Excimer Formation in van der Waals Dimers and Clusters of Aromatic Molecules

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1. Introduction

Aromatic excimers, dimeric species which are associated in an excited electronic state and dissociated in their ground electronic state,[1] play an important role in several areas of photochemistry, including photodimerization.[2] Although these species have been extensively studied in the condensed phase over the past four decades,[1,2] it is only recently that the effective merger of the laser and the supersonic jet[3] has brought us to the state where we can characterize their electronic states and excited-state dynamics in some detail. The low internal temperatures attained in a supersonic expansion allow the formation of weakly bound van der Waals (vdW) dimers and higher clusters of aromatic molecules, which can be laser excited, in a species-specific manner, to produce excimers. In addition to the possible size and geometry dependence of excimer formation, the collision-free conditions of a supersonic jet permit the studies of the excess vibrational energy dependence of the excimer formation and the excimer dissociation on repulsive potential energy surfaces. Thus, the combination of lasers and supersonic jets offers opportunities to study aromatic excimers in ways not possible in condensed phases. Among the kinds of information that are becoming available from the supersonic-jet laser spectroscopy of aromatic dimers and clusters are the shape (bound versus repulsive) of the intermolecular potential wells in various electronic states of the excimers and the role the excimer core plays in elementary photochemical processes of the vdW molecules.

This Account is concerned with an overview of our recent work on the structure and excited-state dynamics of jet-cooled aromatic clusters (naphthalene, in particular), which highlights the types of new information that are emerging from the laser spectroscopic studies of the isolated cold clusters. We first present a very brief summary of the spectral and geometrical characteristics of singlet excimers, as deduced from condensed-phase studies. We then describe the generation and characterization of excimers from photoexcited vdW dimers of aromatic hydrocarbons in a supersonic jet. The repulsive character of the ground state of the excimer, and of the higher-energy electronic states of the excimer, is also described. This is followed by a description of the excimer formation from higher clusters of naphthalene, and the dependence of the excimer formation on cluster geometry and the excess vibrational energy. We conclude this Account by describing evidence for the dimer core structure of the excimer clusters, and the important precursorial role that the excimer core plays in the photodissociation and photoionization of the vdW clusters.

2. Formation of Aromatic Excimers in Condensed Phases

The aromatic excimer was first discovered by Förster and Kasper,[4] who observed the broad, structure-

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less fluorescence from a concentrated solution of pyrene at room temperature. The emission, which appeared only in concentrated solution, was strongly red shifted with respect to the structured monomer fluorescence of pyrene. Since no new spectral feature other than that of the monomeric species was evident in the absorption spectra of the concentrated solutions, the anomalous fluorescence was attributed to a dimeric species which is formed by the diffusive association of an electronically excited pyrene (in its lowest excited singlet state) with a molecule in the ground electronic state. Both the structureless feature of the excimer fluorescence and its lower energy relative to the monomer fluorescence are consistent with the repulsive character of the ground-state potential.[5] A large body of subsequent work has established that the formation of singlet excimers is a rather general property of highly concentrated solutions of aromatic hydrocarbons.[1] The molecular crystals of perylene[6] and pyrene,[7] composed of a face-to-face arrangement of two molecules in the crystal lattice, also exhibit excimer fluorescence, as do the sandwich dimers of naphthalene[8] and anthracene[9] produced by photolytic dissociation of the corresponding photodimers in a rigid glass. These results, as well as the observation of the intramolecular excimer formation from dilute solutions of 1,3-diphenylpropane[10] and 1,3-di-α-naphthylpropane[11] (the only short-chain diarylalkanes that can adopt a face-to-face arrangement of two aromatic rings), led to the conclusion that the preferred conformation of excimers is a symmetrical sandwich structure. This conclusion is supported by semiempirical molecular orbital studies on the naphthalene dimer,[12–16] which indicate that the perfect sandwich-pair D_{2h} structure is the most favored conformation of the singlet excimer due to stabilization by exciton resonance ($M^*M \leftrightarrow MM^*$) and, to a lesser extent, by charge resonance ($M^+M^- \leftrightarrow M^-M^+$). In sharp contrast to the numerous reports of the excimer fluorescence, there is a dearth of information concerning the absorption spectra of the singlet excimers of aromatic molecules. In fact, the absorption spectrum, attributed to the singlet excimer, has only been reported for pyrene in solution.[17,18]

Figure 1. Potential energy diagram for the formation of an excimer, (A·A)*, via local excitation of a ground-state vdW dimer, A···A.

3. Excimers from Photoexcited van der Waals Dimers

3.1. Bimolecular Association at a Well-Defined Geometry. The study of aromatic excimers in a supersonic jet begins with the generation and isolation of a ground-state vdW dimer (and higher order clusters) by an adiabatic expansion of seeded molecular beams. Because the conformation of the ground-state vdW dimer is generally more displaced (and thus less overlapped) than the sandwich-pair geometry of singlet excimers, direct photoexcitation of the excimer state from the ground state of the vdW dimer is not possible. Thus, a generic excimer-formation experiment in a molecular beam involves excitation of the ground-state vdW dimer into its locally excited (LE) state, which then forms an excimer via molecular rearrangement (see Figure 1).

