Laser-induced fluorescence and dispersed fluorescence studies of the donor–acceptor system 4-amino 3-methyl benzoic acid methyl ester and its solvated clusters: Evidence of excited-state charge-transfer reaction

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ABSTRACT

Laser-induced fluorescence (LIF) excitation and dispersed fluorescence (DF) spectra of 4-amino 3-methyl benzoic acid methyl ester (AMBME) and its solvated clusters with solvents such as methanol, water and acetonitrile have been investigated in a supersonic expansion. Spectral signature supports the presence of two conformers in the cooled jet which is in line with theoretical calculations. In addition to structured local emission from the Franck Condon excited state, the molecule AMBME shows red-shifted broad emission from the state attributed to the close-lying charge transfer (CT) state, which is facilitated by exciting low-frequency modes. The molecule readily forms clusters with different solvents and the clusters' electronic excitation bands appear in the low-energy side of the transition origin of the bare molecule. Excitation of the clusters leads to the appearance of red-shifted solvent-polarity dependent CT emission.

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1. Introduction

Since the first observation of photo-induced charge transfer (CT) phenomenon by Lippert et al. [1] from 4-N,N-dimethylaminobenzonitrile (DMABN), the study of photo-induced intramolecular charge transfer reaction in donor–acceptor systems is one of the most encountered photophysical problems. Scientists try to cast light on CT phenomena from both experimental and theoretical points of view, in systems with a variety of donor and acceptor substituents and in different environments [2–19]. It was experimentally found in condensed phase that the CT reaction was favoured in polar solvents due to stabilization of the CT state. However, spectroscopic measurements in jet-cooled conditions have failed most of the time to evidence the CT state. From the very early stage of experimental jet-cooled studies, it was found that only solvated clusters with polar (protic or aprotic) solvents showed CT emission, which well supports the condensed phase results [2]. However, Brutschy et al. reported CT emission from self-clusters in jet-cooled conditions [16]. Mikami et al. reported that (p-cyanophenyl)pentamethyldisilane showed CT emission in

solvent-free conditions, even from the vibration-less level of the locally excited state [17–19]. Their spectral measurements using IR–UV double resonance spectroscopy concluded that the CT state was planar, which contrasts with the twisted ground-state equilibrium geometry.

Theoretical approaches have postulated that low-frequency large-amplitude motion such as twisting or inversion of the donor substituent, or wagging or bending and rehybridization was responsible for the excited state CT process [2]. This resulted to several models such as twisted intramolecular charge transfer (TICT), planarised intramolecular charge transfer (PICT), wagging intramolecular charge transfer (WICT) and rehybridized intramolecular charge transfer (RICT) [2,6–12]. In all these models, coupling induced by excitation of a low-frequency large-amplitude motion allows the molecule to cross from the locally excited (LE) to the CT state. The stabilized CT state then deactivates *via* a solvent-polarity dependent red shifted emission. In the case of jet-cooled (p-cyanophenyl)pentamethyldisilane, this low-frequency promoting mode is assigned to a torsional motion of the disilanyl group relative to the benzene frame [18]. The charge transfer has been explained in terms of transfer of σ electrons from the Si–Si bond to the $2p\pi$ orbital of the cyanobenzene acceptor [17–19].

All studies reported so far concentrate on systems having a tertiary amino group as a charge donor, in which the nitrogen lone pair transfers to the acceptor site. There are few recent

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examples where primary amino donor shows CT emission in the condensed phase [20–22]. However, there is no example where a bare molecule with a standard primary amino donor gives rise to CT emission in jet-cooled conditions. Recently, we have observed a charge transfer emission in 4-amino-3-methyl benzoic acid methyl ester (AMBME) in solution both in homogeneous and heterogeneous media [23]. AMBME clearly shows dual emission in heterogeneous β-CD medium, which is the superposition of emission from molecules in polar and non-polar surroundings. The most important characteristic of AMBME is that it shows red-shifted emission even in non-polar solvents like cyclohexane, which is quite unexpected. The possible explanation of this unusual red-shifted fluorescence of AMBME in non-polar solvents is that the presence of the methyl group in ortho position induces a twist of the amino donor, already in the ground state. The optically excited AMBME therefore possesses the geometry which favours charge transfer. Moreover, the presence of a good acceptor group (ester group), as well as the fact that the lowest excited state is of L_a nature, favours CT reaction [23]. As the CT emission is already observed in non-polar solvents, it is expected that the bare molecule itself has inherent CT character. To investigate the intrinsic nature of the CT state, it is necessary to eliminate solvent effects and spectral broadening. Indeed, the resonant and charge-transfer emission are close in energy in non-polar solvents, as they arise from close lying LE and CT states. It is difficult to assess whether the observed emission band is a single slightly red-shifted emission or two close-lying overlapping bands.

