The photophysics of a photoreactive system in a supersonic jet. Styrene–trimethylamine

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Abstract

The photophysics of styrene clusters with trimethylamine were studied in a supersonic jet using laser induced fluorescence and multiphoton ionization. Two 1:1 adducts were identified, both of which are found to emit exciplex-type emission. The emission intensity strongly depends on the internal energy of the adducts: in one species it is most intense near the origin, while in the other, locally excited fluorescence is observed near the origin, and the exciplex-type appears only upon vibrational excitation. A model proposed for the system's energetics is found to be in good agreement with the experimental data.

1. Introduction

The involvement of exciplexes in bimolecular photochemical transformation has been conjectured in many systems, particularly when electron transfer is believed to be the rate determining step [1,2]. A well studied system of this type is the styrene–tertiary amine one, for which addition products as well as exciplex emission were reported upon irradiation in the ultraviolet. A considerable amount of circumstantial evidence points to the participation of exciplexes in the addition reaction. It includes substitution effects [3–5], solvent effects [3] and work with covalently linked molecules [6–8]. The main evidence comes from the similarity between the quench-

ing rate constants of the photoreaction and that of the exciplex emission [7]. However, some quenching measurements are not in agreement with this hypothesis [9] and no direct link between exciplex formation and photochemical reactivity has yet been established. An added complexity in the solution phase is the possibility of reversible exciplex formation, as deduced from the analysis of non-linear Stern–Volmer plots [10].

To our knowledge, all previous studies of these systems were carried out in liquid solution. It has been shown that the nature of the solvent, in particular its polarity, are of prime importance in determining the rate of the reaction and the distribution of the products. It also strongly affects the exciplex emission, presumably by stabilizing ionic structures. The detailed understanding of the interaction between the two constituents could benefit from a study of the

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isolated pair by itself first, and gradually adding solvent molecules, thereby allowing the separation of solvent-induced effects from intrinsic properties of the interaction.

The technique of seeded supersonic jets allows the facile synthesis and study of weakly bound Van der Waals adducts between neutral molecules in the gas phase. The case of potentially reactive pairs is particularly interesting, since it provides, in principle, an opportunity to study in depth effects such as the importance of cluster geometry, size and composition. In the cold jet, it is possible to measure high resolution spectra, and derive from them structural information on the ground and excited state adducts [11,12]. A recent example of a system of photochemical interest is the study of the cyanonaphthalene–triethylamine adduct [13]. Some time ago we have reported a preliminary study of the fluorescence of some styrene–amine adducts in a supersonic jet [14]. It was found that several different adducts can be formed, some of which exhibit exciplex emission, and some not. Of particular interest was the fact that exciplex emission (albeit quite weak) was observed for the first time from adducts of styrene with secondary amines. The existence of such exciplexes was inferred from kinetic studies in solution [5] but emission from these species was never observed.

In this paper we report the LIF and REMPI spectra of styrene adducts with the smallest tertiary amine trimethylamine (TMA), which is a reactive partner. Two different ground state adducts are identified. Upon excitation, both of them exhibit exciplex emission, one from the origin band onwards, the other when the excitation energy exceeds a small barrier. The fluorescence intensity of both types decrease as the excess energy (ΔE) is increased up to $\Delta E \approx 1200$ cm^{-1}, at which it disappears. The overall intensity decrease over this range is much steeper than for the fluorescence decay time, indicating the existence of a process competing with the *formation* of the exciplex. In contrast with other styrene adducts, no emission from excited bare styrene is observed when the adduct is excited to energies exceeding the dissociation energy of the Van der Waals bound excited state. A very efficient radiationless process is setting in, which may be related to the photochemical activity observed in liquid solutions.

2. Experimental

The LIF and REMPI setups were described in detail in previous communications [14,15]. Briefly, styrene and trimethylamine vapors were mixed with a few atmospheres of helium and expanded through a pulsed valve into a high vacuum chamber. In the LIF experiments, the jet was intersected by a pulsed tunable dye laser 30–50 nozzle diameters downstream. Fluorescence was observed at right angles to both laser and molecular beams, either through a monochromator (3/4 m SPEX model 1702) or through a suitable filter. Emission intensity was monitored by a photomultiplier (Hamamatsu R1332), and the signal digitized (Tektronix 2440), normalized to the laser pulse intensity and processed by a microcomputer. Lifetimes were determined after deconvoluting the signal from the system's response [1]. The shortest decay time measurable with this apparatus is 4–6 ns. In the REMPI experiments, the jet was skimmed by a 2 mm skimmer, and the same laser was used to ionize the resulting molecular beam 25 cm downstream, in the source of a home made Wiley McLaren type time of flight mass spectrometer (TOFMS). The ions were detected by a Daly detector and the signal processed by an on-line microcomputer.

