Styrene Clusters in a Supersonic Jet: Reactive and Nonreactive Systems

S. Kendler and Y. Haas*

Department of Physical Chemistry and the Farkas Center for Light Induced Processes,
The Hebrew University of Jerusalem, Jerusalem, Israel 91904

Received: August 30, 1996; In Final Form: January 21, 1997[⊗]

Clusters of styrene with several atoms and small molecules were prepared and studied in a supersonic jet by laser-induced fluorescence (LIF) from S_1 and resonance-enhanced multiphoton ionization (REMPI) using S_1 as the resonant intermediate state. The dissociation limit can be determined in many cases (e.g., for argon, CO_2, and ammonia) by recording the excess energy at which fluorescence from the cluster disappears and styrene fluorescence appears. Parent ion signals are easily observable from clusters excited to energies exceeding the dissociation threshold in S_1, as determined by LIF. This indicates a relatively long lifetime of the electronically excited cluster on the ionization time scale. The styrene−trimethylamine system, which is reactive in liquid solution, exhibits a very different fluorescence behavior than all others. Two 1:1 styrene−trimethylamine clusters are observed by fluorescence excitation. One of them exhibits locally excited emission upon absorption near the origin, but at higher excitation energies, the emission is exciplex-type. The other shows exciplex emission at all excitation energies, including the 0−0 band. The data indicate at least two nonradiative processes competing with exciplex formation and with its radiative decay. The relation to solution phase photochemistry is discussed.

I. Introduction

The study of samples of 1:1 clusters, easily generated in supersonic expansions, can in principle elucidate details of bimolecular reactions that are difficult to observe in bulk systems.[1−3] Nonetheless, the number of reactive systems studied that way is very limited, particularly when compared to the large number of nonreactive systems that were studied.[4−6] Most studies dealt with ionic species,[7−10] atom transfer reactions,[1,11−14] and proton transfer.[15−18] Exciplex formation in jets was extensively studied, being easily recognized by the appearance of a charge transfer type fluorescence.[19−24] The initially excited state in these systems is usually a locally excited (LE) state, showing that when energetically possible, the formation of an exciplex competes successfully with other processes in the system, including dissociation into the original constituents. These systems were also subject to several theoretical studies in which the nature of the excited states was elucidated by empirical or semiempirical methods.[25,26]

In the bulk, many chemical transformations are initiated by electron transfer, the second step involving atomic motions, such as bond scission and new bond formation.[27,28] Specifically, picosecond time-resolved absorption spectroscopy was used to show that exciplexes are intermediates in the photoinduced hydrogen transfer reaction between a secondary amine and an aromatic acceptor.[29,30]

In this paper we discuss the properties of a potentially reactive cluster composed of styrene and trimethylamine, two molecules that are known to react in the bulk upon optical excitation.[31−35] It is also known that an emitting exciplex is formed, and the question whether the exciplex participates in the reaction or constitutes a competing channel is still open.[35,36] All evidence points to the participation of some strongly polar species, but whether it is the emitting exciplex is not clear. Electron transfer has been suggested as an initial step for both the reaction and the exciplex formation.[32,37] In principle it is rapid enough to compete, under collision-free conditions, with cluster dissociation, making this system attractive for jet-cooled cluster work.

The dissociation mechanism of a cluster to its original constituents upon optical excitation to the first electronically excited state was studied in great detail.[38−48] In many cases, where aromatic molecules are involved, the reaction was found to be adiabatic, the product (i.e., the bare aromatic molecule) being formed in the first electronically excited state. Two processes need to be considered—intracluster vibrational energy redistribution (IVR) and vibrational predissociation (VP), which may take place sequentially or in parallel.[49−51]

The experimental determination of van der Waals (vdW) bond dissociation *rates* turns out to be difficult. Attempts to estimate them from spectral line broadening[52] or from direct time-resolved measurements of the rise time of the products[51,53] are rare. Near the dissociation threshold the reaction rate may be small, but it appears to grow very rapidly with excess energy, reaching typically $10^{10}-10^{12}$ s^{-1} within a few hundred cm^{-1} of excess energy. Picosecond tunable lasers were used in some favorable cases involving large molecule adducts with rare gas atoms,[51,54,55] but more complicated systems were hardly examined. Since light absorption leads initially to an electronically excited state, a natural clock offers itself—the lifetime of that state, which is determined by radiative and/or some nonradiative processes (internal conversion, intersystem crossing, direct dissociation). For aromatic molecules and carbonyl compounds, the most frequently studied systems, this provides a time window in the $10^{-7}-10^{-9}$ s range, allowing the indirect measurement of vdW bond dissociation rate constants.[45,56]

The vibrational state distribution in the product was measured in some cases and sometimes is nonstatistical,[40,45,56,57] indicating state selectivity. The origin of this selectivity, suggested to be due to momentum conservation[58] in small systems, is not yet adequately accounted for when large components are involved. It was found that the order of magnitude of the dissociation rate constants is reasonably well predicted by a statistical theory, such as RRKM,[40,51] even if the product distribution is nonstatistical (i.e., preferential formation of some vibronic states is observed).

We have chosen styrene and its derivatives as a suitable candidate for the study of possible reactivity in jet-cooled

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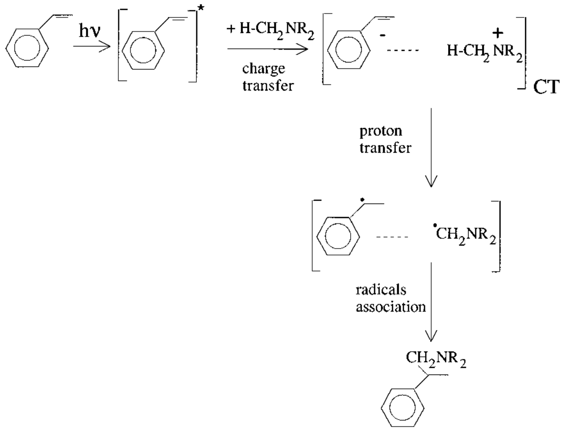
[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S1089-5639(96)02642-4 CCC: $14.00

SCHEME 1



clusters for the following reasons. (1) The spectroscopy of the $S_0 \leftrightarrow S_1$ transition is well understood[59−61] and was amply studied in jet expansions.[62−64] (2) The $S_1 \rightarrow S_0$ fluorescence of styrene is effectively quenched by aliphatic amines with a low ionization potential; exciplex emission often follows in the case of tertiary amines.[37,65,66] The bimolecular photochemistry of styrene (and its derivatives) with aliphatic amines is well studied in solution.[31,66] (3) Intramolecular reactions between the styryl and amine moieties of the same molecule, linked by a covalent $(CH_2)_n$ chain of varying lengths, are more efficient than their corresponding intermolecular analogues.[32,34,36]

The reaction leads in the case of separated reactants to several products, all in poor preparative yield. These include addition compounds as well as hydrogenation of the double bond to form ethyl benzene or 2,3 diphenylbutane.[31,32] These observations were rationalized by a reaction mechanism (Scheme 1) previously suggested for the photochemical addition of amines to stilbene.[67] It was assumed that a key intermediate is a radical pair formed by a hydrogen transfer from the amine to the styrene. Recombination of the two radicals leads to the addition compound, while the hydrogenation products are formed by hydrogen abstraction from a second amine molecule to the styryl radical or by recombination of two styryl radicals. These latter reactions require separation of the two nascent radicals.

Jet cooling offers some distinct advantages for the study of these systems. Solvent-induced quenching processes do not interfere, allowing the study of intermediate species that previously evaded detection. In addition, no energy relaxation is possible in the isolated cluster (in distinction with energy redistribution), making possible the measurement of decay times of excited species at different well-defined energies.