We have therefore studied the photophysics of AMBME and its clusters with usual solvents in isolated jet-cooled conditions. We have used laser-induced fluorescence (LIF) excitation and dispersed fluorescence spectroscopy to precisely study the ground and excited-state properties of the isolated molecule and its jet-cooled clusters with usual solvents.

2. Experimental

The title molecule 4-amino-3-methyl benzoic acid methyl ester (AMBME) molecule has been synthesized in our laboratory using a simple synthetic procedure [23]. In brief, $SOCl_2$ (3.52 ml) was added drop wise to a solution of 4-amino-3-methyl-benzoic acid from Aldrich (6 g, 40.3 mmol) in MeOH (50 ml) under ice-cooled condition. The reaction mixture was stirred for 24 h at room temperature. Volatile solvent was removed under reduced pressure and the residue was dissolved in water, neutralized with aqueous $NaHCO_3$ and extracted with ethyl acetate (50 ml × 3). The combined organic layer was washed with water, brine and dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure to get the desired compound as colourless solid (6.3 g, 95%). The product was recrystallized for getting pure compound. ^{1}H NMR (CDCl$_3$, 60 MHz) δ 2.1 (s, 3H), 3.7 (brs, 2H), 3.95 (s, 3H), 7.6–7.9 (m, 3H).

The experimental set-up for measuring laser-induced fluorescence (LIF) excitation spectra of jet-cooled AMBME and its complexes has been described previously [24–27]. The sample vapours seeded in helium at a pressure of ∼2 atmospheres are expanded into vacuum through a pulsed nozzle (General Valve) and excited by a frequency-doubled dye laser (Sirah, Spectra Physik, 0.2 cm^{-1} resolution) pumped by the second harmonic of a Nd:YAG (GCR 190, Spectra Physics). The fluorescence signal from the sample is collected perpendicular to both the exciting light and the molecular beam by a two-lens collecting system and a 25 cm monochromator under broad band condition and detected by a Hamamatsu R2059 photomultiplier. The output electrical signal of the PMT is averaged by an oscilloscope (Lecroy 9310) and finally processed through a PC.
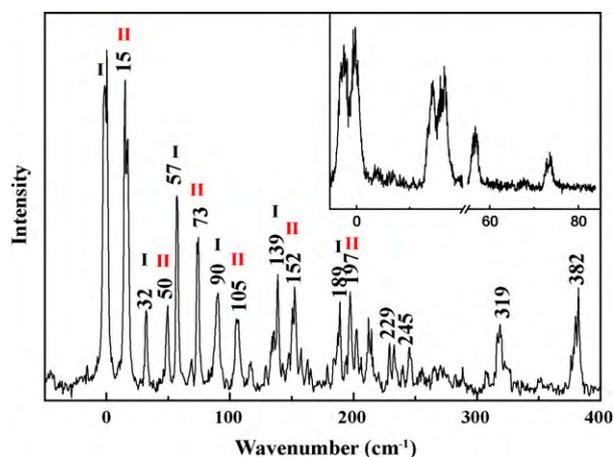

Fig. 1. LIF excitation spectrum of 4-amino-3-methyl benzoic acid methyl ester, inset: higher-resolution scan of the initial portion of the spectrum. The bands due to Conformer I and Conformer II are denoted by I and II, respectively. The zero of the scale is taken at the transition origin at 34251 cm^{-1}.
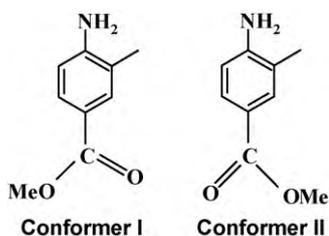
Dispersed fluorescence spectra are measured by focusing the emitted light on the entrance slit of a 60 cm Monochromator (Jobin-Yvon) by a two-lens system. The dispersed light is collected by an intensified gated ICCD camera (Andor Technology). The spectral resolution of the set-up (monochromator and ICCD assembly) is about 12 cm^{-1} in our experimental conditions. Lower resolution spectra are measured using the same monochromator equipped with a PM tube (Hamamatsu R2059). Broad-band spectra have been measured using a 25 cm monochromator (Huet M25).