An excimer laser pumped dye laser (Lambda Physik 3002 pumped by a EMGMSC150 excimer laser) was used as the main light source for both experiments. In some two color experiments a Nd:YAG pumped dye laser was also used.

3. Results

Fig. 1 shows some spectra recorded upon expansion of a mixture of styrene and TMA seeded in a helium jet. The top panel shows the total fluorescence observed through a 7-60 Corning filter. Under these conditions the spectrum is seen to be dominated by intense bare styrene bands; In addition, two types of cluster bands could be discerned, principally

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by their widths: the ones marked by 'w' in Fig. 1a had were found to be somewhat broader than those marked by 'n' (Typically 1.4 vs. 1.1 cm^{-1}). Both band-types appeared in the excitation spectrum as a series of vibronic bands shifted by an almost constant value from the bare styrene bands. The first bands in each series (w$_1$ and n$_1$, respectively), are
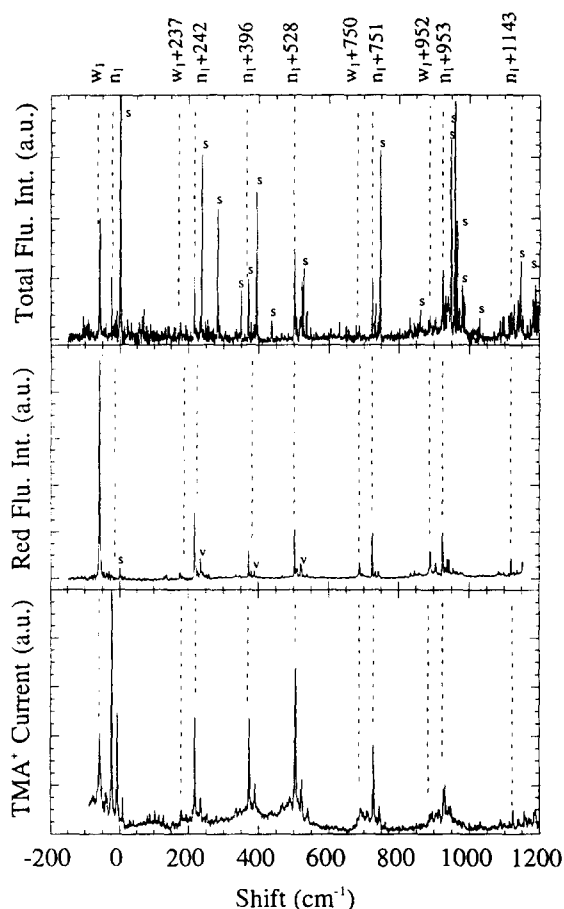

Fig. 1. The LIF and REMPI excitation spectra of the styrene–TMA system. A mixture of TMA (7 Torr) seeded in a helium (4 atm.) was passed over styrene held at 23°C (~ 5 Torr) and expanded through a 0.35 mm pulsed nozzle. See text for further experimental details. Top panel: Total fluorescence observed through a Corning 7-60 cutoff filter (transmitting between 290 and 430 nm). 'S' denotes bare styrene bands. Middle panel: Emission observed through a monochromator set to 385 nm, bandwidth 3 nm. Some weak bands due to intermolecular van der Waals modes are marked with the letter v (only a few were selected for this demonstration, a more complete list is available on request). Bottom panel: Mass selected ion REMPI excitation spectrum, monitoring the TMA$^+$ ion peak at $m/z = 59$.

found to be red shifted with respect to the 0,0 styrene band (located at 34761 cm^{-1} [16]) by 59 and 25 cm^{-1}, respectively. Dilution experiments were found to be consistent with both n- and w-type species being 1:1 adducts.