Indeed, preliminary experiments published some time ago[68] reported for the first time fluorescence due to a styrene−secondary amine adduct that could be characterized as due to an exciplex. The emission was weak, as expected, but distinct. Its most significant property was the unusual *long* lifetime—a few *hundred* nanoseconds compared to 74 ns for the triethylamine−styrene jet-cooled exciplex. This result substantiated the notion that exciplexes are involved in styrene−secondary amine photosystems but raised doubts as to their role in the photoinduced reactions. If the exciplex is so long-lived, the failure to observe its emission in the bulk is readily accounted for—collisional quenching would easily make the quantum yield negligible. However, that would also prevent its participation in the reaction, unless the reaction itself is a strong deactivation channel. If it is, why does it not also eliminate emission in the jet? These difficulties could be settled if the formation of the exciplex and the formationof the precursor to the addition reaction are parallel, rather than consecutive, reactions. We tried to check this point further in the present work.

We found it appropriate to examine the photophysical properties of some simpler styrene adducts before taking on a reactive system. We therefore will begin by discussing an atomic partner (argon), then continue with polyatomic nonreactive ones (CO_2, ammonia), and finally end up with a small amine−trimethylamine. A preliminary report of this work appeared in ref 69.

II. Experimental Details

The clusters were prepared in a system described previously in detail.[70] The carrier gas was usually helium, which was mixed with the desired partner (argon, CO_2, etc.) in a cylinder capable of maintaining a constant pressure throughout the experiment. The mixture was saturated with styrene by flowing it over a styrene container held at a constant temperature. The gas was then allowed to expand through a pulsed valve, operated at 10 Hz with an orifice of 0.45 mm, into a vacuum chamber. The base pressure was 10^{-6}−10^{-7} mbarr and with the valve on, about 10^{-5} mbarr. In the fluorescence experiments, the resulting jet was crossed by a tunable, pulsed laser beam about 15 mm downstream.

Fluorescence was monitored at right angles to both molecular and laser beams, either through a filter or after being dispersed by a monochromator (SPEX Model 1702, 0.75 m) with a resolution of up to 10 cm^{-1}. An excimer-pumped dye laser was used (Lambda Physik Model DL3002 pumped by EMGM-SC150) with a pulse width of about 15 ns and a resolution of 0.2 cm^{-1}. The laser was not transform limited and could actually be considered as a burst of a sequence of short (subpicosecond) pulses having an overall envelope of 15 ns. The emission was detected by a photomultiplier (Hamamatsu R1332) digitized (Tektronix 2440) and analyzed on a personal computer. Decay times were obtained either directly or by comparison of the signal with an assumed exponential decay convoluted with the system's response function. This procedure allowed attainment of decay times down to 4−6 ns, depending on the S/N ratio.

REMPI spectra were obtained in a similar apparatus except that the molecular jet was skimmed by a 2 mm skimmer (Beam Dynamics) 40 mm downstream from the nozzle. The molecular beam formed in this way entered a differentially pumped chamber and was directed into the source of a Wiley McLaren time-of-flight mass spectrometer (TOFMS).[71] Ionization was achieved by crossing the slightly focused laser beam at right angles with the molecular beam inside the source. To avoid saturation, laser power densities had to be limited to 10^3−10^4 W/cm^2 for bare styrene vibronic bands. The ions were accelerated in two stages to about 2500 V and then allowed to drift in a field-free zone for about 130 cm. A Daly type detector[72,73] was used to monitor the ion current. With a 15 ns laser pulse, the mass resolution of the instrument ($m/\Delta m$) was about 630. The system was pumped to a background pressure of about 10^{-7} Torr, and when the system was operated at 10 Hz with a 5 atm source pressure, the field-free zone's pressure was about 10^{-6} mbarr. A scheme of the apparatus is shown in Figure 1.

The ionization potential of styrene is 68 267 cm^{-1},[74] while the origin of the $S_0 \rightarrow S_1$ transition is at 34 761 cm^{-1} .[59] Thus, in a REMPI experiment using a single light source, two photons resonant with the origin transition suffice to ionize styrene. This resonance one-color two-photon ionization (R1C2PI) scheme was used in the previous report.[70] The ionization potential of styrene clusters is usually smaller than that of the bare molecule, so absorption of two photons suffices also to ionize all 1:1 clusters studied in this paper. Moreover, as discussed for the styrene−argon cluster in ref 70, the combined energy of the

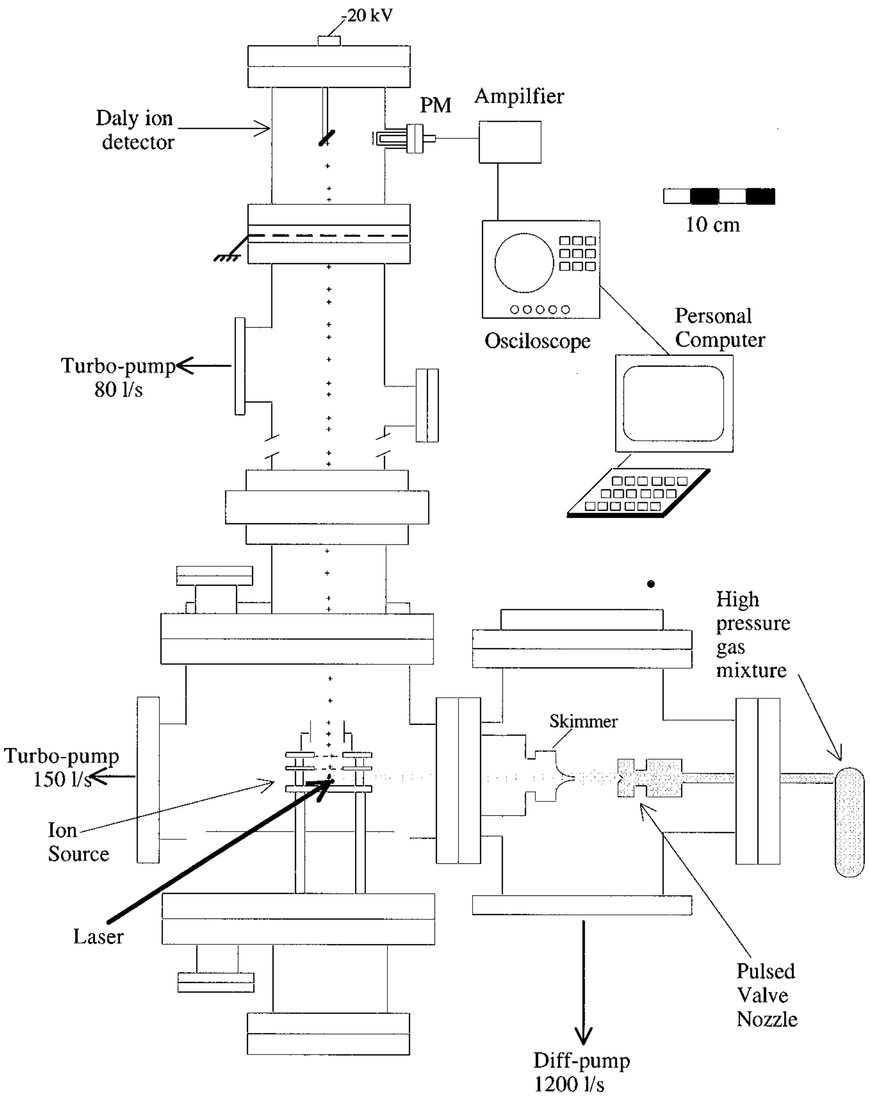


Figure 1. Scheme of the REMPI apparatus.

two photons resonant with the 0−0 transition of the cluster is sufficient not only to ionize but also to dissociate it (the dissociation energy of the styrene−argon cluster ion is reported to be only slightly higher than that of the neutral cluster (by 116 cm^{-1}[74]). Therefore, in the R1C2PI experiments reported below, the parent ion signal was always accompanied by a daughter ion signal. The ratio of the two signals was fairly constant as long as the photon's energy was below the dissociation threshold of the cluster in S_1.

