ formation involves a (1 + 2) photon process. Figure 7 offers a schematic representation of the energy level diagram.

The leveling off of the power dependence at higher fluences (Figure 6a) cannot be readily explained, although two possible processes may be suggested: (1) the intracluster process competes with molecular fragmentation processes as the parent ion absorbs additional photons, or (2) the $C_{11}H_9^+$ fragment also absorbs at this photolysis wavelength, resulting in further fragmentation. However, we failed to observe any fragments other than this species even at much higher fluences (500 μJ), for which result we offer no further explanation at present.

The lack of $C_{11}H_9^+$ formation for the smaller cluster ions, namely $(C_{10}H_8)_2^+$ and $(C_{10}H_8)_3^+$, provides strong evidence of solvent cage effects on the reaction probability. While various types of intracluster ion−molecule reactions are known to proceed for specific cluster sizes and hence display significant variation with degree of solvation,[1-4,30] none to date appear to be quite as specific as the example presented here. A similar, but not identical, behavior was reported by Schriver et al. for the formation of $C_7H_7^+$ in benzene clusters.[13] They suggested that the solvated cluster ions $(C_6H_6)_nC_7H_7^+$, produced upon photoionization at 12.8 eV, arise from dissociative ionization of the neutral clusters $(C_6H_6)_{n+2}$. The observation that the relative abundance of $(C_6H_6)_nC_7H_7^+$ to $(C_6H_6)_{n+2}^+$ increases slowly with cluster size up to $n \approx 7$, was used to propose that this process is intrinsic to condensed benzene systems. Although the behavior is qualitatively in agreement with our result, we were unable to detect solvated ions involving $C_{11}H_9^+$ under the experimental conditions described above. This is to be expected if the binding energy of solvent molecules around the dimer ion core is considerably smaller than that of the dimer core. Since, as demonstrated in Figure 2b, even one-photon excitation of the cluster ions results in multiple monomer evaporation, it is reasonable to expect that the multiphoton excitation leads to a complete loss of solvent molecules.

We believe that the formation of a strongly bound dimer ion plays a key role in the photochemistry of these cluster ions at the intervalence band excitation. The dimer core is assumed to possess a nearly parallel overlapped configuration, where the equilibrium spacing between the two component molecules should be much shorter than those of surrounding neutral molecules. Since the positive charge is largely confined within the pair, this dimer core may be regarded as the elementary unit in the excitation of a cluster ion. The idea of the dimer core structure has also been used to explain the observation that the benzene cluster ion systems exhibit the intervalence transition band near 920 nm, irrespective of cluster size.[31] Based on the results for the benzene and naphthalene cluster ions, we propose that this type of photochemistry could be viewed as a *unimolecular* reaction of a strongly bound dimer ion core which is surrounded by a solvent cage, rather than an ion−molecule reaction.

Compared to the near-IR photolysis, the visible excitation at 580 nm (2.13 eV) produces no $C_{11}H_9^+$ fragment ion. At higher laser power, fragment ions corresponding to destruction of the monomer ion appear at lower masses. Previously, multiphoton dissociation behaviors of the naphthalene molecular ion in the visible and UV regions were studied using ICR[32] and supersonic expansion[33] techniques. The minimum energy dissociation threshold of the naphthalene cation, corresponding to either loss of C_2H_2 or loss of H, was found to lie near 7.4 eV. This implies that the dissociation process requires four photons in the visible (600 nm and longer). Although we observe similar photofragment ions upon photodissociation at 580 nm, these fragments can be assigned as arising from the cluster ions. Under the irradiation condition employed for the cluster ions, no detectable

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depletion was observed for the monomer ion intensity. Based on the assignment of the visible absorption band as a local excitation, the 580-nm excitation is expected to promote the dimer ion into a state where charge resonance interaction would be smaller, and thus the interplanar separation would be larger, than in the ground state. This situation is apparently unfavorable for the photochemical rearrangement, and could be used to explain the absence of such photochemistry upon excitation through this intermediate.

Conclusions

The photofragmentation behaviors of naphthalene cluster ions $(C_{10}H_8)_n^+$ in the near-IR and visible regions have been investigated as a function of cluster size using mass-selected photoionization–photodissociation mass spectrometry. Following multiphoton excitation of cluster ions with $n \geq 4$ into the intervalence transition band, production of a $C_{11}H_9^+$ fragment ion is detected, while no such photochemistry is observed for cluster ion sizes $n \leq 3$. This process is described as a reaction of the strongly bound dimer ion core produced within the initially ionized cluster. The reaction probability is found to be strongly dependent on cluster size, which suggests that the reaction requires a solvent cage involving at least two neutral molecules surrounding the dimer core. Although the $C_{11}H_9^+$ fragment could possess benzotropylium structure, further study is needed for structural determination. In contrast, analogous experiments with visible photons lead to intramolecular fragmentation pathways, and no $C_{11}H_9^+$ fragment is observed.

We believe that the observation of $C_{11}H_9^+$ following excitation of the naphthalene cluster ions via the intervalence transition band has important implications for intracluster photochemistry of aromatic molecules in the near-IR wavelength region.

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