The first band in the w series (w$_1$) is about twice as intense than the n$_1$ band; The other w-type ones, being much weaker than the n-type ones, were harder to separate from the background. Observing the spectrum through a monochromator set at 385 nm eliminated almost completely the bare molecule's bands, and reduced the background considerably, facilitating the observation of w-type bands (middle panel in Fig. 1). The absence of the first band in the n-series (n$_1$) under these conditions is noted. In addition to intramolecular styrene bands shifted by cluster formation, bands due to intermolecular vibrations of the Van der Waals bonds were observed for both n- and w-type series. Some of them are denoted by 'v' in the spectrum. These bands are usually much weaker than the intramolecular ones, and will not be further considered in this work.

The bottom panel shows the excitation spectrum of the same system, when the REMPI signal (monitored as the TMA$^+$ ion current) was recorded. In this case the n-type bands are seen to dominate the spectrum, the only strong w-type band being the w$_1$ one. The broad background signal is probably due to clusters larger than the 1:1 ones. Table 1 lists the observed frequencies and decay times of the adduct bands (with proposed assignments). No fluorescence could be observed upon excitation to $\Delta E \approx 1200$ cm^{-1}; it is noted that in many other styrene adducts, fluorescence from excited styrene could be easily observed upon excitation to bands beyond the dissociation limit of the cluster. A prominent band, expected at $\Delta E \approx 1209$ cm^{-1} (due to the 18^1_0 band) [17,18], is found in the case of the styrene–ammonia and styrene–argon adducts [19], whose dissociation energies are much smaller; the fluorescence originates from the bare styrene molecule produced upon dissociation of the Van der Waals bond. In the same vein, no ion formation was detected beyond the same excess energy, again in contrast with other styrene adducts [15].

Dispersed emission spectra obtained upon excitation of the w$_1$ and n$_1$ bands are shown in Fig. 2. Despite the low resolution used in these spectra, it is
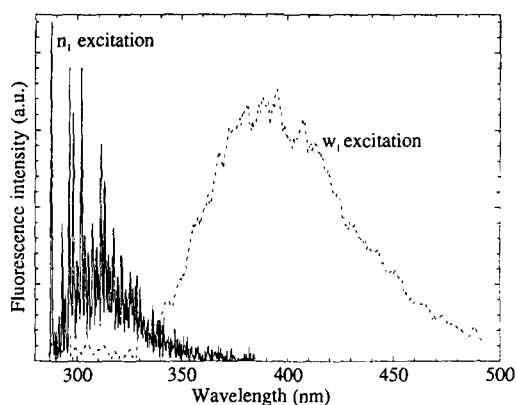
Fig. 2. The emission spectra observed upon exciting the styrene–TMA adducts at the bands indicated in Fig. 1 by w_1 (dashed line) and n_1 (solid line).

evident that excitation of the n_1 band leads exclusively to typical Van der Waals type, locally excited (LE) emission, while excitation of the w_1 one results in a qualitatively different emission whose origin is

strongly red shifted with respect to the excitation frequency. This emission, centered around 385 nm, is very similar to that observed for exciplexes in non polar solvents [8], and is tentatively assigned to an exciplex. The absence of the n_1 band from the spectrum shown in Fig. 1b is readily accounted for —only a negligible part of its emission intensity occurs around 385 nm, excitation the $n_1 + 242$ cm^{-1} band led to mixed emission spectra— showing both LE and exciplex type bands. Excitation of higher vibronic transitions of n series gave pure CT-like emission.

As seen from Table 1, the decay times of the n- and w-type bands are similar for any given vibronic band, and monotonously decrease. The shortest decay times (obtained for the 23_0^1 band, $(\Delta E \approx 966$ cm$^{-1})$ are a factor of two smaller than those measured for the 29_0^1 band, $(\Delta E \approx 236$ cm$^{-1})$. The intensity of each vibronic cluster band was normalized to that of the corresponding bare styrene; The normalized intensity of the $n_1 + 242$ cm^{-1} excitation

Table 1
Observed vibronic transitions in the excitation spectrum of styrene–TMA clusters [a]