The internal clock in the REMPI experiments is not the fluorescence lifetime but rather the ionization rate, which in turn depends on the photon flux density. Since the temporal behavior of the dye laser within the 15 ns pulse used is irregular, a second photon may be absorbed by the excited cluster after an indeterminate time interval that may vary from less than a picosecond to a few nanoseconds. As long as the excess energy of a cluster beyond the dissociation limit is small (a few hundred cm^{-1}), the dissociation rate is of the same order as the ionization one. The parent ion signal is thus expected to depend on the laser power used, and the dissociation energy of the cluster in S_1 determined by the disappearance of the parent ion signal tends to be too high. The presence of a sharp feature in the mass-resolved R1C2PI spectrum[75] is therefore not a sufficient condition for establishing a low limit for the cluster dissociation energy. Rather, it provides an upper limit. A resonance two-color two-photon ionization (R2C2PI) scheme is often used to alleviate this problem.

It was found experimentally that the ionization signal saturated very easily, and typically, laser fluxes of $(2-30) \times 10^5$ W/cm^2 were used to avoid saturation.

III. Results

IIIa. Determination of van der Waals Bond Dissociation Energies of Styrene 1:1 Adducts. *Styrene−Argon.* In a preliminary report on this system,[70] the dissociation energies of the 1:1 cluster in S_0 and S_1 were estimated using REMPI to be 385 and 416 cm^{-1}, respectively, from the dependence of the parent-to-daughter ion signal ratio ($[styrene-Ar]^+/[styrene]^+$) on excess energy. These estimates, which were found to agree with previous determinations[76] and with calculations based on atom−atom pairwise potentials, are in fact upper limits, since an R1C2PI method was used. By use of LIF, it was found that the decay time of the emission from the styrene−Ar cluster upon excitation at the 0−0 band (shifted 31 cm^{-1} to the red from the 0−0 of the bare molecule) is 12 ± 1 ns, i.e., considerably shorter than that of styrene itself (21 ns). When the excitation energy was increased to beyond 288 cm^{-1} (the $40^1 42^1$ band[60]), the decay time was found to be 21 ± 1 ns. A plausible cause for this change is that the cluster dissociates adiabatically to yield electronically excited styrene, indicating a lower dissociation energy. This was checked by recording the dispersed emission obtained upon excitation of the 1:1 styrene−Ar cluster to different excitation energies. Figure 2 shows the emission spectra obtained from styrene and the 1:1 styrene−Ar cluster

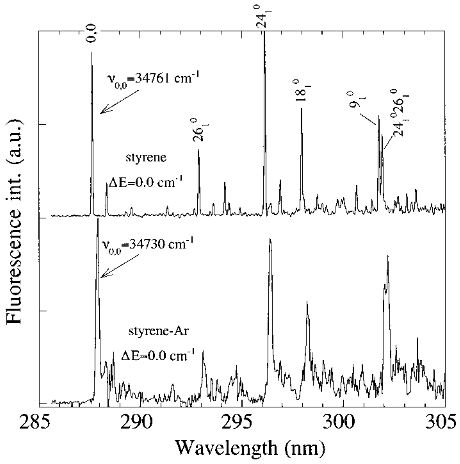


Figure 2. Emission spectra of styrene (upper panel) and the styrene–argon 1:1 cluster (lower panel) obtained upon excitation to the 0–0 bands.

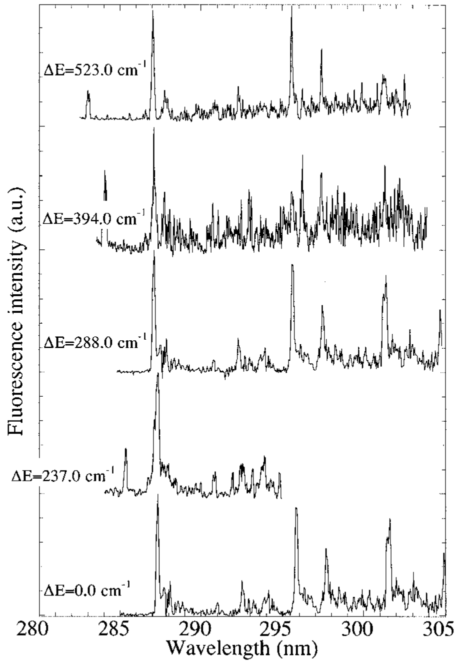


Figure 3. Emission spectra of the 1:1 styrene–argon cluster obtained upon excitation to various vibronic levels.

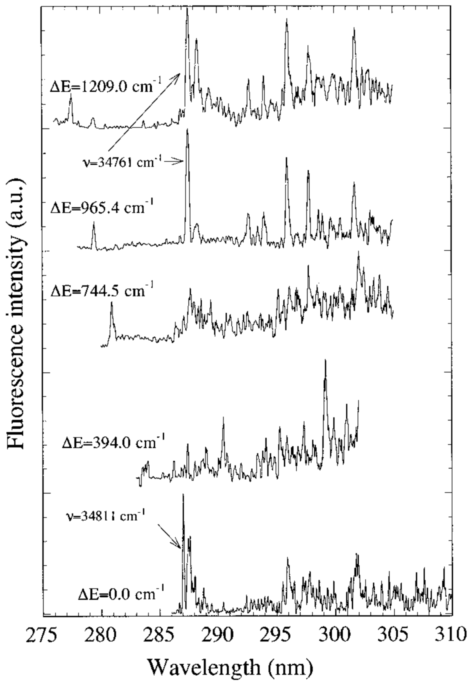


Figure 4. Emission spectra of the 1:1 styrene–CO_2 cluster obtained upon excitation to various vibronic levels.

excited at their respective 0,0 bands. It is seen that the cluster spectrum reproduces the spectrum of the bare molecule except for a red shift of the intramolecular bands and the addition of bands due to vdW vibrations. Figure 3 shows the emission spectra of the cluster after excitation to some higher vibrational levels. It is found that up to an excess energy of 237 cm^{-1}, the emission is due to the intact cluster. Beyond 288 cm^{-1}, the emission is essentially that of bare styrene. Thus, the dissociation energy of the cluster on the S_1 surface ($D_0(S_1)$) is between 237 and 288 cm^{-1}. (The lower boundary is valid provided that dissociation is faster than the fluorescence lifetime). Using the observed red shift of the 0–0 band, the dissociation energy of the cluster on the ground-state surface ($D_0(S_0)$) is between 206 and 257 cm^{-1}. We note in passing that this revised value leads also to a revision of the dissociation energy of the styrene–argon cluster ion, which is 116 cm^{-1} higher than that of the neutral.[74] The proposed value of D_0(ion) is between 322 and 373 cm^{-1} rather than 512 cm^{-1}.

Styrene–CO_2. The 0–0 band of this cluster is *blue* shifted by 51 cm^{-1} with respect to that of the bare molecule. The LIF and REMPI excitation spectra reveal only one 1:1 isomer. Figure 4 shows some emission spectra recorded after excitation to different excess energies. Inspection of the spectra shows that they are due to the bound cluster for all excitation energies below ΔE = 746 cm^{-1} ($25^{1\,60}$). The emission spectra become progressively more congested as ΔE increases apparently because of IVR. Excitation to the $35^1 39^1$ level (ΔE = 965 cm^{-1}) leads to a much less congested emission spectrum, which is almost identical with the emission of the bare molecule, when excited to the 0–0 band. At still higher energy ΔE = 1208 cm^{-1} (the 18^1 level) the spectrum begins to be congested again. These results indicate a dissociation energy ($D_0(S_1)$) between 746 and 965 cm^{-1} on the S_1 surface and between 797 and 1016 cm^{-1} on the ground-state surface.