The photoexcited vdW dimer of benzene is characterized by an anomalously low fluorescence yield[19] and a short lifetime[20,21] with respect to the monomer, which has been taken as an indication that this species undergoes a structural change into an excimer geometry in the first excited singlet (S_1) state. Direct evidence for such vdW dimer–excimer transformation was first obtained by Saigusa and Itoh through the observation of excimer fluorescence from a photoexcited vdW dimer of fluorene.[22] Since the dimer is initially excited into the S_1 state with well-defined vdW geometry, its excitation spectrum resembles the monomer spectrum (Figure 2a). The formation of the fluorene excimer was evidenced by the observation of a broad, structureless fluorescence (Figure 2b) which closely mimics the excimer fluorescence from concentrated solutions of fluorene. The extension of the study to naphthalene,[23] dibenzofuran,[24] and anthracene[25] dimers indicates that the electronic excitation of these species into their LE state also leads to the formation of excimers. The excimer formation

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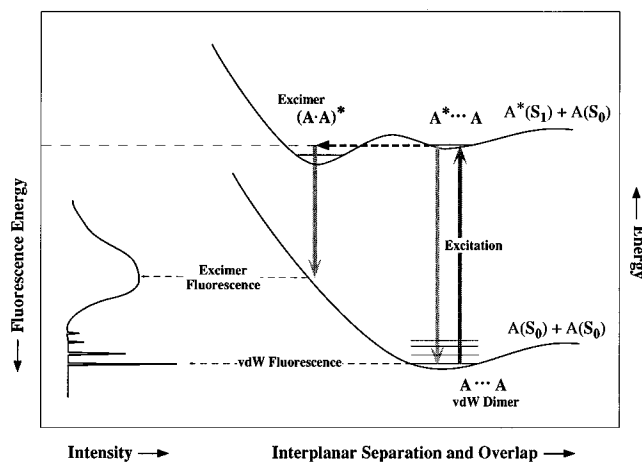(18) Post, M. F. F.; Langelaar, J.; van Voorst, J. D. W. *Chem. Phys. Lett.* **1971**, *10*, 468.

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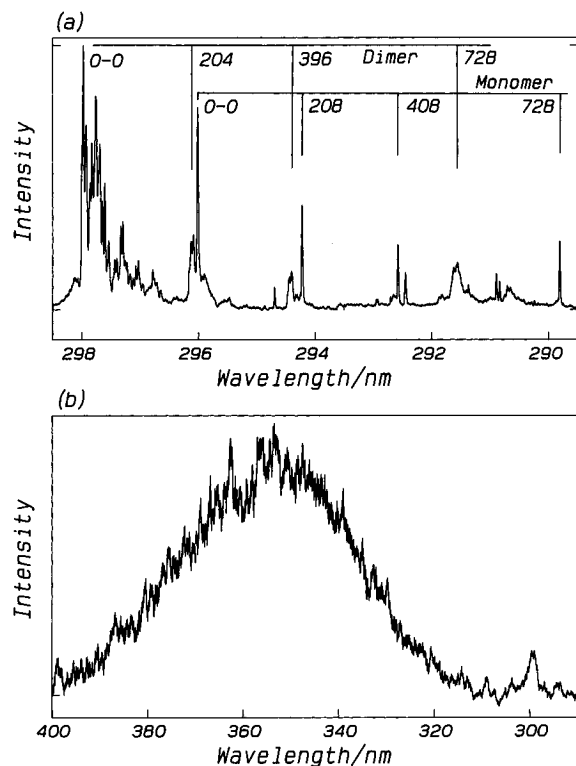
Figure 2. (a) Fluorescence excitation spectra of the monomer and vdW dimer of fluorene in the $S_1 \leftarrow S_0$ region obtained by detecting the fluorescence at >360 nm. The vibrational frequencies of the main bands with respect to the electronic origin (0−0) are shown in inverse centimeters. (b) Dispersed fluorescence spectrum obtained subsequent to excitation of the most intense peak of the dimer (a).

appears to be a barrierless process which takes place even in the absence of excess vibrational energy. Thus, the excimer fluorescence appears very rapidly (compared with the pulse width of the nanosecond laser) even when the dimers are excited into the zero-point vibrational level of their LE state. These results indicate that the Franck−Condon excited states of the vdW dimers of aromatic hydrocarbons (whatever their geometries might be) can easily rearrange to the face-to-face geometry of two monomer units favored by the singlet excimers.

The lifetimes of the excimer fluorescence from the photoexcited vdW dimers of fluorene,[22,26] naphthalene,[23] and dibenzofuran[24] are generally long, consistent with the symmetry-forbidden nature (g−g) of the radiative transition. However, the excimer fluorescence of anthracene decays with a laser-pulse-limited lifetime of <5 ns,[27] which is about 3 orders of magnitude shorter than the ~1 μs decay time of the excimer fluorescence of the compound in a solid matrix at low temperature.[28] The very short lifetime of the anthracene excimer in a supersonic beam can be attributed to the efficient dimerization of the gas-phase excimer leading to the formation of dianthracene.