The most stable conformations of AMBME have been calculated within the frame of the density functional theory (DFT) with the standard B3LYP functional and the 6-311++g(d,p) basis set. All calculations have been done using the Gaussian 03 software [28]. Excitation energies were calculated using the time dependent density functional theory (TDDFT) method using the same functional and basis set as for the two ground-state optimized geometries. Computed excitation energies are the vertical transition energy without zero point energy (ZPE) correction. The energy barrier for the conversion from one conformer to the other has been calculated in the ground electronic state at the same level by twisting the acceptor group step by step and optimizing all the remaining degrees of freedom at each step.

3. Results and discussion

3.1. LIF excitation spectrum of the bare molecule

The LIF spectrum of bare AMBME is shown in Fig. 1 and is much more complex than that of the related molecule 4-amino benzoic acid methyl ester (ABME) [29]. It shows two intense bands at 34251 cm^{-1} and 34266 cm^{-1} and several bands with weak to moderate intensity in the high energy side of these two strongest bands. The first pair of bands is separated by 15 cm^{-1}. All the other higher frequency bands appear pair wise and the difference between them is always ∼15 cm^{-1}. This spectral pattern, with regular pairing of bands, usually indicates the presence of two species with their own vibrational signature. We assume therefore that the first two bands correspond to the 0–0 transitions of two conformers, namely, Conformer I and Conformer II. The pairwise bands observed at higher energy side correspond to the excitation of similar vibrational modes for the two isomers. The similar molecule m-aminobenzoic acid shows similar conformational isomerism as two 0–0 band origins are observed in jet-cooled conditions and the separation of the 0–0 transitions of the two conformers of m-aminobenzoic acid

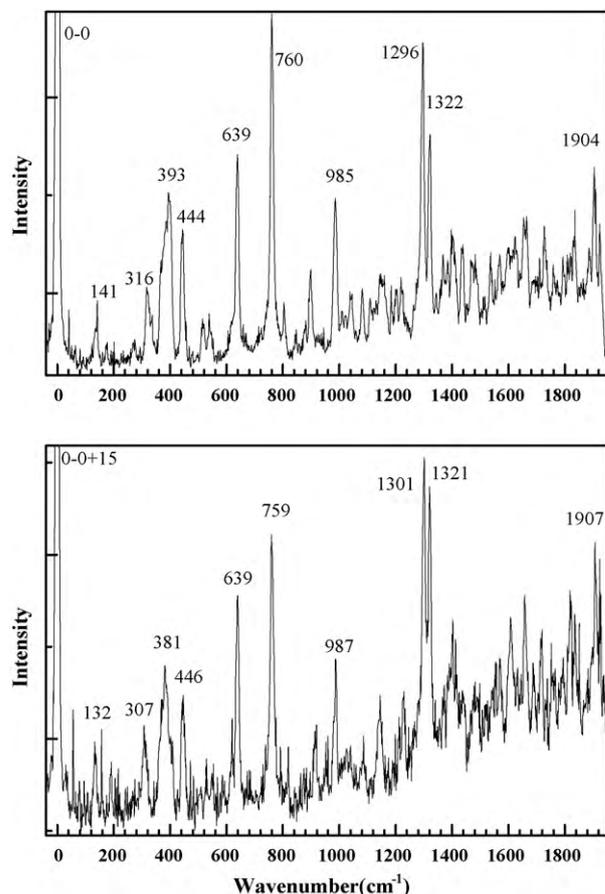**Scheme 1.** The two low-energy structures of AMBME.

Fig. 2. Dispersed fluorescence spectra of AMBME resulting from the excitation of the 0–0 (top) and 0–0+15 cm^{-1} (bottom) bands (initial portion with a resolution of 12 cm^{-1}). These spectra are shown without elimination of scattered light. The zero of the scale is set at the excitation wavelength.

is about 27 cm^{-1} [30–32]. Structural optimisation of the molecule AMBME generates two low-energy structures (Scheme 1) with respect to the orientation of the ester C=O group, which can be at the same or at opposite sides of the methyl substituent. This is very similar to what has been reported in m-aminobenzoic acid [30–32]. At the DFT level of calculation (B3LYP/6-311++g(d,p)), it is found that the ground-state energy difference between the two low-energy conformers is only 29 cm^{-1} and that the inter-conversion barrier from one conformer to the other is about 2800 cm^{-1} [23]. This may indicate that both conformers should be populated in jet-cooled conditions.