Styrene–Ammonia. In the LIF spectrum, the 0–0 band, *blue* shifted by 52 cm^{-1}, is by far the most intense one. Its intensity relative to the higher vibronic bands is much larger than that observed in the bare molecule. A weaker band found 30 cm^{-1} to the blue of the bare molecule is assigned to a different 1:1 cluster. R1C2PI excitation spectrum shows a prominent 0–0 band, along with considerable nonresonant signal. At higher frequencies, the ionization excitation spectrum is found to consist of doublets separated by 22 cm^{-1}, in which the intensity of the higher frequency component progressively increases. The two systems are tentatively assigned to 1:1 styrene ammonia clusters based on dilution experiments and on the vibrational spacings that correlate with the two lowest frequency bands observed in the LIF excitation spectrum. Dispersed fluorescence spectra were obtained for the sequence based on the +52 cm^{-1} band. Some are shown in Figure 5. The low intensity of the emission dictated the use of rather low resolution in these experiments (~30 cm^{-1}). It is seen that the spectra are highly congested for excess energies in the range ΔE = 193–523 cm^{-1}, while excitation at ΔE = 746 cm^{-1} leads to a spectrum essentially indistinguishable from that of styrene excited at the 0–0 band (Figure 5b). It is concluded that the dissociation energy on the excited surface $D_0(S_1)$ is between 523 and 746 cm^{-1}, while on the ground state the limits are 52 cm^{-1} larger.

Styrene–Trimethylamine. LIF could not be used to determine the vdW bond dissociation energy for this system. As shown in the next paragraph, the emission characteristics are completely different from those of the former pairs, and no emission from

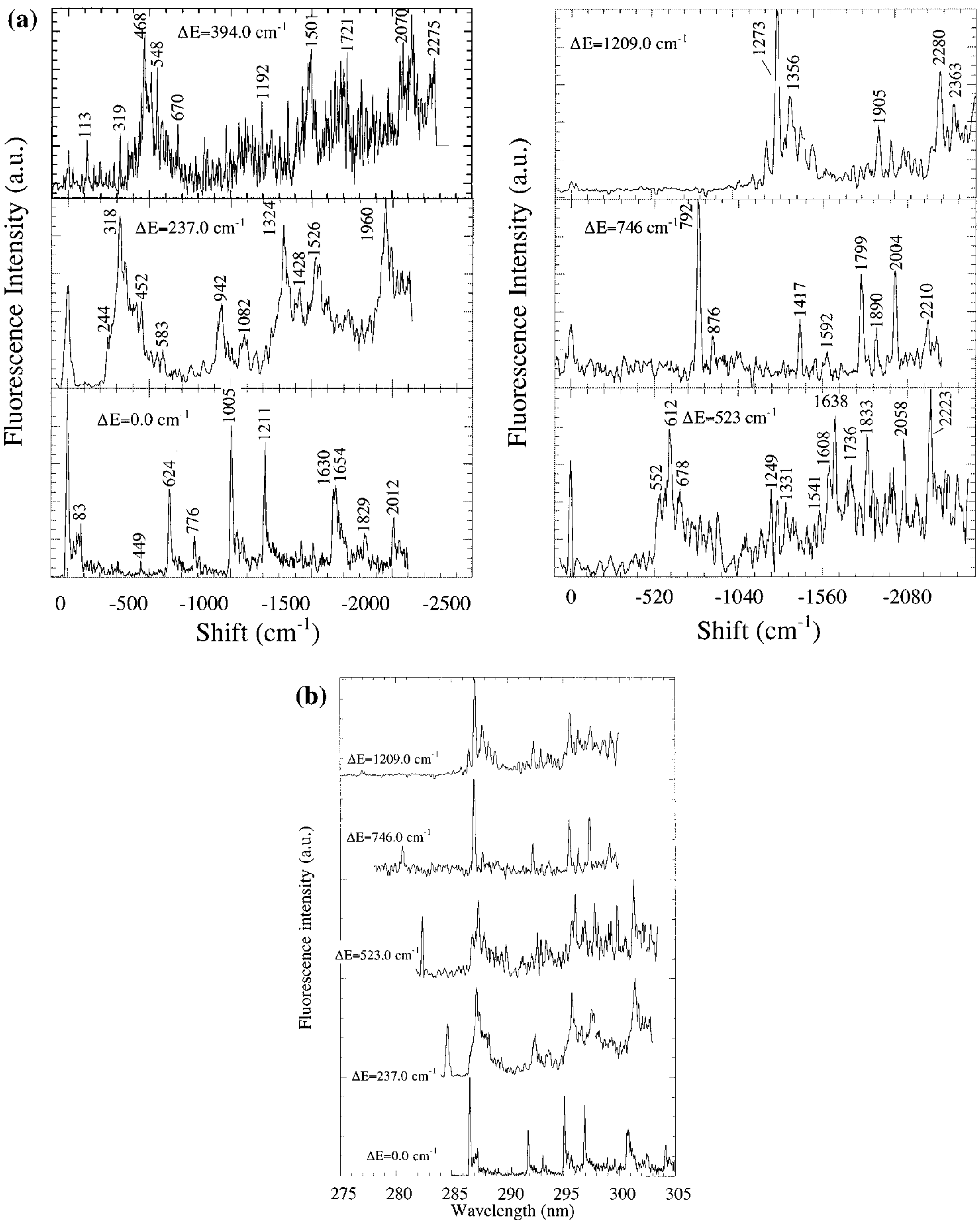


Figure 5. (a) Emission spectra of 1:1 styrene−ammonia clusters obtained upon excitation to various vibronic levels, plotted on an energy scale, the origin being the excitation frequency. Note the large change in spectral congestion between $\Delta E = 523$ and 746 cm^{-1}. (b) Same data plotted on a wavelength scale, showing that the spectrum obtained upon excitation of the $\Delta E = 746$ cm^{-1} is identical with that of bare styrene excited at the 0−0 band.

bare styrene could be observed upon excitation of the cluster to any energy on the S_1 surface. In this case, R2C2PI REMPI was used to determine the dissociation energy. A Nd:YAG-pumped dye laser (Quanta-Ray's PDL-1 pumped by DCR-1A) was tuned to the 0−0 band of the S_0−S_1 styrene−TMA (a n type band; see Figure 7 below) transition (shifted 24 cm^{-1} to the red of the styrene origin). This laser beam and that of the excimer-pumped dye laser were allowed to cross the molecular beam in the source of the TOF mass spectrometer and were synchronized so that the Nd:YAG-pumped dye laser was fired to maximize the two-color signal (zero delay). The excimer laser-pumped dye laser was scanned across the 340−370 nm wavelength range. Figure 6 shows the ion current as a function of the combined energy of the two photons. The sharp onset of the parent ion signal ($M/Z = 163$) at 61 900 cm^{-1} is assigned to the appearance potential of that ion. The appearance energy of the daughter ion ($M/Z = 59$, due to singly ionized TMA) at 64 150 cm^{-1} provides an estimate for the dissociation energy of the cluster ion:

$$[\text{styrene}-\text{TMA}]^+ \rightarrow \text{styrene} + \text{TMA}^+ \quad D_0(\text{ion}) = 2250\ \text{cm}^{-1}$$

From this value, and the ionization energy of TMA (7.82 eV[77]), the cluster dissociation energy on the ground-state surface, $D_0(S_0)$, can be estimated from the relation

$$D_0(S_0) = \text{IP(styrene}-\text{TMA)} + D_0(\text{ion}) - \text{IP(TMA)}$$

to be 1080 ± 200 cm^{-1}, the large error bar being primarily due to the error reported for IP(TMA). The dissociation energy on

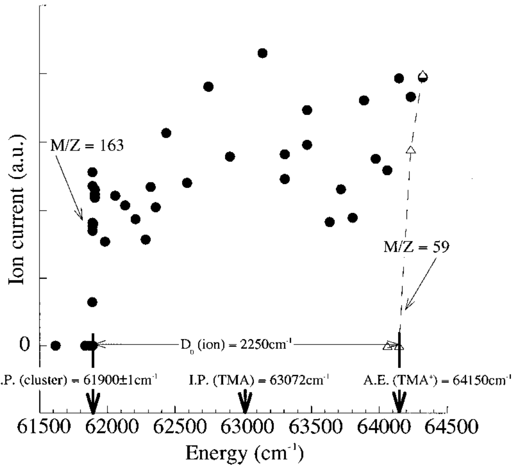


Figure 6. Ion currents of the parent ($M/Z = 163$) and daughter ($M/Z = 59$) ions as a function of the combined two-photon energy in the R2C2PI spectrum of the styrene−TMA system. Experimental conditions are 10 Torr TMA, 7 atm of helium, and styrene held at 0 °C.