3.2. Radiative Dissociation of Excimers. In the condensed phase, spectroscopic evidence for the repulsive character of the ground-state potential of aromatic excimers comes, only in an indirect manner, from the absence of an absorption spectrum attributable to a stable dimeric species.[1] Direct experimental

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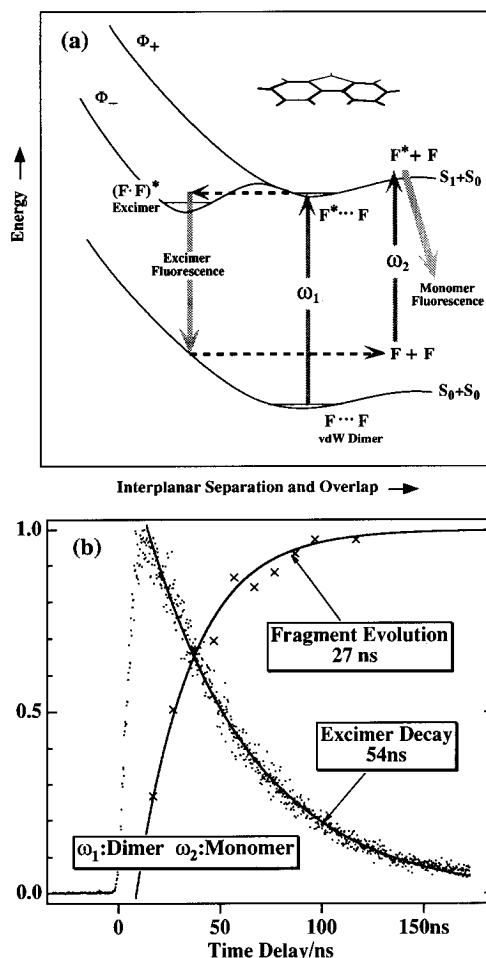

Figure 3. (a) Schematic diagram illustrating the pump−probe technique employed to probe dissociation of the fluorene excimer in the ground state. The vdW dimer F···F, excited into its S_1 by the pump pulse ω_1, rearranges into the excimer (F·F)* at <100 ps and dissociates into monomers via radiative transition. The vibrationally excited fragments are probed by detecting the monomer fluorescence induced by the second laser pulse ω_2. (b) Fragment fluorescence intensity (×) detected at 315 nm as a function of the pump−probe delay. The dotted curve represents the excimer fluorescence induced by the pump laser alone.

proof for the repulsive ground-state potential would require the observation of the monomer fragments following the dissociative radiative transition of an excimer into its ground electronic state. Unfortunately, such measurements are very difficult in condensed phases. The solute−solvent interactions rapidly change the initial internal-state distribution of the monomer fragments, such that the fragment molecules cannot easily be distinguished from the solute molecules which did not go through the excimer formation−dissociation cycle. Under the collision-free conditions of a supersonic jet, a subensemble of the monomer fragments produced by the excimer dissociation can be selectively detected by means of a double-resonance pump−probe spectroscopy.

The pump−probe study of the molecular fragmentation in the ground state of an excimer has been carried out for the fluorene excimer,[26] which is believed to decay mainly by a radiative transition to the ground electronic state. The experiment begins with the electronic excitation of the fluorene vdW dimer to its S_1 origin by a pump laser (ω_1), which generates the excimer as schematically illustrated in Figure 3a. A time-delayed probe laser (ω_2) then detects the fluo-

rescence of the monomer fragments generated by the radiative decay of the excimer by exciting the vibrationally hot fragment at wavelengths not absorbed by the cold fluorene molecule. By varying the time delay between ω_1 and ω_2, the time evolution of the monomer fragments can be followed and compared with that of the excimer fluorescence. The result,[26] which is shown in Figure 3b, demonstrates that the rise time of the fragment fluorescence is half the decay time of the excimer fluorescence, consistent with the fact that two monomer fragments are produced from the radiative dissociation of the excimer. The result of this pump–probe experiment therefore confirms that the excimer emits and returns to the repulsive inner wall of the ground-state potential energy surface (which is weakly bound at the vdW geometry, as shown in Figure 3a).