In AMBME, the calculated 0–0 vertical transition energy difference between the two isomers is found to be 19 cm^{-1} [23]. This value correlates well with the experimental 0–0 transition energy separation of 15 cm^{-1}. This difference in energy allows us assigning the most red shifted band in the LIF spectrum to the 0–0 transition of the most stable Conformer I and the 0–0+15 cm^{-1} transition to the 0–0 of the next stable Conformer II.

The LIF spectrum of AMBME recorded with a slow frequency scan of the exciting laser has been recorded for the first pair (0–0 and 0–0+15 cm^{-1}) and the second one (0–0+57 cm^{-1} and 0–0+73 cm^{-1}) and is shown in the inset of Fig. 1. It clearly appears that the first pair of bands is composed of a doublet, with a splitting of ∼2 cm^{-1}. The second pair of lines, i.e. the 0–0+57 and 0–0+73 cm^{-1} bands, do not show this splitting. Despite the fact that the L$_a$ and L$_b$ terms are no really appropriate in AMBME, because the presence of the methyl group reduces the symmetry of the system, we will still refer to the L$_a$ or L$_b$ character of the electronic transition. The shape of the rotational contour of the 0–0+57 and 0–0+73 cm^{-1} bands is easier to analyse than that of the transition origin, because they do not show splitting of the bands. It is clearly of a type, i.e. the transition moment is oriented along the main molecular axis. This indicates that these bands correspond to vibronic transitions of L$_a$ character. These results are in line with the TDDFT calculations which indicate a very strong oscillator strength for the first electronic transition located at 4.59 eV (f = 0.244 and 0.241 for the two conformers), while the second excited state located 0.121 eV higher in energy shows an oscillator strength of 0.08 or 0.09, much closer to what is expected for a L$_b$ type transition. This contrast with the parent molecule ABME for which the rotational contour of the transition origin has been shown to be typical of L$_b$ type transition [29]. In DMABN, the L$_b$ transition is lower in energy than L$_a$, but in ester-substituted donor–acceptor systems these two transitions are close in energy; their ordering is extremely sensitive to minor modifications of the molecular structure [33]. In methyl 4-N,N-dimethylaminobenzoate for example, solutions studies have shown that the lower excited state is of L$_a$ character with increased radiative rate constant k_r [33,34]. On the other hand, the first electronic transition is of L$_b$ character in AMBE but of L$_a$ character in the corresponding ethyl ester [29]. It seems here that the presence of the methyl in ortho position is enough to invert the ordering between L$_a$ and L$_b$ transitions when going from AMBE to AMBME, and the lowest-energy transition of AMBME is of L$_a$ type.

We now come back to the doublet observed for the 0–0 and 0–0+15 cm^{-1} bands. The vibrational pattern observed for each conformer is much richer than that of the parent molecule AMBE. It is reminiscent of that observed for o- or m-fluorotoluene, which has been assigned to transitions between methyl internal rotation levels [35]. Here also, the 0–0, 0–0+2 and 0–0+32 cm^{-1} bands can be assigned to transitions involving the internal methyl rotation in Conformer I, while those located at 0–0+15, 0–0+17, 0–0+50 cm^{-1} are assigned to the corresponding transitions in Conformer II. This hypothesis is reinforced by the fact that no mode in this low-frequency range has been obtained for the calculated optimized structure. Indeed the lowest calculated frequency is 52 cm^{-1}. This calculated mode mainly corresponds to the torsion of the ester group coupled with a CH$_3$ out-of-plane motion. It is thus tempting to assign the band observed at +57 cm^{-1} to the lowest calculated frequency of 52 cm^{-1}. Last, examination of Fig. 1 shows that the bands at 90 and 105 cm^{-1} correspond to the combination of the 57 cm^{-1} mode with the 32 cm^{-1} methyl torsion, for conformer I and conformer II, respectively. The bands at 90 and 105 cm^{-1} are more intense relative to the 57 and 73 cm^{-1} bands than the +32 and +50 cm^{-1} relative to the origin transitions. This gain in intensity can be due to coupling between the pure methyl torsion and the +52 cm^{-1} mode, which also involves deformation of the methyl group.