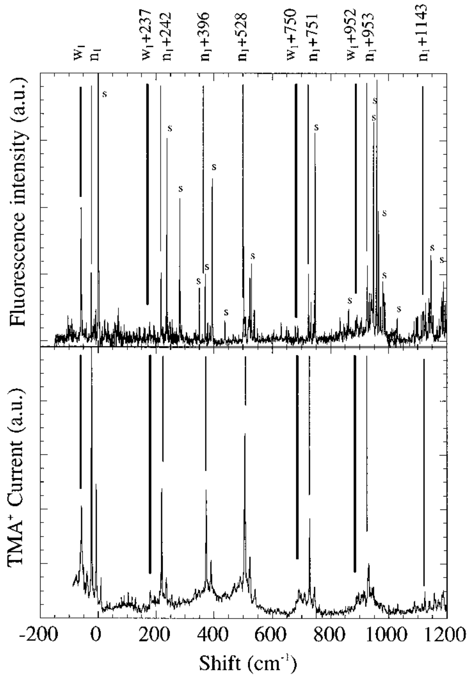


Figure 7. Fluorescence and R1C2PI excitation spectra of the styrene−TMA system. Experimental conditions as in Figure 6. The bands denoted by "S" are due to bare styrene. Some bare styrene bands are also seen in the REMPI spectrum. This is due to the difficulty in completely suppressing the very intense nonresonant signal due to the molecular styrene. (The resonant one is typically 2−3 orders of magnitude stronger than the cluster signal.)

TABLE 1: Some Characteristics of Styrene Clusters[a]

partner	origin[b]	$D_0(S_0)$	$D_0(S_1)$	lifetime[c] (ns)
argon	−31	$205 < E < 251$	$236 < E < 282$	11 ± 1
CO_2	+51	$797 < E < 1016$	$746 < E < 965$	22 ± 1
ammonia	+52	$575 < E < 798$	$523 < E < 746$	24 ± 1
TMA ("n" type[d])	−24	1080 ± 200	1104 ± 200	23 ± 1

[a] All energies in cm^{-1}. [b] Wavenumber shift of origin with respect to bare styrene. [c] At the origin band. [d] See section IIIb.

the S_1 surface, $D_0(S_1)$, is obtained from the red shift of the 0−0 band to be 1104 cm^{-1}.

Table 1 summarizes the vdW bond dissociation energies measured in this work, and some other properties of the clusters.

Inspection of Figures 3−5 reveals a considerable spectral congestion in the dispersed emission even at relatively low excess energies. The dispersed emission of styrene itself[78] and even of the larger *trans-β*-methylstyrene[61] shows broadening assigned to IVR only at higher excess energies (>800 cm^{-1}). The increased congestion of the cluster emission spectra can be accounted for assuming that in the cluster, energy transfer from in-plane vibrations to out-of-plane ones is promoted (for a discussion of the vibrational energy levels of styrene in S_0 and in S_1, please see ref 60). This efficient cluster-induced IVR is expected to hold also for TMA adducts, whose dispersed emission spectra are very different. It will be assumed that the IVR rates in styrene−polyatomic clusters are very rapid compared to fluorescence rates, i.e., with rate constant larger than 10^9 s^{-1}.

IIIb. Spectroscopy and Photophysics of the Styrene−TMA System. The excitation spectrum of the undispersed fluorescence of the styrene−TMA adduct was found to consist of two band series separated by 34 cm^{-1} from each other. Their origins were found to be *red* shifted with respect to that of bare styrene by 25 and 59 cm^{-1}, respectively. Dilution experiments indicated that both are due to 1:1 clusters, a proposition supported by REMPI data. The widths of the bands were somewhat different, 1.1 cm^{-1} for the series beginning with the −25 cm^{-1} band and 1.4 cm^{-1} for the other. They will be referred to as the "n" and "w" series, respectively. The fluorescence and R1C2PI excitation spectra are reproduced in Figure 7. It is seen that the relative intensities of the individual bands in the two series vary considerably across the spectrum and are different for the LIF and REMPI spectra. As shown in the preliminary report,[69] excitation of the "n" type origin band led to a locally excited type fluorescence, as observed for all previously discussed styrene clusters. However, excitation to higher energy members of this series or to "w" type bands at any frequency (including the 0−0 band) led to a different emission spectrum whose characteristics resemble exciplex emission as observed in solution and in other jet-cooled systems.[24] The spectrum was considerably red shifted with respect to the excitation frequency, peaking at 385 nm, broad, and with almost no vibrational structure. At higher excitation energies, the fluorescence intensity was found to be strongly reduced, resulting in poor *S*/*N* ratio. The slits of the monochromator had to be opened, reducing the spectral resolution and also increasing the background due to remnants of the ever-present room temperature styrene molecules. Figure 8 shows the spectra obtained upon excitation to the 29_0^1 and 28_0^1"n" type cluster band (at $\Delta E = 242$ and 396 cm^{-1}, respectively). It is seen that at $\Delta E = 242$ cm^{-1} absorption leads to an emission spectrum of a mixed character—both the locally excited (LE) and the exciplex type bands are present. At higher excitation energies LE type emission is absent, the spectra becoming essentially of pure exciplex character.

Both the decay times and the intensity of the emission decreased as the excitation energy increased, but not to the same extent. To compensate for differences in absorption cross sections of different vibronic bands, the intensity of each cluster band was normalized to that of the corresponding band in the LIF excitation spectrum of the bare molecule. This normalization procedure assumes that the relative Franck−Condon factors of the 1:1 adduct are essentially the same as those of the bare molecule. Figure 9 displays the data. Over the excess energy range 240−970 cm^{-1}, the decay time decreased by a factor of 2 in a rather smooth fashion, while the variation of the emission intensity was found to fluctuate as the energy increased. Nonetheless, for a given ΔE, the intensity decreased at least by a factor of 2 more than the decay times and often by an order of magnitude for both "n" and "w" type bands. Beyond $\Delta E = 1000$ cm^{-1}, both decay times and intensities became too small

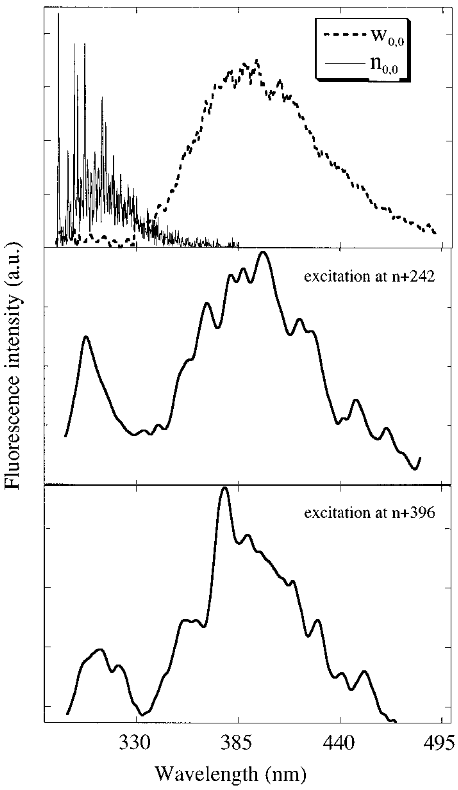


Figure 8. Emission spectra of the styrene−TMA system after excitation to the following: (top) the origin of the "n" and "w" type series; (middle) the 29_0^1 band of the "n" series ($\Delta E = 242$ cm^{-1}); (bottom) the 28_0^1 band of the "n" series ($\Delta E = 396$ cm^{-1}). The locally excited fluorescence is still apparent at $\Delta E = 242$ cm^{-1} and is much weaker at $\Delta E = 396$ cm^{-1}. The signal seen in this spectrum is due mainly to residual background warm styrene.