3.3. Photodissociation of the Excimer. Another important photoprocess which appears to be common to the vdW dimers of aromatic hydrocarbons is the near-IR absorption by their excimers which leads to the fragmentation of the species.[29,30] The photofragmentation of the vdW dimer is a sequential two-photon (two-color) process in which the first photon (ω_1) produces an excimer core via the photoexcitation of the vdW dimer and the second photon (ω_2) induces the dissociation of the excimer on the higher-energy repulsive potential surface. The photodissociation of the vdW dimer can be followed by monitoring the fluorescence from the electronically excited monomer fragment or by measuring the decrease in the intensity of the excimer fluorescence. A schematic diagram illustrating the formation and photodissociation of the fluorene excimer is shown in Figure 4a. The time evolution of the fragment fluorescence can be measured by varying the time delay between ω_1 and ω_2. The result obtained at a photodissociation wavelength of 860 nm (Figure 4b) clearly indicates that the fragment fluorescence decays out as the time delay is increased. The decay behavior is almost identical to that of the excimer fluorescence, which confirms that the excimer absorbs the near-IR photon and gives rise to the excited-state monomer fragment. The absorption spectrum of the excimer (to a higher-energy, repulsive excimer state) can be obtained by recording the photodepletion of the excimer emission (or the increase in the intensity of the fragment emission) as a function of ω_2. Figure 5a displays the photodepletion yield spectrum of fluorene, measured by varying the photodissociation wavelength at a fixed laser power.[29,30] The spectrum exhibits a broad, structureless band with an intensity maximum in the near-IR region. We have assigned the photodissociation spectrum (i.e., absorption spectrum) to the intervalence transition between two exciton resonance (ER) states, Φ_+ and Φ_-, which represent in-phase and out-of-phase combinations of locally excited $\phi^*\phi$ and $\phi\phi^*$, i.e., $\Phi_\pm = (1/\sqrt{2})(\phi^*\phi \pm \phi\phi^*)$. The observed intervalence transition energy of about 1.44 eV ($\sim$860 nm) is in good agreement with a computed value of $\sim$1.5 eV,[31] suggesting that the excimer states Φ_+ and Φ_- correlate with the S_1 and S_0 states of the monomer. The importance of the S_1 exciton resonance interaction as the principal source of the excimer stability is supported by the observation that the vdW complex of fluorene with
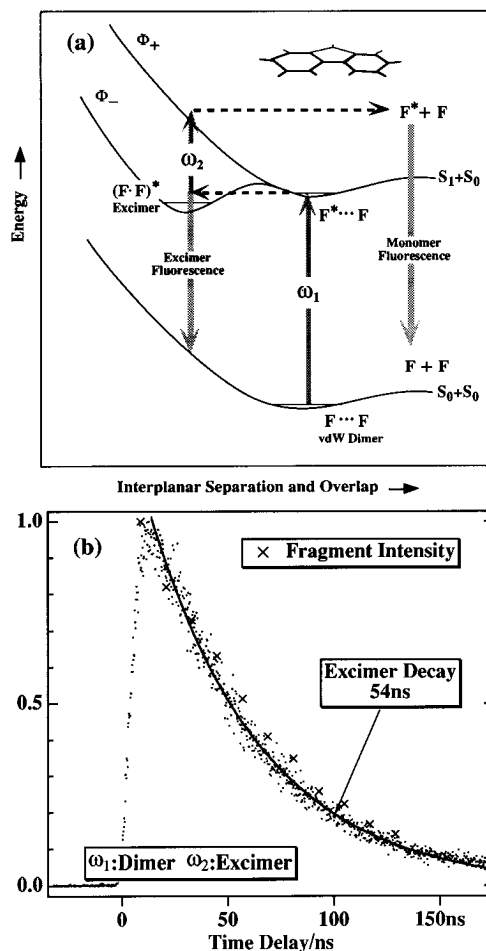
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Figure 4. (a) Schematic diagram illustrating the photodissociation technique employed to probe the intervalence absorption band ($\Phi_+ \leftarrow \Phi_-$) of the fluorene excimer. The occurrence of the transition is probed by detecting either the depletion of excimer fluorescence or the evolution of fragment fluorescence. (b) Fragment fluorescence intensity ($\times$) detected at 315 nm as a function of the time delay. The photodissociation wavelength is 860 nm. The dotted curve represents the excimer fluorescence induced by ω_1 alone.
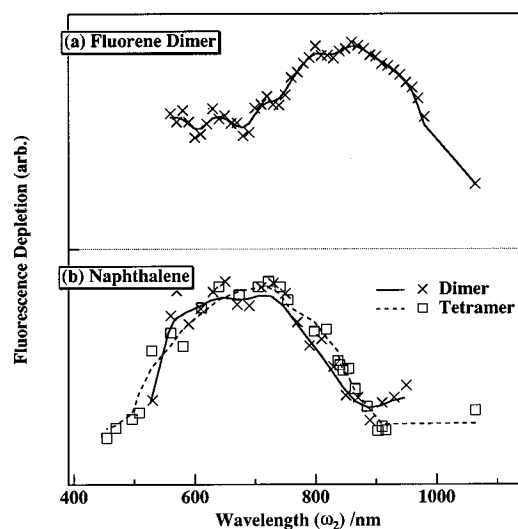

Figure 5. Photodepletion efficiency curves of excimer fluorescence obtained for (a) the fluorene dimer and (b) the dimer and tetramer of naphthalene. The photodissociation laser power is kept at 0.5 mJ/pulse.