Transition	Assignment	Ion current [b]	Relative fluorescence intensity [d]		Decay time (ns) [e]
			measured [b]	normalized [c]	
w_1	0–0	0.70	10.87	0.97	16
n_1		2.17	0.0	0.0	20
$w_1 + 237$	29_0^1	0.15	0.25	0.25	14
$n_1 + 242$		1.0	1.0	1.0	16
$w_1 + 395$	28_0^1	–	0.05 <	0.05 <	12
$n_1 + 396$		0.87	0.65	0.6	13
$w_1 + 527$	27_0^1	–	0.05	0.15	12
$n_1 + 528$		1.37	0.89	2.73	12
$w_1 + 750$	25_0^1	0.11	0.18	0.07	9
$n_1 + 751$		0.67	0.68	0.26	9
$w_1 + 952$	24_0^1	0.07	0.11	0.04	8
$n_1 + 953$		0.15	0.62	0.24	8
$w_1 + 967$	23_0^1	–	0.07	0.03	7
$n_1 + 966$		–	0.24[f]	0.09[f]	8
$n_1 + 970$	$35_0^1 39_0^1$	–			–
$n_1 + 987$	$25_0^1 29_0^1$?	–	0.05	0.25	–
$n_1 + 1136$	$25_0^1 28_0^1$	–	> 0.05	0.01	–
$n_1 + 1143$	20_0^1	–	0.25	0.35	–

[a] Only molecular transitions are listed, bands involving the van der Waals modes are omitted.
[b] Intensities are relative to $n_1 + 29_0^1$ band in the n-series.
[c] Intensities are normalized to the corresponding bare styrene vibronic intensity, see text for details.
[d] Measured at 385 nm.
[e] $\pm$ 1 ns.
[f] Intensity could not be measured due to incidental overlap with a Van der Waals band.
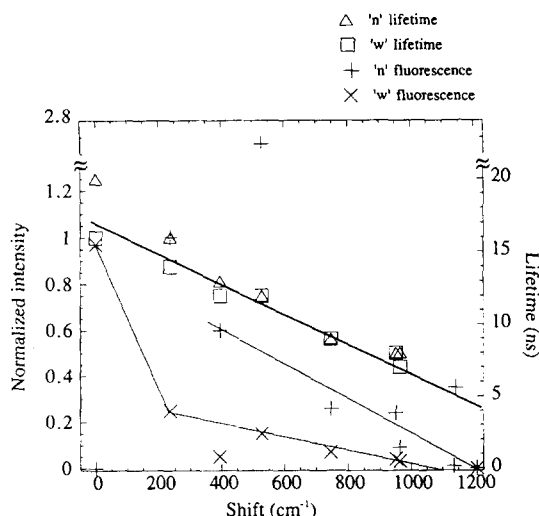
Fig. 3. The measured fluorescence decay times and normalized fluorescence intensities (monitored at 385 nm) of styrene–TMA clusters as a function of excess energy relative to the 0,0 band of the n and w series. The fluorescence intensities are normalized to that of the $n_1 + 29_0^1$ band (see text for details). Lines are drawn through the experimental points as a visual aid.

band (29_0^1 transition) obtained in this manner was arbitrarily set to unity and that of all other bands scaled to it; the fourth column of Table 1 lists the resulting relative intensities of the observable cluster bands. Both n- and w-type normalized fluorescence intensities undergo a steeper decrease over the $\Delta E =$ 0–1200 cm^{-1} excess energy range than the decay times (Fig. 3). Intensities decrease by a factor of four to ten over this interval, while decay times are reduced only by a factor of two over this range. The large uncertainty in the intensity reduction factor is due to the very small experimental intensity of the cluster bands observed beyond $\Delta E = 900$ cm^{-1}.

The detailed changes of the n- and w-type emission band intensities over this range differ considerably. Fluorescence intensities are determined by the absorption cross section and by competitive non radiative processes. Normalization to the bare molecule's excitation band intensity was performed in order to cancel out differences in the absorption intensities of different vibronic bands, assuming cluster formation has a negligible effect on the vibronic bands' transition intensities. Experiments on other styrene clusters [19] have shown that this as-

sumption holds for most bands, but breaks down completely for the 27_0^1 band (at $\Delta E \approx 527$ cm^{-1}), found to exhibit a strong intensity enhancement upon clustering with inert species. A similar enhancement is seen in Fig. 3 for the n-type band, but not for the w-type one; the strong normalized intensity of the n-type 20_0^1 band at $\Delta E = 1143$ cm^{-1} may be due to a similar effect; it was not noticed in previous studies on other adducts, possibly due to the much larger spectral congestion in this range. The overall intensity changes along the n-type series fluctuate strongly with excess energies. The decrease in the w-type emission intensities as the excess energy is very steep at low excess energies and much more gradual than that of the n-type series at higher energies.