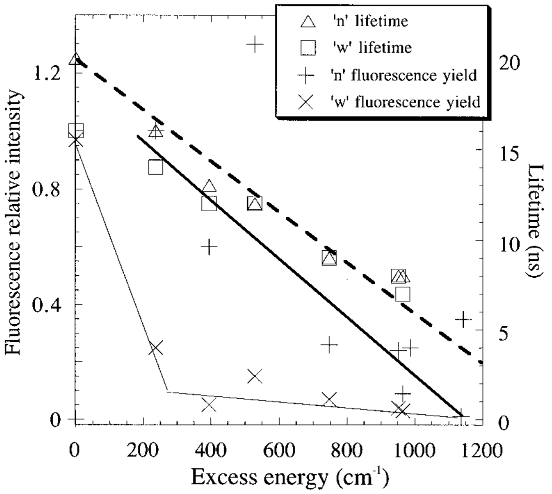


Figure 9. Normalized relative fluorescence intensity (see text for normalization procedure) and the decay times of the fluorescence of the styrene−TMA clusters of the "n" and "w" type series as a function of excess energy.

to measure. It is noted that in contrast with the other clusters discussed in this work, *no emission from bare styrene* could be detected beyond the measured dissociation limit of the "n" type band.

TABLE 2: Predicted Binding Energies of Some Hydrocarbons with Argon[a,b]

molecule	D_e(GS) calcd	D_0(GS) calcd	D_0(GS) exptl	$D_e(1^1B_{2u})$ calcd	$D_e(1^1B_{2u})$ exptl
methane	115		116[c]		
benzene	257	206[d]	340−358[e]	235	300, 375[c]
styrene	287	240	206−257[f]	271	237−288[f]
indene	316	274		307	
naphthalene	315	275		309	
phenanthrene	353	313		350	
anthracene	350	310			
pyrene	373	333			
perylene	409	369	<274[g]		
tetracene	372	332			

	S_0		$S_1(B_{2u})$	
	ϵ (cm^{-1})	σ (Å)	ϵ (cm^{-1})	σ (Å)
C−Ar	28.7	3.48	32.4	3.41
H−Ar	26.4	3.208	26.4	3.208

[a] Based on the Lennard-Jones parameters derived in this work. [b] All energies in cm^{-1}. The zero-point energy of the M−Ar adduct is assumed to be 40 cm^{-1} for all aromatic hydrocarbons unless otherwise stated. GS, ground state; calcd, calculated; exptl, experimental. [c] Reference 84 (spherically averaged potential). [d] $\text{ZPE}_{\text{benzene}} = 51$ cm^{-1},[99] $\text{ZPE}_{\text{styrene}} = 47$ cm^{-1}, $\text{ZPE}_{\text{indene}} = 42$ cm^{-1} [work from this laboratory]. [e] References 47, 100, and 101. [f] This work. [g] Reference 83.

IV. Discussion

IVa. Cluster Dissociation Energies. The use of fluorescence excitation to measure the dissociation of styrene clusters leads, in the case of argon, to lower values than previously estimated on the basis of REMPI measurements. Competition between predissociation and photoionization was observed previously (for instance, in the pyrimidine−argon case[41]). The combination of dispersed fluorescence measurements and changes in the observed decay times between $\Delta E = 237$ and 282 cm^{-1} leaves little doubt that these are the lower and upper limits of D_0 on the S_1 surface. Atom−atom pairwise empirical potentials of the Lennard-Jones form

$$V_{ij} = 4\epsilon_{ij}[(\sigma_{ij}/R)^{12} - (\sigma_{ij}/R)^{6}]$$

have been used in the literature to provide an estimate for the interaction between aromatic molecules and rare gas atoms.[79,80] These potentials require only two parameters, the energy parameter (ϵ_{ij}) and a geometric parameter (σ_{ij}), and are easily transferable between different systems. The present results necessitate a revision of the parameters used for styrene in previous publications.[70] In Table 2 we show that the experimental values may be reproduced by changing only the energy parameter of a previously used potential for the C−Ar pair. Parameters are proposed for both the ground and S_1 states. Assuming that the ground-state parameters are valid also for other hydrocarbon molecules, an estimate of their binding energies with argon may be made, as also shown in the table. It is seen that the predicted bond dissociation energies are much smaller than proposed earlier,[81,82] though still a bit higher than the experimentally determined one for tetracene.[83] The good agreement with the experimental value (isotropic part;[84] see also ref 85) for methane may be fortuitous or may indicate that the pairwise potential approximation represents an essential part of the real potential.

No emission from bare styrene was observed upon excitation up to $\Delta E = 1200$ cm^{-1}, i.e., beyond the dissociation limit determined by R2C2PI, for the "n" type styrene−TMA cluster. Unlike the other clusters dealt with in this work, dissociation to the molecular components does not take place on the S_1 surface. In this energy range rapid transitions between different potential surfaces take place in this system, providing, in principle, an opportunity to observe other photochemical processes. The role of the charge transfer state will be discussed in the next subsection.

Charge exchange between the partners appears to be rapid on the REMPI time scale. Initial excitation in the resonance experiments is of the styrene moiety, but formation of TMA$^+$

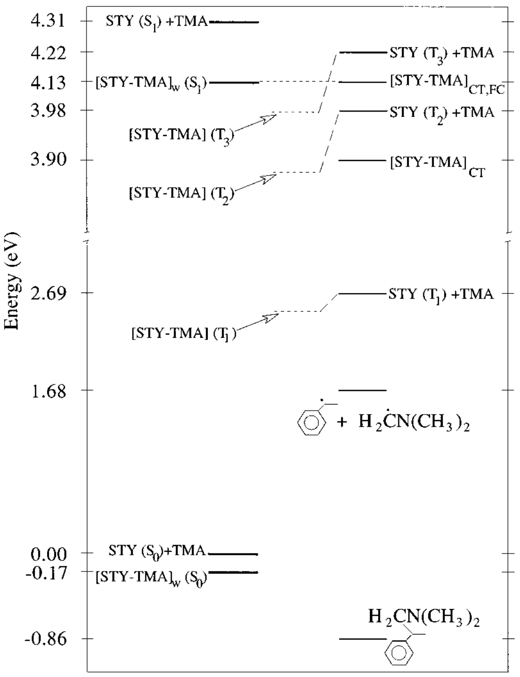


Figure 10. Energies of species relevant to the styrene−TMA system. See text for sources of experimental data and for the method of calculation for the computed ones. Note the different vertical scales used in the lower and upper parts of the plot.

is found to dominate the mass spectrum. For all other clusters the main daughter ion was styrene$^+$, following the energetically preferred path. This is also the case for the styrene−TMA cluster, since the ionization energy of styrene (8.44 eV) is higher than that of TMA (7.82 eV). In contrast with the other systems, here we have direct evidence for intracluster charge transfer.