1,2,4,5-tetrachlorobenzene, in which the two chromophores possess slightly different S_1 energies, un-
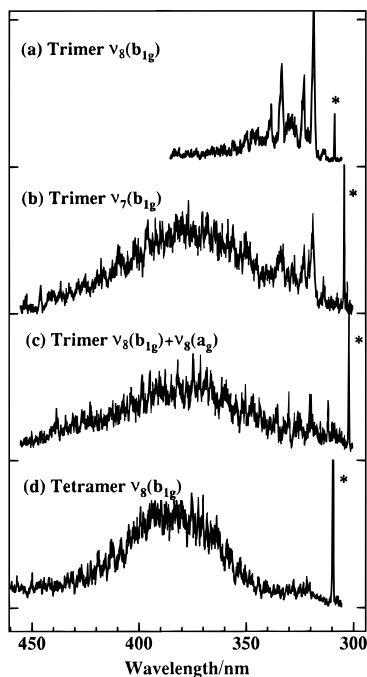
Figure 6. Dispersed fluorescence spectra obtained subsequent to excitation into (a) $\nu_8(b_{1g})$, (b) $\nu_7(b_{1g})$, and (c) $\nu_8(b_{1g}) + \nu_8(a_g)$ of the trimer and into (d) $\nu_8(b_{1g})$ of the tetramer.

dergoes less efficient excimer formation.[32] The photodissociation of excimers has also been observed for the vdW dimer of naphthalene[30] (Figure 5b).

4. Excimers from Photoexcited van der Waals Clusters

4.1. Geometry-Controlled Isomerization Dynamics. The neutral clusters of benzene, $(C_6H_6)_n$, with $n = 2-20$, as well as those of naphthalene, $(C_{10}H_8)_n$, with $n = 2-7$, can be easily produced by conventional supersonic-jet expansions. The absorption spectrum of the species can be characterized by mass-resolved, resonantly enhanced multiphoton ionization, and its excited-state dynamics probed by species-selective excitation. The study of the fluorescence-detected excited-state dynamics of naphthalene clusters ($n > 2$) shows that electronic excitation of these species into their LE states leads to the appearance of the excimer fluorescence,[23,33] as in the corresponding dimer. However, unlike the case of the dimer, the excimer formation in the higher clusters requires vibrational energy above a threshold value. This is illustrated for the trimer and tetramer in Figure 6, which displays the dispersed fluorescence from various S_1 (LE) vibronic levels. It should be noted that the sharp, discrete fluorescence from the low-lying vibronic level $[S_1 + \nu_8(b_{1g})]$ of the trimer transforms into the broad, structureless excimer fluorescence at high excitation energies $[S_1 + \nu_7(b_{1g})$ and $S_1 + \nu_8(b_{1g}) + \nu_8(a_g)]$. The threshold excess energy required for the excimer formation is significantly smaller for the tetramer than for the trimer. Thus, while the excimer formation in the trimer requires an excess vibrational energy of ~870 cm^{-1} (the vibrational energy of the $\nu_7(b_{1g})$ mode), the tetramer requires an energy of less than 400 cm^{-1}, as evidenced

by the observation of the excimer fluorescence following the $\nu_8(b_{1g})$ excitation (Figure 6d). In both cases, no isomerization dynamics is promoted at the S_1 electronic origin. These results strongly suggest that the geometry of the initially excited vdW cluster determines the efficiency of the excimer formation. Apparently, the trimer has a vdW geometry which renders its transformation (in the excited state) into the excimer more difficult. The conclusion that the excited-state dynamics are geometrically controlled is also supported by the fact that the trimer excited into the $S_1 + \nu_7(b_{1g})$ transition shows an anomalously long rise time of 32 ns for excimer formation, in sharp contrast to the $S_1 + \nu_8(b_{1g})$ tetramer which does not exhibit a measurable rise time even at a 100 ps time resolution. The rise time of the excimer fluorescence from the trimer decreases sharply with increasing excess vibrational energy. At excess energies where both the LE fluorescence and the excimer fluorescence are observed, the decay time of the former is identical to the rise time of the latter, indicating that the excimer is formed directly from the LE state of the vdW cluster.[33]

The geometry-restricted isomerization dynamics are also evident in the mixed clusters of naphthalene with durene (1,2,4,5-tetramethylbenzene) $[(C_{10}H_8)_2(C_{10}H_{14})_n]$, with $n = 1$ or 2.[33] In contrast to the pure dimer of naphthalene where excimer formation takes place very rapidly (<100 ps) even at the S_1 origin, the excimer formation in the 2:1 mixed cluster requires an excess vibrational energy of ~400 cm^{-1}. Even at this relatively large threshold energy, the rise time of the excimer fluorescence is very slow (~60 ns), indicating that the addition of durene strongly impedes excimer formation.[33] For the 2:2 mixed cluster, both the threshold excess energy for the excimer formation and the rise time of the excimer fluorescence are significantly smaller than those of the trimer.[33] It may be concluded from these results that the cluster geometry of the 2:2 mixed cluster must be more favorable than that of the 2:1 mixed cluster for the excited-state structural isomerization leading to excimer formation.