Binding energies of the n-type clusters in the S_0, S_1 and in the ion were measured by two color REMPI using a method previously described [15]. One laser was tuned to the frequency of the n_1 band, and the parent ion signal ($m/z = 163$ amu) was monitored as a function of the frequency of the second laser. The latter was tuned across an energy range from below the ionization energy of the cluster, to the lowest appearance energy of the daughter ion ($m/z = 59$ amu, corresponding to TMA$^+$). The ionization potential of the cluster was found to be 61900 ± 1 cm^{-1}, and the appearance potential of the daughter ion, 64150 ± 40 cm^{-1}. The difference, 2250 ± 40 cm^{-1}, is the cluster ion's binding energy (D(ion)) for the reaction (STY is an abbreviation for styrene):
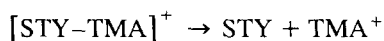
$$[STY-TMA]^+ \rightarrow STY + TMA^+$$

The binding energy for the neutral cluster in the ground state ($D(S_0)$) is obtained from the relation

$$D(S_0) = IP(STY-TMA) - IP(TMA) + D(ion)$$

where IP(x) is the ionization potential of species x. IP(TMA) is 63072 ± 161 cm^{-1} [20], leading to $D(S_0) = 1078 \pm 200$ cm^{-1}, the main contribution to the error coming from the uncertainty in IP(TMA). The dissociation energy of the cluster in S_1 can be obtained from the spectral shift of the n_1 band with respect to the styrene origin (-25 cm^{-1}), leading to 1103 ± 200 cm^{-1}. The corresponding measurement for the w-type cluster could not be made, as the ion signal was too small.

4. Computer simulations of the clusters' properties

The energies of different cluster structures were calculated by the method described in Ref. [15], using a pair-wise atom atom potential of the form Eq. (1):

$$
V_{A-B} = \sum_i^a \sum_j^b \left(C_6^{ij} \times \frac{\rho_{ij}^6}{2 \times r_{ij}^{12}} - \frac{C_6^{ij}}{r_{ij}^6} + m \times \frac{q_i q_j}{r_{ij}} \right) \tag{1}
$$

V_{A-B} is the potential between molecule A and molecule B in cm^{-1}, C_6^{ij} is the attractive term between atom i and atom j in $Å^6 cm^{-1}$. ρ_{ij} is $1/2(\rho_i + \rho_j)$ were ρ_i is the Van der Waals radius of atom i in Å, m is a constant ($m = 116110\ cm^{-1}$ · $Å/e^2$), q_i is the partial charge on atom i in units of electronic charge (e). The parameters used in the calculation were obtained by the usual combination rules from the atomic parameters of Ref. [21].

The charge distributions in styrene and TMA were obtained from a CNDO calculation [22], and are available on request. Simulated annealing [23] was used to obtain the structures of the stable configurations. Two main minima were obtained for the styrene–TMA cluster, with binding energies of 1311 and 1076 cm^{-1}. Their structures are shown in Fig. 4; it is seen that in the more stable isomer, the lobe of the non-bonding orbital of the nitrogen points towards the styrene molecule and can have good overlap with its π electrons. This is a favorable condition for forming a charge transfer complex, so that this form suggests itself as the adduct leading to the w-type excitation bands. In the other isomer the corresponding overlap is expected to be much smaller, and it is tentatively assigned to the n-type one. The excellent agreement between the calculated and experimentally obtained binding energy (1078 $\pm$ 200 cm^{-1}) is noted. The barrier for the transformation of the less stable form to the more stable one is found to rather small, about 106 cm^{-1}. The structure of the transition state was obtained by assuming that the reaction coordinate is a rotation of TMA with respect to the styrene is also shown in Fig. 4. The
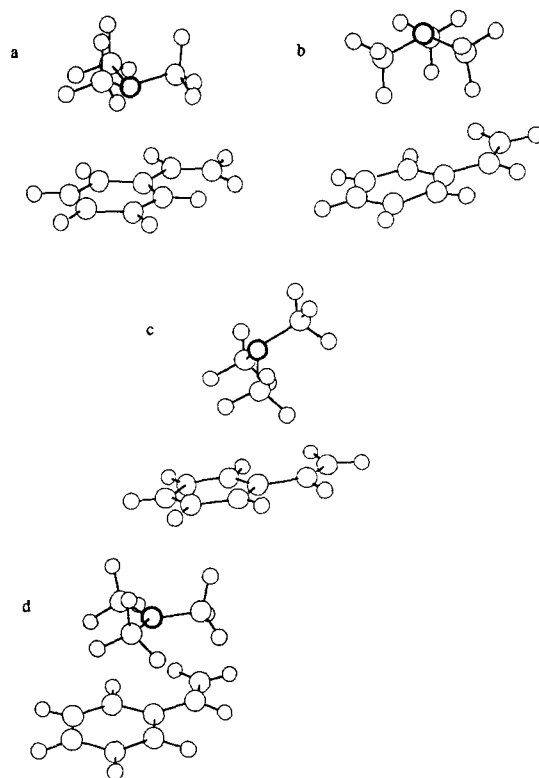