IVb. Photophysics of the Styrene−Trimethylamine System. The energetics of this system for the energy interval relevant to this work is summarized schematically in Figure 10. The data shown are based partially on experiment (energies of S$_1$,[59] T$_1$, and T$_2$ of styrene[86]) and partially on calculations done in this work. AM1 was used for the radical pair energy, while the CT state energy calculation is detailed in ref 69. Three species are calculated to be energetically stable on the ground-state surface: the van der Waals adduct, the addition product, and the radical pair. Several triplet states of styrene are expected corresponding to $\pi-\pi^*$ transitions. One was observed by direct absorption[87] with an origin at about 462 nm (21 645 cm^{-1}). This value of the vertical triplet energy was confirmed by energy transfer studies[88,89] and by low-energy electron energy loss spectroscopy.[86] The vertical Franck−Condon state is expected to undergo rapid relaxation to the perpendicular form with an estimated minimum at 51 kcal/mole (17 850 cm^{-1}).[88] Triplet states are very short-lived because of efficient intersystem crossing to S$_0$ (∼23 ns[88]), and they are believed to be unreactive as far as amine addition is concerned.[32] Intersystem crossing to the triplet manifold is therefore expected to lead to a reduced photochemical yield. Its quantum yield in solution has been estimated to be 0.4.[90] The observed decay time of S$_1$ styrene in the jet is 21 ns (0−0 band[62,64]), while the calculated radiative one is about 60 ns.[91] It is apparent that a major nonradiative process responsible for the shorter observed decay time is intersystem crossing. Analogous processes are expected to be important also in styrene clusters. We have seen that argon adducts are characterized by shorter decay times than bare styrene, while for the other adducts, a somewhat *longer* decay time was found. The heavy argon atom is likely to increase the ISC rate, as also proposed for other molecular adducts with argon.[40]

The minimum of the singlet charge transfer state, responsible for the observed exciplex emission, was calculated[69] to be at 3.9 eV (31 453 cm^{-1}) with respect to the separated components. The energy of the radical pair was calculated by the AM1 semiempirical method as implemented in the Gaussian package[92] to be 38.8 kcal/mol (13 550 cm^{-1}). Several mechanisms for its formation may be proposed: two-step processes in which charge is separated in the initially excited van der Waals pair; initial electron transfer followed by a proton transfer or by a single step direct hydrogen transfer. The single step process is expected to have a higher activation barrier, being probably prohibitively large under the conditions of this work. The radical pair itself is a plausible intermediate en route to the addition compound.[32−34]

Two types of styrene−TMA adducts were observed by LIF and REMPI. The “n” species appears much more conspicuously in the REMPI spectrum than the “w” one. The first vibronic band shows distinct locally excited fluorescence, while at excitation energies higher than 350 cm^{-1} only exciplex type emission is observed. This indicates a barrier to the formation of the charge transfer state. At $\Delta E = 242$ cm^{-1}, both types are found. It may be concluded that at this excess energy, the transition to the charge transfer state takes place at the same rate as the combined radiative and nonradiative deactivation of the excited cluster, i.e., about 10^{-8} s. In contrast, the “w” type adduct is converted to the charge transfer state without a barrier. This accounts for the absence of locally excited emission and the prompt appearance of the exciplex emission, as well as for the low efficiency of two-photon ionization. Charge transfer states are inefficient stepping stones in resonance-enhanced ionization, whereas locally excited ones promote it probably because of more favorable Franck−Condon factors. The larger ion signal obtained from the “n” type species is, according to this view, due to clusters ionizing before the transition to the exciplex state takes place.

The geometries of the species giving rise to the “n” and “w” type series were calculated using pairwise potentials as described before.[69] (The geometries of styrene[93] and of TMA[94] were assumed to be unchanged by cluster formation.) Their forms are reproduced in Figure 11. It is seen that in one structure, the overlap between the nonbonding orbital of the amine and the π electron structure of styrene is much larger than for the other. The first is assigned to the “w” isomer and the other to the “n” one. It was proposed that the latter must rotate by 180° in order for the electron to transfer, and the barrier for this rotation was calculated to be about 100 cm^{-1}.[69] It is noted that a recent calculation on the similar naphthalene−triethylamine system[26] arrived at similar conclusions—the exciplex state may be reached by a barrier-free process from one ground-state conformer, whereas excitation of a different conformer yields initially a state that can transform to the exciplex only by surmounting a barrier. These results are in qualitative agreement with the experimental data of ref 95.

Furthermore, an ab initio calculation of two structures of the benzene−TMA 1:1 cluster[96] gives very similar binding energies to those calculated here for the styrene−TMA cluster. In that work, two structures were calculated: one similar to that assigned herewith to the “n” species, the other in which the C_3 axis of TMA coincides with the C_2 axis of benzene (a “hydrogen bond” form). The latter was not identified as a minimum by us using the simulated annealing method. Since the ab initio calculation of a structure similar to that assigned by us to the “w” species was not reported, it is not clear whether it might have a lower energy than the hydrogen-bonded form.

The relative fluorescence *intensity* of the exciplex emission, originating either from the “n” or the “w” isomers, was found

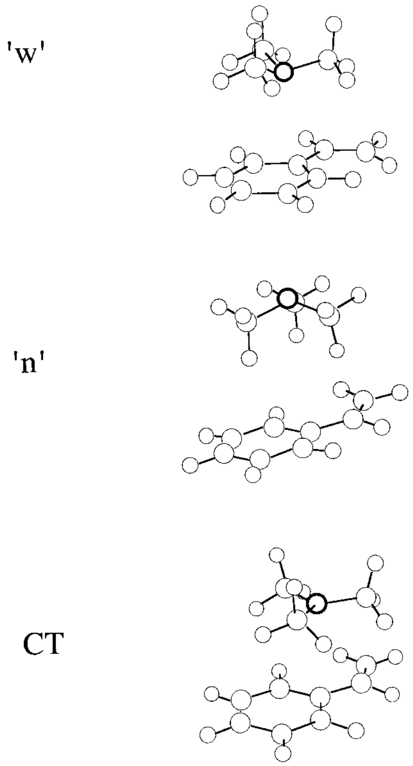
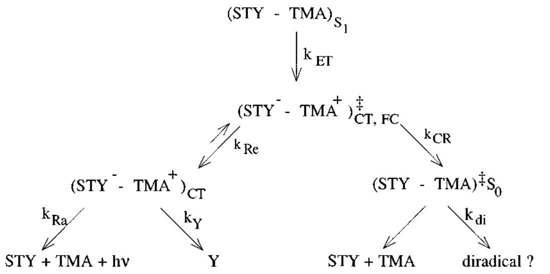


Figure 11. Proposed geometries of the "n" and "w" isomers of the styrene−TMA 1:1 adduct and of the charge transfer (CT) exciplex. The separation between the amine nitrogen and the center of mass of styrene is 4.18, 3.15, and 3.00 Å for the "n", "w", and CT, respectively.

SCHEME 2



to decrease much more rapidly than the fluorescence *lifetime* as the excitation energy was increased. A kinetic scheme consistent with this result is shown in Scheme 2. The main assumption is that the nascent species formed upon electron transfer (the Franck−Condon state, ((STY$^-$−TMA$^+$)$^{\ddagger}_{FC}$ in the scheme) is practically nonfluorescent because efficient nonradiative processes compete with light emission. One is skeletal reorganization to form the fluorescent exciplex, (STY$^-$−TMA$^+$)$_{CT}$, whose observed decay rate is determined by the radiative rate constant, k_R and a nonradiative one, k_Y. The other process is crossing to the ground-state surface at the conical intersection, leading to charge recombination (with a rate constant k_{CR}) whose product is a vibrationally highly excited adduct (STY−TMA)‡. This latter species, in turn, can either decay to the separated ground-state components or form a diradical pair by proton transfer. Reaction follows only from the diradical pair.

IVc. Photochemical Consequences. In the jet, IVR is rapid, but the total energy is preserved. Therefore, the charge transfer exciplex state is formed with about 2000 cm^{-1} of vibrational energy upon excitation at the origin band of the "w" or "n" series. The much steeper dependence of the exciplex emission intensity on the excitation energy (as compared to the decay rate) must be due to radiationless processes competing with the formation of the emitting exciplex. Once formed, only intersystem crossing (assuming internal conversion from this state to be negligible) competes with emission, accounting for the moderate energy dependence of the decay times. The transition from the LE to the exciplex FC state becomes progressively faster at higher energies, leading to the disappearance of the LE fluorescence. Assuming that a quantum yield of 1% is easily observable, this sets a lower limit of 10^{10} s^{-1} on the rate of the exciplex FC state formation at excess energies beyond ∼400 cm^{-1}. An upper limit may also be established, since the observed bandwidth of the vibronic transitions, as observed by REMPI or LIF, is less than 1.5 cm^{-1}. This sets an upper limit to the homogeneous width due to any dissipation process of 3×10^{11} s^{-1}. Dissociation of the cluster to styrene and TMA (on the S$_1$ surface, below $\Delta E = 1200$ cm^{-1}) is apparently too slow to compete with the intracluster reorganization. Return from the exciplex state to the locally excited one is statistically unlikely, making the disappearance of the initially formed LE state irreversible. The absence of fluorescence from bare styrene upon excitation of the styrene−TMA adduct to energies beyond (though close to) the dissociation limit found in the R2C2PI experiments is therefore accounted for.

