Mass resolved excitation spectroscopy and dispersed emission spectroscopy are employed to study van der Waals (vdW) clusters of jet-cooled fluorene with ammonia, water, and piperidine. For fluorene(H$_2$O)$_1$ and fluorene(NH$_3$)$_1$ clusters, cluster geometries and binding energies can be suggested based on the experimental results and Lennard-Jones (LG) potential (6-12-1) energy calculations. As the number of solvent molecules in the cluster is increased, spectra of the clusters become more complex and broad probably due to the many possible stable configurations for these vdW clusters. Although the pK$_a$ for fluorene in its first excited singlet state (Förster cycle calculations) is quite acidic (~8.6), and solvent molecules can coordinate to the aliphatic hydrogens of the fluorene molecule in at least some cluster configurations, no direct evidence is found for the occurrence of proton transfer in S$_1$ in these systems.

**TABLE I: Atomic Partial Charges for the Fluorene Molecule**

<table>
<thead>
<tr>
<th>atom</th>
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<th>atom</th>
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<tr>
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* See structure I for details. *Geometry data are obtained from ref 21.

**TABLE II: Partial Atomic Charges for Water and Ammonia Molecules**

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<tr>
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<td>H</td>
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</table>

molecular proton-transfer reaction in fluorene complexes will be discussed on the basis of experimental observations and calculations.

**Experimental Procedure**

The supersonic jet apparatus has been described in detail previously. For time-of-flight mass spectroscopy, the doubled output of two pulsed dye lasers, each of which is pumped by the doubled output of a Nd:YAG laser, is used to excite the fluorene molecule and clusters to S$_1$, and then ionize it. The pump laser (S$_1\rightarrow$S$_1$ excitation) is scanned while the ionization laser (ion → S$_1$ excitation) is held at a fixed frequency. The energy of the ionization laser is kept lower than that of the pump laser so as to minimize the fragmentation of the clusters. The two laser beams are made collinear and intersect the expansion gas at right angles. The ions produced are accelerated up the flight tube and detected by a microchannel plate. For the dispersed emission (DE) detection system a 1-m McPherson monochromator with a 1200 g/mm grating is used in the third order to resolve the fluorescence. The emitted light is detected by a photomultiplier tube.

Supersonic expansions are created in a vacuum chamber by using a pulsed nozzle with a 0.7 mm diameter orifice, or a CW.

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The concentration of each solvent is monitored to be 1 or 1.5% in He. Symmetric vibrations of transition, for the origin is about 3-4 atm. Mixtures of helium with NH₃, ND₃, H₂O, D₂O, and piperidine are prepared before they enter the nozzle. The concentration of each solvent is monitored to be 1 or 1.5% in He. The samples are heated to 70 °C in the pulse nozzle and 150 °C in the CW nozzle.

The expansion gas is typically helium and the backing pressure is about 3-4 atm. Mixtures of helium with NH₃, ND₃, H₂O, D₂O, and piperidine are prepared before they enter the nozzle. The concentration of each solvent is monitored to be 1 or 1.5% in He. Fluorene is purchased from Aldrich and used without additional purification.

The stable geometries of various clusters are calculated by using empirical atom-atom potential energy calculations developed by Scheraga et al. The potential function form is described in detail in a previous publication. The partial charges for each molecule are calculated from the MOPAC (v. 5.0) programs. Table I contains the partial charges of the solute molecule (fluorene), and in Table II the partial charges of the solvent molecules are presented. The atomic numbering of the fluorene molecule is shown in structure 1.

Results and Discussion

A. Isolated Fluorene Molecule. The fluorescence excitation and TOFMS of jet-cooled fluorene have been reported previously. The TOFMS of fluorene (m/e = 166) is shown in Figure 1 and is similar to that reported by Leutwyler et al. The origin is identified at 33 778.1 cm⁻¹. The other two intense peaks in the spectrum at +208 and +408 cm⁻¹ from the spectral origin are assigned as the totally symmetric vibrations v₁ and v₂, respectively. The assignments are based on those given in ref 14b.