4.2. Gross Geometries of Small Naphthalene Clusters. The differing behaviors of the naphthalene trimer and tetramer with respect to excimer formation point to the major structural differences between the two clusters. Gross geometries of these clusters can be obtained from an analysis of the splittings of the mass-resolved $S_1 \leftarrow S_0$ resonant two-photon ionization (R2PI) spectra.[34] Our analyses of the tetramer spectra[35] suggest that this species possesses an asymmetric structure and the band splitting is induced by the S_2 excitation exchange (excitonic) interaction among chromophore molecules, which is transmitted to the S_1 state through vibronic coupling. (The S_1 excitonic interaction is expected to be very small compared to the S_2 interaction in naphthalene; see section 4.3.) The observed band splitting is therefore a direct reflection of the magnitude of the excitonic interaction in S_2, which in turn is related to the relative orientation of the monomer moieties within the cluster. This model for the band splitting is supported by the observation that the multiplet structure (and splitting) in the $S_1 \leftarrow S_0$ spectrum is observed only for the nontotally symmetric b_{1g} modes

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(ν_8, ν_7, etc.),[34,36] which are active in the S_1-S_2 vibronic coupling. In contrast, the analysis indicates a symmetric, nonoverlapping cyclic (C_3) structure for the naphthalene trimer.[35]

These structures are in agreement with the cluster geometries proposed by Felker and co-workers based on the ionization-detected stimulated Raman spectroscopy.[37] They have shown that the C−H stretching fundamentals of the tetramer consist of four clearly resolved bands, whereas the trimer exhibits a single feature. These observations led them to the conclusion that the tetramer is composed of four monomer sites that are all symmetry inequivalent, whereas the trimer is composed of monomer moieties that occupy equivalent (or near-equivalent) sites.[37] The intermolecular vibrational bands in the Raman spectra also exhibit clear manifestations of a high-symmetry geometry for the trimer and a low-symmetry structure for the tetramer.[37] The likely cyclic structure of the naphthalene trimer suggested by these studies is such that the long axes of the three monomer moieties lie parallel, and each moiety has one of its long edges pointing into the plane of one of its neighbors and has its plane pointed into by the long edge of its other neighbor. On the other hand, the tetramer appears to be composed of "interior" structural sites containing a pair of nearly overlapping naphthalene moieties and "exterior" sites containing nonoverlapping monomer moieties, which are very weakly coupled to the molecules in the interior sites.[35] Given these gross geometries, the greatly reduced efficiency of excimer formation in the trimer relative to the tetramer is reasonable since the transformation of the nonoverlapping trimer structure to the excimer geometry would be much more difficult as compared to the structural isomerization of the tetramer with a nearly overlapping dimer site.

4.3. Core Structure of Excimer Clusters. As in the case of the dimeric excimer, the excimer produced in the higher clusters of naphthalene strongly absorbs in the near-IR region and dissociates into monomer fragments (one of which is electronically excited).[29,30] The pump−probe experiment, identical to that for the vdW dimer, shows that the photofragmentation does not occur when the pump laser is tuned to the energies below that needed to form an excimer (i.e., $S_1 + \nu_8(b_{1g})$ or lower excitation of the trimer and S_1 origin excitation of the tetramer). This indicates that the monomer fragments are produced from the photodissociation of the excimer cluster. Consistent with this conclusion, the rise time of the fragment fluorescence is nearly identical with the decay time of the excimer fluorescence.

The photodissociation spectra of the naphthalene dimer and tetramer are compared in the bottom panel of Figure 5. It should be noted that the two photodissociation spectra are essentially identical and reveal a maximum at 700 nm, which is red shifted from that of the fluorene dimer (Figure 5a). The trimer spectrum is also very similar to the dimer spectra.[30] Since the excitation delocalization would lead to a size-dependent absorption spectrum, the results indicate that the excimer clusters of naphthalene consist of a strongly bound dimeric core, where

the excitation is localized, and weakly bound ground-state molecules, i.e., $(C_{10}H_8)_2{}^*(C_{10}H_8)_{n-2}$. The 700-nm absorption band can be assigned to the intervalence transition between the bound (Φ_-) and repulsive (Φ_+) excimer states with an energy separation of 1.7 eV. Assuming symmetric splitting of the two excimer states, the dissociation energy of the naphthalene excimer can be estimated at ∼0.85 eV (i.e., half of the intervalence transition energy). This is in agreement with the estimated experimental value (0.78 eV) based on the sum of the measured solution-phase dissociation energy of ∼0.30 eV[38] (which represents the dissociation into S_1 and S_0 monomers) and the S_1-S_2 electronic energy gap (0.48 eV). Thus, we conclude that the bound and repulsive excimer states of naphthalene are correlated with the S_2 and S_0 monomers at infinite interplanar separation. This is in sharp contrast to the case of the excimer states of fluorene which correlate with the S_1 and S_0 states of the monomer (section 3.3). The differing behavior of naphthalene can be traced to the very small oscillator strength of the $S_1 \leftarrow S_0$ transition ($f < 0.001$) relative to that of the $S_2 \leftarrow S_0$ transition ($f \approx 0.11$), which renders the S_1 excitonic interaction very small in naphthalene.

4.4. Photoionization of Excimers. In analogy with aromatic crystals, photoionization of aromatic clusters may be expected to occur by a conventional two-step process involving the creation and subsequent excitation of the exciton or by exciton−exciton annihilation.[39,40] These mechanisms can lead to formation of higher excited states which undergo autoionization. Our recent two-color pump−probe photoionization study of naphthalene clusters reveals a third ionization mechanism involving the photoionization of the excimer core,[41] which is schematically illustrated in Figure 7.