Fig. 4. The calculated structures of some species in the styrene–TMA system: (a) The most stable ground state 1:1 adduct (binding energy 1311 cm^{-1}). (b) The second stable 1:1 adduct (binding energy 1076 cm^{-1}). Structures (a) and (b) are proposed to give rise to the observed w-type and n-type series, respectively. (c) The transition state between the two stable ground state structures (a) and (b). Its energy is 106 cm^{-1} above that of structure (b). (d) The structure of the charge transfer adduct (complete transfer of an electron from TMA to styrene was assumed). Binding energy 30367 cm^{-1}.

Van der Waals adducts in the excited state are assumed to have similar structures.

The structure of the charge transfer (exciplex) adduct was calculated in a similar fashion, assuming that the it is mainly determined by the ionic configuration $STY^- -TMA^+$. According to this simplified model the anion (STY^-) and the cation (TMA^+) consist of an assembly of point charges centered on the nuclei. The structure and charge distributions of the separate STY^- and TMA^+ species were calculated at the ROHF/3-21 + G* level of theory. The main geometry change is the transformation of TMA to a planar form. The potential energy of the system

was the same as given in Eq. (1) plus the energy at infinite separation which is IP(TMA) + EA(styrene), EA being the electron affinity of styrene, 0.15 eV [24]. The Lennard-Jones parameters were the same as for the neutral. A single minimum was found for the ionic adduct, whose structure is also shown in Fig. 4.

5. Discussion

5.1. Locally excited and exciplex type emission from styrene–TMA clusters

The emission spectrum shown in Fig. 2 (obtained upon excitation of the w_1 band) is assigned to an exciplex since it is strongly red shifted with respect to the excitation and apparently carries no vibrational structure. These are typical characteristics of jet-cooled exciplexes [25,26]. The weakness of a REMPI signal upon excitation of this band is in line with this assignment, since charge transfer bands, being broad and weak, do not support efficient ionization by a second photon. Excitation of the n_1 band leads, in contrast, to LE emission *only*. Both bands are assigned to 1:1 adducts, based on two color REMPI results for the n-type and dilution experiments for both w- and n-series. It was not possible to completely avoid formation of larger adducts, but they usually seemed to appear mainly as a broad background signal in both LIF and REMPI spectra.

The appearance of higher energy n-type bands in the excitation spectrum of the 385 nm emission indicates that they lead also to the formation of an exciplex. The regular sequence of vibronic bands with frequency intervals characteristic of styrene rules out the possibility that these bands arise from a different species. It is concluded that the formation of an exciplex from the n-type adduct involves a barrier, located below 242 cm^{-1} — the energy of the first observed n-type excitation band yielding exciplex emission. A low limit for the barrier can be established at 16 cm^{-1}, the highest energy at which an n-type band is observed showing no exciplex-type emission; This band is assigned to an intermolecular Van der Waals cluster vibration (satellite to the n_1 band).

Therefore, the combined evidence of the LIF and REMPI data point to the existence of at least two

distinct styrene–TMA 1:1 adducts, one leading to the w-type bands, and one to the n-type ones. It is proposed that in both cases, initial excitation is to a Van der Waals excited state adduct, which transforms to an exciplex-type one. For the w-isomer, no barrier is involved in this transition, while for the n one, the process is slower and involves a barrier. Since we assume that the binding energies and geometries of the n- and w- type clusters in the S_1 state are very similar to those calculated for the S_0 ones, shown in Fig. 4, we tentatively propose that the n-type excited cluster isomerizes to the w-type one, which transforms to the CT adduct by electron transfer. Thus, the barrier for the formation of the exciplex from the n-type cluster is expected to be (as the calculation suggests) about 100 cm^{-1}, in agreement with experiment.