The DE spectrum of jet-cooled isolated fluorene, excited at the origin (33 778.1 cm⁻¹), is shown in Figure 2. The two vibrational modes ν₁ and ν₂ in the ground state are identified at 210 and 411 cm⁻¹, respectively.

The stable geometries of various clusters are calculated by using empirical atom-atom potential energy calculations developed by Scheraga et al. The potential function form is described in detail in a previous publication. The partial charges for each molecule are calculated from the MOPAC (v. 5.0) programs. Table I contains the partial charges of the solute molecule (fluorene), and in Table II the partial charges of the solvent molecules are presented. The atomic numbering of the fluorene molecule is shown in structure 1.

![Fluorene Clustered with H2O, NH3, and Piperidine](image)

**Figure 1.** Two-color TOFMS of jet-cooled fluorene. The origin, 0g transition, for the S₁ → S₀ transition is at 33 778.1 cm⁻¹. The two features +208 and +408 cm⁻¹ from the origin are assigned to the totally symmetric vibrations v₁ and v₂.

**Figure 2.** Dispersed emission spectrum of jet-cooled fluorene. The excitation energy is 33 778.1 cm⁻¹, corresponding to the origin transition.

**Figure 3.** TOFMS of fluorene(H₂O)₁ clusters as a function of ionization energy, Eᵢₒᵣ. (a) Eᵢₒᵣ = 33 333.0 cm⁻¹. (b) Eᵢₒᵣ = 31 250.0 cm⁻¹. (c) Eᵢₒᵣ = 30 769.2 cm⁻¹.

**Figure 4.** Dispersed emission spectrum of jet-cooled isolated fluorene. In the origin region, the spacing between the origin peak and the next peak in this figure is exactly the same as that in the DE of fluorene(H₂O)₂ (32.4 cm⁻¹, Figure 4c) and that between the origin peak and the second peak is exactly the

B. Fluorene/Water Clusters. Figure 3 shows the TOFMS of fluorene(H₂O)₁ as a function of ionization energy. As ionization energy is decreased, the intensity of two peaks, positioned at 33 834.8 cm⁻¹ (I) and 33 840.0 cm⁻¹ (II), remains strong. Such an intensity dependence on the ionization energy in the fluorene-(H₂O)₁ mass channel demonstrates that many of the features attributed to fluorene(H₂O)₁ are actually due to fragmentation of larger clusters (mostly the (H₂O)₂ cluster), caused by excess vibrational energy in the cluster ion. With the exception of the intense feature at 33 840.0 cm⁻¹ all the coincident features in the observed (H₂O)₁ and (H₂O)₂ cluster spectra are probably due to fragmentation of the fluorene(H₂O)₂ cluster. Although this latter peak is coincident in energy with a feature in the (H₂O)₂ cluster spectrum, its intensity behavior with ionization energy is not indicative of fragmentation of larger clusters.

The DE spectra of the fluorene(H₂O)₂ cluster excited at 33 834.8 cm⁻¹ (I) and 33 840.0 cm⁻¹ (II) and the fluorene(H₂O)₂ cluster excited at 33 821.3 cm⁻¹ (III) are presented in Figure 4. The DE spectrum of fluorene(H₂O)₂ excited at 33 834.8 cm⁻¹ (I) (Figure 4a) evidences two strong peaks in the origin region with a spacing of 51.6 cm⁻¹. Figure 4c presents the DE spectrum of fluorene(H₂O)₂ excited at 33 821.3 cm⁻¹ (III), which shows a vibrational progression with the spacing of 32.4 cm⁻¹. Figure 4b shows three strong peaks in the origin region. The spacing between the origin peak and the next peak in this figure is exactly the same as that in the DE of fluorene(H₂O)₂ (32.4 cm⁻¹, Figure 4c) and that between the origin peak and the second peak is exactly the
Figure 4. Dispersed emission spectra of fluorene\(\left(H_2O\right)_n\), \((n = 1, 2)\) clusters: (a) excitation at \(33 834.3 \text{ cm}^{-1}\), the feature marked I in Figure 3; the transition pumped is assigned to the fluorene\(\left(H_2O\right)_1\) cluster exclusively; (b) excitation at \(33 840.3 \text{ cm}^{-1}\), the feature marked II in Figure 3; the transition pumped is assigned as coincident fluorene\(\left(H_2O\right)_1,\left(H_2O\right)_2\) cluster transitions; (c) excitation at \(33 821.3 \text{ cm}^{-1}\), the feature marked III in Figure 3; the transition pumped is assigned exclusively to the fluorene\(\left(H_2O\right)_1\) cluster.