Figure 8a compares the time evolution of the trimer ion signal, measured by varying the time delay between the pump laser ω_1 (which excites the trimer into $S_1 + \nu_7(b_{1g})$) and the ionization laser ω_2 (at 325 nm), with the time evolution of the excimer fluorescence generated by the pump laser alone. It is evident that the photocurrent signal is characterized by a slow rise time which corresponds well to that of the excimer fluorescence (35 ns). This demonstrates that the ionization of the naphthalene clusters occurs more efficiently from the excimer state when $\omega_2 = 325$ nm. In contrast, the tetramer ionization signal obtained at $S_1 + \nu_8(b_{1g})$ exhibits no slow rise time (shown in Figure 8b), which also parallels the fluorescence behavior. The important precursorial role of the singlet excimer in photoionization of the clusters can be attributed to the conformational similarity between the excimer and corresponding dimer cation (section 2), which renders a large Franck−Condon factor for ionization of the excimer.[41,42]

For both the trimer and tetramer of naphthalene, the two-color ionization enhancement is observed at total energies well below the one-color two-photon (1 + 1) ionization limit.[41] Thus, the excimer formation

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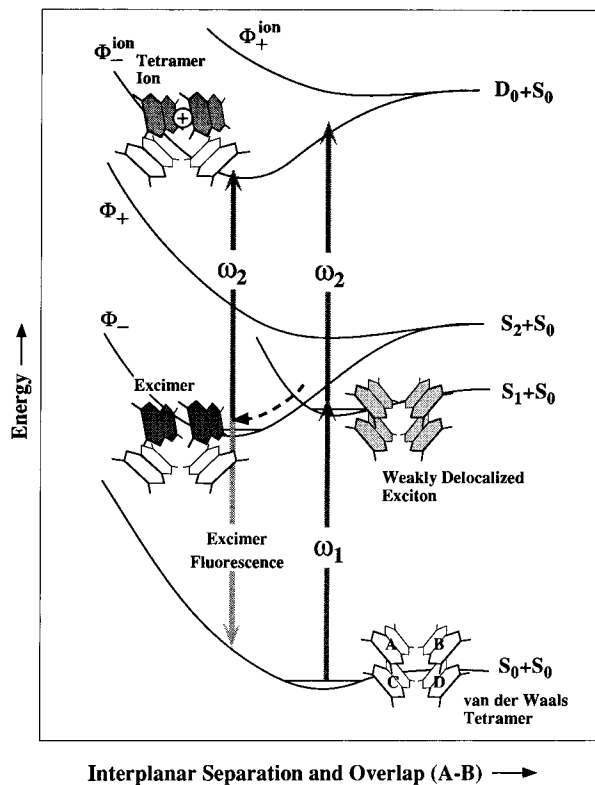
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Figure 7. Schematic diagram illustrating the two-color photoionization processes of naphthalene clusters. The pump laser ω_1 promotes a vdW cluster into an S_1 level undergoing excimer formation, and the ionization laser ω_2 is used to ionize the excimer cluster.

Figure 8. Photoionization signal of (a) the trimer ($\triangle$) and (b) the tetramer ($\square$) obtained as a function of the time delay between ω_1 and ω_2. The ion signals are obtained subsequent to excitation of the neutral trimer and tetramer into the respective $\nu_8(b_{1g})$ intermediates. The dotted curves represent the excimer fluorescence generated by the pump laser alone.

Figure 9. Photoionization efficiency curves of the trimer and tetramer obtained by scanning the ionization laser ω_2 near the ionization threshold. The neutral clusters are excited into the respective $\nu_8(b_{1g})$ intermediate levels.

not only enhances the ionization efficiency of the clusters but also lowers their ionization thresholds. This lowering of the ionization threshold is most likely due to the charge-resonance stabilization of the sandwich-pair dimer cation, $A^+A \leftrightarrow AA^+$, which leads to a decrease in the ionization potential of the excimer core (as schematically shown in Figure 7).[42] Figure 9 compares the photoionization yield curve of the trimer and tetramer, as measured by tuning the pump laser to the respective $\nu_8(b_{1g})$ levels. Note that the appearance potential is significantly smaller for the tetramer than for the trimer, which does not form an excimer at this energy of excitation. This again demonstrates the importance of excimer formation in the photoionization of aromatic clusters.

The cluster ionization by photoionization of the excimer core demonstrated here is expected to be a general and important mechanism for the photoionization of aromatic clusters.

5. Summary and Concluding Remarks

In this Account, we have described the structure and excited-state dynamics of the neutral clusters of naphthalene in seeded supersonic molecular beams.