5.2. Energetics and mechanisms of charge transfer formation

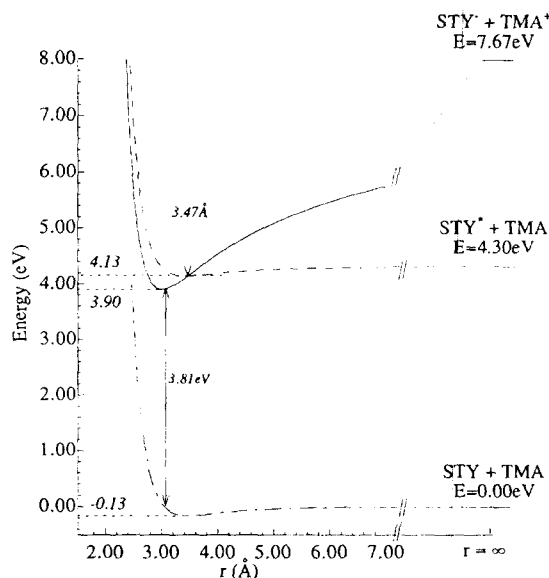Fig. 5 shows a plot of the calculated potential energy of the system as a function of the styrene–

Fig. 5. A cut of the energy level diagram of the styrene–TMA system along the intermolecular center-of-mass separation r. All energies are relative to the energy of the separated pair in the ground state. The minimum of the excited singlet state of the w-type van der Waals adduct is calculated to be at 4.13 eV and that of the charge transfer adduct at 3.90 eV.

TMA separation, when the energy is minimized along all other coordinates. The figure shows the results of the simplified model calculations described in Section 4 for the w-type adduct and the charge transfer (CT) state. It is seen that the charge transfer potential surface crosses the Van der Waals (LE) one very near the minimum of the latter. This is in line with observed barrierless appearance of exciplex emission from the w-type species. The energetics of the species giving rise to the n-type series are likely to be similar, in view of the similar binding energies of the ground state adducts. The small experimentally observed barrier for this species may be due to the need to reorient the two components to allow efficient electron transfer.

Fig. 5 predicts that at the minimum of the CT state is at 3.00 Å; At this separation, the ground state potential curve is repulsive, accounting for the lack of vibronic structure; the energy separation between the two surfaces at this intermolecular separation is about 3.81 eV, corresponding to 325 nm. This value is in reasonable agreement with the onset of the exciplex type emission shown in Fig. 2 (340 nm).

The processes relevant to the system are summarized in Scheme 1, which includes for simplicity only singlet species. The possible involvement of triplet states in the photochemistry of this system

was considered to be negligible [6] in solution, and is assumed to be so also in the gas phase clusters. However, the data indicate that at least two dark (non-emissive) states (designated as X and Y in the scheme) are implicated in this system. The evidence for X arises from the different dependence of the measured exciplex fluorescence decay times on the excess energy, from that of the fluorescence intensity. The former is lowered by a factor of about two as ΔE increases from 237 to 968 cm^{-1}, while the latter is reduced by a factor of at least four, and more likely, ten over the same range. These values hold for both n- and w-type bands. The discrepancy is larger than warranted by uncertainties in the experimental determination of these properties. The fluorescent exciplexes arising from the n- and w-type clusters appears to have the same emission spectrum and decay times, and according to this evidence may be considered as a single species. The decrease of the fluorescence intensity (ascribed to the competition between the formation of the emissive exciplex and the dark state X) as a function of excess energy is drastically different: for the w-type isomer, the main decrease is at relatively low excess energies (between 0 and 237 cm^{-1}); the intensity of the n-type isomer fluoerescence shows much larger fluctuations with excess energy. It is not possible to