937 cm\(^{-1}\)

Figure 5. Minimum-energy configuration and binding energy for fluorene\(\left(H_2O\right)_1\), obtained using a LJ potential calculation. The above DE behavior supports the following conclusions: the peak at \(33 834.3 \text{ cm}^{-1}\) (I) is only generated by the fluorene\(\left(H_2O\right)_1\) cluster; the peak at \(33 840.0 \text{ cm}^{-1}\) (II) is generated by both the fluorene\(\left(H_2O\right)_1,\left(H_2O\right)_2\) clusters; the second peak (II) in the TOFMS of fluorene\(\left(H_2O\right)_1\) is due to a vDW vibrational mode since the DE spectra excited at both positions I and II (Figure 3) evidence the same spacing; and only one origin (at \(33 834.8 \text{ cm}^{-1}\)) is observed for fluorene\(\left(H_2O\right)_1\).

Only one stable configuration of fluorene\(\left(H_2O\right)_1\) (binding energy \(= 937 \text{ cm}^{-1}\)) is obtained from LJ potential energy calculations. The structure of this minimum energy cluster is depicted in Figure 5. The oxygen atom of coordinated water is displaced from the center of mass of the fluorene molecule by \(0.66 \text{ Å}\) along the \(X\) axis and is \(3.3 \text{ Å}\) above the fluorene ring. The water hydrogen atoms are \(2.8 \text{ Å}\) above the ring.

The two-color TOFMS of fluorene\(\left(H_2O\right)_2\) clusters and the one-color TOFMS of fluorene\(\left(D_2O\right)_1\) cluster are presented in Figure 6. The TOFMS of fluorene\(\left(D_2O\right)_1\) is taken with a high ionization energy (ca. \(33 800 \text{ cm}^{-1}\)), so that both the mono- and disolvate cluster spectra are present. The fluorene\(\left(H_2O\right)_1\) cluster spectrum (Figure 6b) shows a progression in a low-frequency mode with a spacing on the order of \(\sim 1 \text{ cm}^{-1}\). The spacing of this progression decreases to \(\sim 6 \text{ cm}^{-1}\) upon deuteration of the water molecule (see Table III). This isotope effect clearly demonstrates that the observed progression is associated with motion of the water molecule and the Franck-Condon intensity profile in this spectrum indicates that a large displacement of the water molecule occurs in the excited state relative to the ground state.

The isotope effect (11 cm\(^{-1}\) vs 6 cm\(^{-1}\)) for this vDW progression suggests that the motion of the active vDW mode could be a free rotation of the water molecule about an axis that bisects the H–O–H angle because the moment of inertia for this rotation changes by a factor of 2 upon water deuteration. Nonetheless, the harmonic behavior of this vDW mode contradicts the free-rotor explanation. At present, one can only conclude that the active vDW mode is related to the motion of hydrogen atoms most likely (but not definitely) on the water molecule. The spectra for the mono- and dihydrate fluorene complexes are blue-shifted with respect to the isolated fluorene origin by \(\sim 57\) and \(\sim 36 \text{ cm}^{-1}\), respectively. Cluster features for both the mono- and disolvate complexes are also built on the \(11\) vibration \(208 \text{ cm}^{-1}\) to higher energy. The cluster features built on this vibration are identical with the cluster features built on the origin.