These studies indicate that the ability of the photoexcited neutral clusters to form excimers depends on the cluster size as well as the excess vibrational energy in their locally excited state. Thus, while the vdW dimer forms an excimer even at zero excess energy, the excimer formation in higher clusters requires excess vibrational energies beyond certain threshold values. The threshold energy required for the excimer formation is substantially greater, and the rate of the
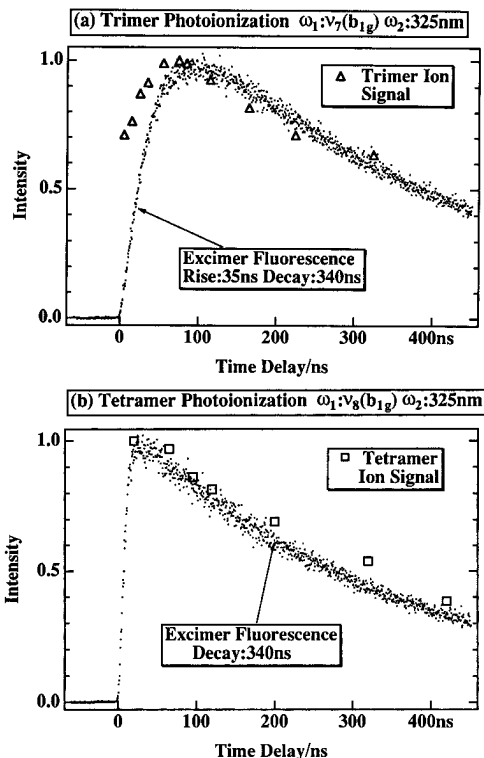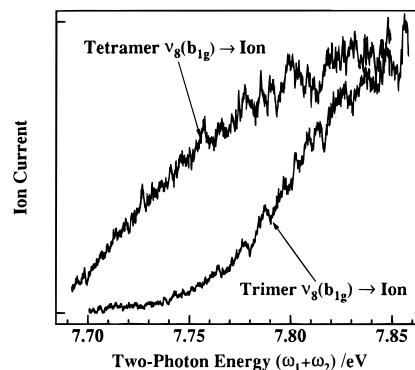
excimer formation considerably smaller, for the trimer than for the tetramer, suggesting that a significantly larger structural rearrangement is involved for the trimer to form an excimer. Both the ionization-loss stimulated Raman spectroscopy and the analyses of the $S_1 \leftarrow S_0$ spectra of the isotopically mixed clusters provide strong evidence that the trimer is composed of nonoverlapping naphthalene molecules arranged in a symmetric cyclic geometry. For the tetramer, the analyses of the S_1 spectra lead to an asymmetric structure, which is characterized by "interior" structural sites composed of a pair of nearly overlapping naphthalene molecules and "exterior" sites consisting of "solvated" naphthalene molecules. The transition from the nonoverlapping trimer structure to the overlapping sandwich-pair conformation of the singlet excimer would be much less efficient than the photo-

isomerization involving a nearly overlapping dimer core in the tetramer.

The studies described here also demonstrate the repulsive, or very weakly bound, character of the ground state and the higher-lying electronic states (created by intervalence excitation) of the excimer. The repulsive character of these states is responsible for the radiative dissociation of the excimer and photofragmentation of the aromatic clusters. Measurements of the photodepletion of the excimer as a function of the wavelength of the photodissociation laser yield the absorption spectra for the excimer clusters. The spectra obtained are independent of the cluster size for $(C_{10}H_8)_n$ with $n = 2-4$, indicating that the excimer clusters are composed of a strongly bound dimer core to which the ground-state naphthalene molecules are weakly bound.

Finally, it has been shown that the aromatic clusters photoionize very efficiently through a new mechanism, involving generation and ionization of the excimer core. The important precursorial role of the excimer in the photoionization has been attributed to the conformational similarity between the excimer and the dimer cation, which provides a large Franck−Condon factor for the ionization.

While the above results based on nanosecond experiments represent significant advances in the understanding of the excited-state dynamics of aromatic clusters, and their dependence on cluster structure, additional experiments are needed for the full elucidation of the structure−reactivity relationship. The most critical of these is the rigorous structural characterization of the clusters which is central to the understanding of the dynamics of the species. Because of the large size of the clusters, frequency-domain rotational spectroscopies (e.g., microwave and rotationally-resolved electronic spectroscopies) are not expected to be practical methods for rigorous structural determination. The only viable experimental method for structure determination is mass-selective rotational coherence spectroscopy (RCS),[43] which monitors the manifestation of quantized rotational motion (rotational recurrence) in the picosecond time domain. Ionization-detected RCS experiments, in combination with ionization-detected stimulated Raman spectroscopy, may provide rigorous structural information for small aromatic clusters. Equally important, it is essential to extend the work described here to dimers and high clusters of other aromatic hydrocarbons to test the generality of the conclusions derived from the studies of naphthalene clusters, and to carry out real-time picosecond studies of excimer formation in naphthalene and other aromatic clusters. We anticipate that these studies will provide detailed insights into the structure−reactivity relationship pertaining to isomerization of photoexcited vdW clusters into excimers and the concurrent transition from weak to strong extremes of exciton interaction as the system evolves from the vdW to excimer geometries. In addition, they will lead to an increased general understanding of the intermolecular aromatic−aromatic interactions and the microscopic details of energy flow and isomerization in geometrically restricted systems.

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