We can now attempt to correlate these results with the situation in the bulk, particularly in liquid solution. In contrast with the jet environment, vibrational deactivation to the bottom of the potential well is very efficient in the bulk, making any vibrationally excited species very short-lived. This would make the processes following the crossing at the conical intersection practically irreversible. The nascent exciplex, formed in the other route, is also quickly vibrationally equilibrated. However, in contrast with the situation in the jet, thermal reactivation may take place, so the exciplex may contribute to the formation of final products by this indirect manner. The detection of long-lived ($\tau = 400-800$ ns) exciplex emission from styrene−secondary amines in the jet[68] is significant in this context. The absence of exciplex emission from these systems in the bulk is easily accounted for by the presence of competing deactivation processes. The rapid and efficient reaction in the bulk in these systems may involve a mechanism similar to that shown in Scheme 2, requiring that charge transfer and proton transfer are rapid enough to compete with vibrational relaxation. The conflicting data concerning the quenching of the reaction and exciplex fluorescence in the case of linked styrylamines[34,36] can also be considered in view of the proposed mechanism. Both the emitting (vibrationally relaxed) exciplex and the precursor of the reaction are formed from the nascent CT state. The nonlinear Stern−Volmer plots reported by Aoyama et al.[36] may be due to interaction of biacetyl not only with the relaxed exciplex but also with its precursor. The linear plot for the reaction is due to the quenching of the precursor only.

Figure 12 shows a schematic energy level diagram that displays graphically the energy levels of the system and the major radiative and nonradiative processes. Absorption is initially into a locally excited (LE) state, since the excitation spectra exhibit the characteristic vibronic structure of solvated styrene. The "FC state" is the nascent CT state formed upon transition from the LE state. It undergoes reorganization at a fixed energy along two different routes. One leads to the geometry of the emitting CT state, which has a local minimum. In solution, vibrational deactivation would populate the bottom of the well, but in the jet, the system remains at the original total energy. The exciplex type emission observed in the jet has a spectrum similar to the solution phase spectrum, since in most of the other degrees of freedom (not shown in the figure) the two are essentially indistinguishable. A nonradiative process (most likely, intersystem crossing) competes with the radiative deactivation of this state. Another route starting from the FC

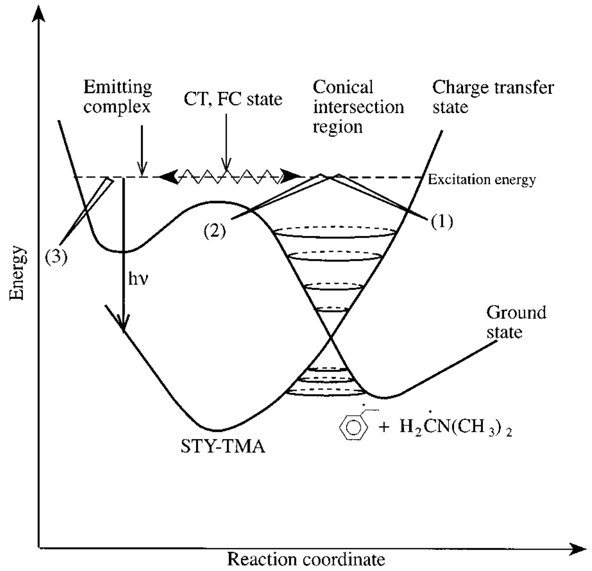


Figure 12. Simplified energy level diagram showing the energetics and main processes taking place after the charge transfer state was formed from the initially excited state. It is assumed that the electron is transferred at a rate faster than nuclear rearrangement so that the CTFC (charge transfer Franck−Condon) state is formed at the geometry of the LE state. It then proceeds to move along two possible reaction coordinates: one leading to the emitting exciplex, whose minimum energy configuration is at a smaller intercomponent separation than that of the LE state; another leading to a conical intersection with the ground state. From the conical intersection, the system may move on to form the radical pair en route to the final reaction products (process 1) or separate back to styrene and TMA (process 2). Process 3 is a nonradiative loss mechanism from the emitting exciplex, such as intersystem crossing.

state along a proton transfer reaction coordinate leads to a conical intersection with the ground-state potential surface (shown schematically in the figure). The system can cross over to the ground state, forming a radical pair, a process that is irreversible in solution because of rapid vibrational relaxation. In the jet, it is also likely to be practically irreversible, since the density of states on the ground-state surface is much higher than on the excited-state surface. This scheme accounts for the qualitative features of the jet results, such as the different decreasing rates of the decay times of the exciplex emission and its intensity.[97]

It is also in line with the available information on solution-phase kinetics. A nonlinear Stern−Volmer plot is usually associated with quenching of two electronic states. In the case at hand, the excited state is a precursor of both the exciplex and the radical pair *but along two different routes.* That would lead to a complicated Stern−Volmer behavior if the quenching rates depend on the different conformations of the CT state *en route* to the conical intersection even in solution. Evidence for kinetically distinguishable ion pairs (designated as “loose ion pairs”, “contact ion pairs”, etc.[30,98]) is abundant in solution chemistry of exciplexes. The solvent-free system, however, provides a good starting point for the analysis of solvent-induced effects.

V. Summary

The dissociation energies of several styrene clusters with inert partners (argon, CO_2, and ammonia) and a potentially reactive one (TMA) were measured in the first electronically excited state by REMPI and dispersed LIF. The ground-state dissociation energies are derived from these data using the measured shift of the 0−0 band in the cluster with respect to that of the bare molecule. It is found that one-color REMPI results tend to overestimate the dissociation energies. In the case of the styrene−argon system, new parameters for the Lennard-Jones atom−atom pairwise potentials are proposed.

The photophysics of the styrene−TMA 1:1 cluster was studied in detail. Two separate optical absorption systems were observed by both LIF and REMPI. They are assigned to two isomeric forms of the adduct, both capable of forming a charge transfer exciplex upon excitation to the locally excited state. In one, the conversion is instantaneous on the time scale of the experiment ($\sim 10^{-9}$ s) so that only exciplex emission is observed upon excitation at any frequency. For the other, a barrier to the conversion is found and assigned to a 180° rotation of the TMA molecule with respect to styrene. Analysis of the intensity and decay time variations as the internal energy of the cluster is increased leads to the conclusion that the exciplex is not an intermediate leading to the reaction products. Rather, it is formed in a competing channel. Extrapolation of these results to the liquid solution phase must be done with care, since solvation is expected to affect the energetics of the system. Nevertheless, the species revealed in these experiments are expected to be relevant to the solution chemistry of the system and may help in understanding some as yet unresolved issues. The emerging viewpoint resulting from this work is summarized in Scheme 2 and Figure 12.

Acknowledgment. The Farkas Center for Light Induced Processes is supported by the Minerva Gesellschaft, mbH, Munich. This work was supported in part by the Binational German-Israel James Franck program for Laser-Matter Interaction. We thank Dr. Wolfgang Drescher and Eyal Zingher for their experimental help and Dr. Shmuel Zilberg for his help with the calculations and many inspiring discussions.

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(97) The scheme shown in Figure 12 assumes that the electron transfer process from the LE state to the CT, FC state occurs without *any* nuclear reorganization, as would be the case in optical excitation (hence, the use of the Franck−Condon terminology). This sequence of events is not essential for the main conclusions of this work, namely, that the routes leading to the emitting exciplex and to the reaction are different. A partial charge transfer accompanied by concurrent nuclear motion along two separate channels is also consistent with the data.

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