The spectra of fluorene\(\left(H_2O\right)_n\) \((n = 3–5)\) are shown in Figure 7. The cluster spectra become increasingly broad as the number of water molecules increases. The position of the maximum

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**Table III:** Observed vDW Vibrational Energy Levels (cm\(^{-1}\)) for \(S_1\) of Fluorene\(\left(H_2O\right)_2\) and Fluorene\(\left(D_2O\right)_2\)

<table>
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<th>Fluorene-(\left(D_2O\right)_2)</th>
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</table>

\(33 821.3 \text{ cm}^{-1}\), \(33 832.9 \text{ cm}^{-1}\).
Fluorene Clustered with H₂O, NH₃, and Piperidine

Figure 7. TOFMS of fluorene(H₂O)ₙ (n = 3–5). The spectra are all broad with sharp features built on the broad background. The negative peak at 33,982 cm⁻¹ is due to saturation of the microchannel plate from the ν₁ vibration of isolated fluorene.

Figure 8. TOFMS of the fluorene(NH₃)ₙ cluster for both NH₃ and ND₃. The spectra consist of sharp features. In contrast to the results for water clusters, an isotope shift is not observed for the van der Waals modes upon deuteration of ammonia.

Figure 9. Minimum-energy configurations and binding energies for fluorene(NH₃)₁ obtained by using a LJ potential calculation.

Figure 10. TOFMS of fluorene(NH₃)ₙ, n = 2–4 and 6. The origin of the TOFMS of fluorene(NH₃)₁ (taken as the lowest energy doublet) is red-shifted by 51 cm⁻¹ from that of the isolated molecule. The spectrum of the solvate is quite complex consisting of sharp features built on a broad background. As the number of ammonia molecules increases in the cluster, the number of sharp features in the spectrum diminishes and the spectrum becomes broad and featureless.

C. Fluorene/Ammonia Clusters. The TOFMS of fluorene-(NH₃)₁ (m/e = 183) is shown in Figure 8a. The spectrum is quite sharp and well resolved. The origin for the cluster is red-shifted by 4 cm⁻¹ with respect to that of the isolated molecule. Figure 8b depicts the TOFMS of fluorene(ND₃)₁ (m/e = 186). The first few features of the fluorene(NH₃)₁ and fluorene(ND₃)₁ spectra are nearly identical, showing little or no isotopic shift. One can conclude from this observation that at least the first few features correspond to clusters of different configurations.

LJ potential energy calculations support this expectation. Several different minimum energy conformers are obtained from the calculations; for example, one has a geometry in which the...
an ammonia molecule above the fluorene molecule central ring and another has a geometry in which the ammonia molecule coordinates to the aliphatic hydrogens and is displaced from the fluorene ring (see Figure 9).

The TOFMS of fluorene(NH$_3$)$_3$ is shown in Figure 10a. The origin of this cluster appears as a doublet in the spectrum, red-shifted by 51.3 cm$^{-1}$ with respect to the origin of the isolated molecule. The spectrum of the fluorene(NH$_3$)$_3$ clusters becomes increasingly more complex at higher energy with several sharp features built on a broad background. The same pattern, both broad and sharp features, is seen to occur in the spectra region (≈208 cm$^{-1}$ above the origin). The width of this broad peak is on the order of 100 cm$^{-1}$. The cause of the broadening for this relatively small cluster could be thought to be either dynamical processes or congestion from many possible cluster configurations.

The TOFMS fluorene(NH$_3$)$_n$ ($n = 3$–6) are also shown in Figure 10. The spectra are all similar: broad, diffuse, and red-shifted with respect to the isolated molecule. As in the TOFMS of larger fluorene/water clusters, the position of the maximum-intensity peak does not change significantly with fluorene/ammonia cluster size for $n = 2$–6. The position of this maximum intensity peak is ≈33 810 cm$^{-1}$.

DE spectra for fluorene(NH$_3$)$_1$ and fluorene(NH$_3$)$_3$ obtained by excitation at the cluster $0_0^+$ are presented in Figure 11. In both cases ($n = 1$ and 2), the spectra of the clusters are quite similar to that of the bare molecule with exception of the superimposed vDW cluster structure present in the cluster emission.