$$(STY\text{-}TMA) + h\nu$$
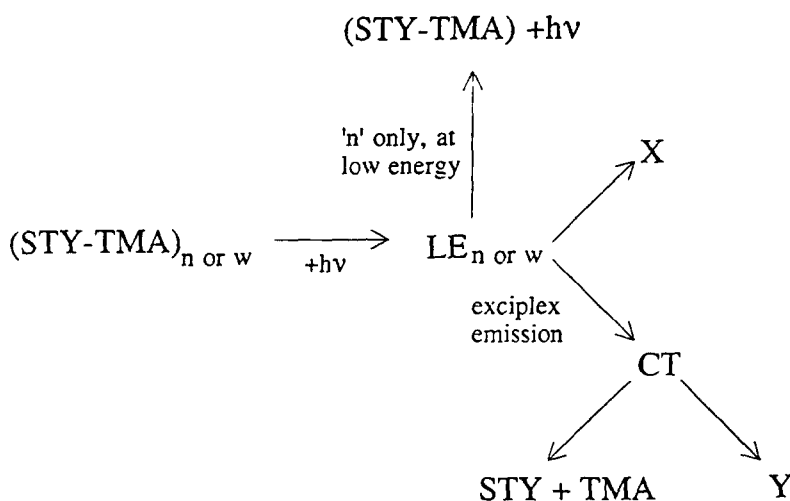
Scheme 1. A proposed simplified kinetic scheme of the styrene–TMA system. Two ground state adducts are assumed; upon excitation, both initially form van der Waals excited species (LE). The n-type one fluoresces at the origin, while the w-type one transforms immediately to two different species X and the emitting exciplex (CT). The n-type isomer also transforms to these two species, but needs to overcome a small barrier to do so. The CT state decays radiatively by exciplex type emission, as well as by forming another dark state Y.

verify at this point whether the same species X is formed from both isomers.

The formation of Y is proposed as the main reason for the decrease in the decay time over the same range. The complete absence of emission for energies exceeding $\Delta E \approx 1200$ cm^{-1} indicates a very rapid non-radiative process. The calculated dissociation energy of the CT state is much higher (~ 30367 cm^{-1}, Fig. 5) ruling out this route as the reason for the disappearance of the emission. According to the REMPI data, the dissociation energy of the Van der Waals bound excited cluster is approximately 1000 cm^{-1}, suggesting the possibility that the absence of emission beyond that energy is related to the dissociation of that adduct. However, this would require that the exciplex should reform the Van der Waals adduct. In that case observation of fragment ion signals and bare molecule's fluorescence signal upon exciting the cluster above dissociation threshold, are expected, as found for styrene clusters with other partners [15]. The absence of such signals is in line with the formation of a different species which is not easily ionized. Furthermore both the n- and w-type vibronic bands sequences terminate at the same excess energy. The most likely reason is the opening of another decay channel, whose barrier is about 200 cm^{-1} above the origin for the n-isomer, and whose rate of formation increases with energy. In view of the known bulk phase properties of this system, a likely candidate for this process is the formation of a new chemical intermediate.

Non-emissive excited states that were proposed as precursors for adduct formation in some styrene–amine systems. A proton transfer reaction following the electron transfer, leading to the formation of a biradical was suggested by Lewis and coworkers [7]. This biradical could possibly be the dark species formed from X of scheme 1, as it is non emissive, and its formation is expected to involve a small barrier. Aoyama et al. concluded that the formation of a fluorescent exciplex is competitive with that of a similar biradical in a covalently bound styrylamine [9], which is the precursor of the final photo products. Our results are consistent with the existence of a dark species, formed at rather low excess energies, that competes with the formation of the emissive exciplex. Its nature is not clear at the moment, but it

might be the biradical proposed by these workers, which is expected to be formed with a large excess of vibrational energy. It is certainly non-emitting, and may be difficult to observe by REMPI due to insufficient enhancement of the ioniztion probability by an intermediate state.

6. Summary

Two types of 1:1 adducts are experimentally observed in the LIF and REMPI spectra of the jet cooled styrene–trimethylamine system. Their emission spectra differ at the origin bands of the $S_0 \rightarrow S_1$ transition, one giving rise to locally excited emission, the other to an exciplex type one. Excitation of higher vibronic bands leads to exciplex emission from both species. The emission intensity, normalized to that of the bare molecule decreases more steeply upon vibronic excitation than the observed decay times. This is taken to indicate the existence of two dark states, as summarized in Scheme 1. The complete absence of fluorescence from this system upon excitation to energies exceeding $\Delta E = 1200$ cm^{-1}, contrasts with the pattern found for non-reactive styrene clusters. It is proposed that the dark states formed beyond these energies may be intermediates en route to photochemical products, which were proposed by previous solution phase work.

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