A careful search for anion emission (generated by proton transfer from larger fluorene(NH$_3$)$_n$ ($n ≥ 3$) clusters was also performed with excitation at 33 810 cm$^{-1}$. No additional broad fluorescence could be observed in the region 370–550 nm. Moreover, dispersed emission spectra, taken with excess vibrational excitation energy in $S_1$ of nearly 1500 cm$^{-1}$, look identical with those presented in Figure 11. These observations suggest that the broadness of the fluorene(NH$_3$)$_3$ TOFMS is most probably caused by a variety of different cluster conformations for a given cluster mass and not proton transfer/fluorene anion generation.

**D. Fluorene/Piperidine Clusters.** The TOFMS of fluorene/piperidine clusters are present in Figure 12. The spectrum of the monosolvate cluster (Figure 12a) is complex, consisting of both broad and sharp features. The first sharp feature observed in the fluorene(piperidine) monosolvate spectrum is assigned to be the origin of the cluster. The cluster origin transition is red-shifted by ≈90 cm$^{-1}$ compared to the bare fluorene molecule origin. The disolvate spectrum is broad with little or no sharp features (Figure 12b).

DE spectra of piperidine complexes do not show direct evidence for an intermolecular proton-transfer reaction: no broad, red-shifted fluorescence is observed from this system.

**E. Proton-Transfer Reaction.** Although a Förster cycle calculation of $pK_a$ for the aliphatic hydrogen atoms of fluorene indicates that they are very acidic ($pK_a = \sim 8.6$) in the excited state and both calculations and experiments suggest that NH$_3$ and H$_2$O solvent molecules can coordinate to the aliphatic hydrogens of the fluorene molecule, none of the spectra of these vDW clusters gives any direct evidence for the occurrence of an intermolecular proton-transfer reaction in $S_1$, i.e., the generation of the fluorenyl anion. Excited-state proton transfer can only be observed if the proton transfer occurs at least on the same time scale as the lifetime of the excited singlet state $S_1$ ($\tau(S_1) < 10$ ns). Förster cycle calculations also indicate a large change in $pK_a$ for naphthalene upon excitation ($pK_a(S_1) = -4.0$, $pK_a(S_1) = 11.7$), however, protonation of naphthalene does not occur upon singlet excitation. Protonation and deprotonation at carbon atoms are apparently quite slow compared to that at oxygen or nitrogen atoms and therefore may not be competitive with deactivation of the singlet excited state. Solution-phase studies of proton transfer between the fluorene molecule and methoxy sodium show the rate of this reaction is $\sim 4 \times 10^4$ M$^{-1}$ s$^{-1}$. Proton transfer occurs in tens of microseconds. A large barrier to proton transfer must therefore exist for this excited-state reaction.

**Conclusions**

Fluorene(H$_2$O)$_n$ and (NH$_3$)$_n$ vDW clusters show sharp mass-resolved excitation spectra. As the number of solvent molecules is increased ($n ≥ 2$) for these clusters, the TOFMS become more complex and broad due to spectral congestion from the many possible stable cluster configurations. In fluorene(H$_2$O)$_n$, immature emission is assigned to the generation of the fluorenyl anion.

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**References**

only one cluster structure is observed with a (calculated) binding energy of 937 cm$^{-1}$. In fluorene(H$_2$O)$_2$, a significant displacement along the vdW coordinates occurs upon $S_1 ightarrow S_0$ excitation. Studies of fluorene(NH$_3$)$_2$ and fluorene(ND$_3$)$_2$ suggest that at least two stable configurations of vdW clusters are possible in fluorene(NH$_3$)$_2$; one has a structure in which ammonia coordinates to the fluorene ring and the other has a structure in which ammonia is coordinates to the aliphatic hydrogens and is displaced from the fluorene ring.

On the basis of both calculations and interpretation of the fluorene/ammonia, water, and piperidine cluster spectra, one expects that the solvent molecules can coordinate to the aliphatic hydrogens of fluorene molecule in at least some cluster configurations. Nonetheless, no evidence (e.g., broad, red-shifted fluorenyl anion emission) which substantiates an excited-state intramolecular proton-transfer reaction can be found in these systems. The absence of any observed anion emission suggests that the proton-transfer reaction at the carbon center occurs at too slow a rate to be observed given the excited-state lifetime of ca. 10 ns.

Acknowledgment. This work was supported by Office of Naval Research and the National Science Foundation.

Registry No. Fluorene, 86-73-7; ammonia, 7664-41-7; water, 7732-18-5; piperidine, 110-89-4.

Vibrational Structure and Temperature Dependence of the Electronic Absorption (1$^1$B$_u$ $\rightarrow$ 1$^1$A$_g$) of all-trans-$\beta$-Carotene

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(Received: June 12, 1989)

The vibrational structure of the absorption spectrum (1$^1$B$_u$ $\rightarrow$ 1$^1$A$_g$) of all-trans-$\beta$-carotene has been analyzed by the second-derivative method and spectral simulation. Estimates of the following quantities have been obtained: the vibrational frequencies and vibrational relaxation rate of the strongly Franck-Condon active modes in the 1$^1$B$_u$ state, parameters representing the displacement of potential minimum along these modes on going from 1$^1$A$_g$ to 1$^1$B$_u$, and the magnitude of modulation of the 0-0 wavenumber due to intermolecular interactions. Against the primitive inference based on the weakening of bond alternation in the 1$^1$B$_u$ state, the frequency of the C=C stretch in the 1$^1$B$_u$ state is higher (though not greatly) than that of the corresponding mode in the 1$^1$A$_g$ state. On the other hand, the frequency of the C=C stretch in the 1$^1$B$_u$ state is higher by about 90 cm$^{-1}$ than that in the 1$^1$A$_g$ state, in agreement with the primitive inference. The vibrational relaxation time in the 1$^1$B$_u$ state is estimated to be of the order of 50 fs. Analysis of the temperature dependence of the absorption spectrum indicates that it is not accompanied by a change in the structure of all-trans-$\beta$-carotene.

Introduction

all-trans-$\beta$-Carotene, a representative polypeptide having a relatively long chain, is an interesting molecule from spectroscopic and biophysical viewpoints. It has been particularly useful in the studies of second-order optical processes. In those studies the Raman excitation profile resonant with the electronic transition 1$^1$B$_u$ $\rightarrow$ 1$^1$A$_g$ has been analyzed. However, it is surprising to find how scarce is the definite knowledge of the excited state 1$^1$B$_u$.

For instance, the vibrational frequencies of relatively large molecules in excited electronic states are most directly determined by the transient Raman method or the method of fluorescence excitation of jet-cooled polyenes. For shorter polyenes, this kind of frequency upshift had long been proposed from the absorption or fluorescence excitation spectra at low temperatures and it was clearly observed in the absorption spectra of jet-cooled hexatriene and octatetraene. The frequencies of both the C=C and C=C stretches are higher in 1$^1$B$_u$ than those in 1$^1$A$_g$. Furthermore, the parameters used in the analysis of the absorption spectrum and the Raman excitation profile of tetrademethyl-$\beta$-carotene have also indicated the higher frequency shifts. It is therefore expected that all-trans-$\beta$-carotene (hereafter simply called $\beta$-carotene) would be in a similar situation.

Vibrational frequencies of relatively large molecules in excited electronic states are most directly determined by the transient Raman method or the method of fluorescence excitation of jet-cooled polyenes. The frequencies of the two modes in 1$^1$B$_u$ are the same as those in the ground state 1$^1$A$_g$. On this assumption, however, one fails to reproduce the absorption spectrum in the visible region, as shown below (see also Figure 2 of ref 13). This implies that the frequencies become higher (at least on the average) on excitation. For shorter polyenes, this kind of frequency upshift had long been proposed from the absorption or fluorescence excitation spectra at low temperatures and it was clearly observed in the absorption spectra of jet-cooled hexatriene and octatetraene. The frequencies of both the C=C and C=C stretches are higher in 1$^1$B$_u$ than those in 1$^1$A$_g$. Furthermore, the parameters used in the analysis of the absorption spectrum and the Raman excitation profile of tetrademethyl-$\beta$-carotene have also indicated the higher frequency shifts. It is therefore expected that all-trans-$\beta$-carotene (hereafter simply called $\beta$-carotene) would be in a similar situation.