3.2. Dispersed fluorescence spectra (DF)

The dispersed fluorescence (DF) spectra resulting from the excitation of the first two strong transition origins (0–0 and
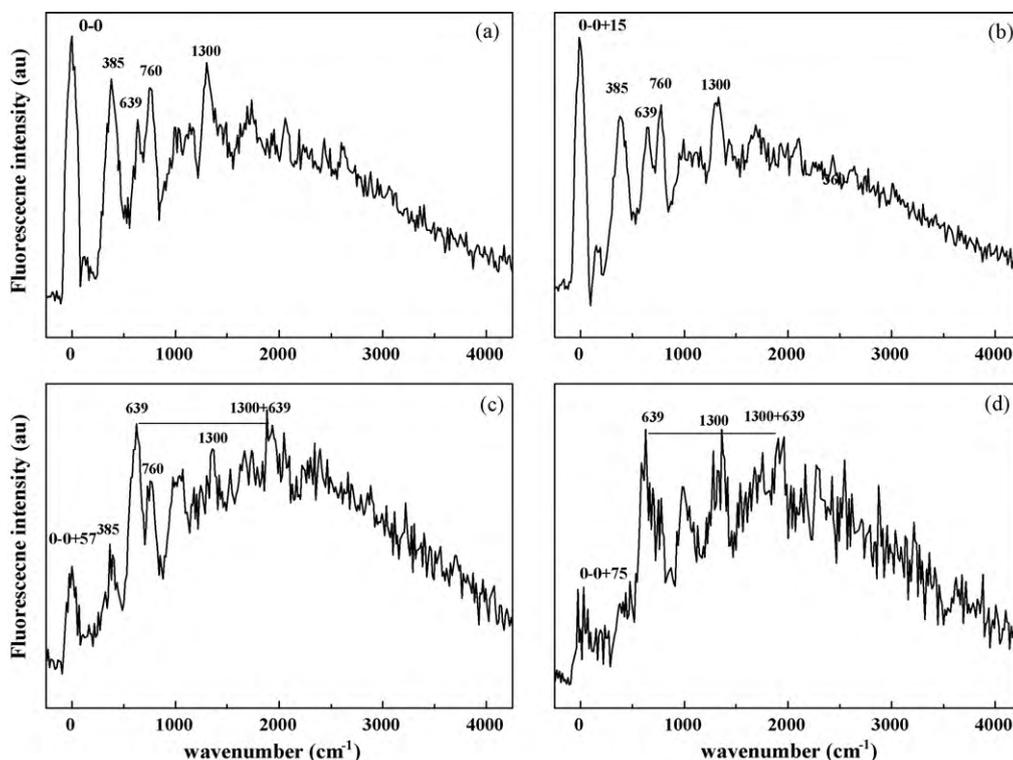
Fig. 3. Dispersed fluorescence spectra of AMBME resulting from the excitation of different vibronic levels at low resolution. Excitation set on (a) 0–0, (b) 0–0+15 cm^{-1}, (c) 0–0+57 cm^{-1}, and (d) 0–0+73 cm^{-1}. The spectra are given with subtraction of scattered light. The zero of the scale is set at the excitation wavelength.

0–0+15 cm^{-1}), recorded at a resolution of ~12 cm^{-1}, are shown in Fig. 2. These DF spectra are typical of the emission arising from a transition origin, which confirms that the two 0–0 and 0–0+15 cm^{-1} bands are due to two different conformers. The two spectra are similar to each other; they show a strong resonance emission with several lower intensity bands with similar patterns for both excitation bands. It is worth noting that a background appears at the low-energy side of the spectrum, starting at ~1600 cm^{-1} from the excitation. Fig. 3 shows the same spectra, as well as those recorded after excitation of the 57 and 73 cm^{-1} bands, recorded under lower resolution condition over a wider emission range. The DF spectrum for 0–0+32 cm^{-1} band cannot be observed due to its weak intensity. But the DF spectra obtained from the 0–0+57 cm^{-1} and 0–0+73 cm^{-1} bands (Fig. 3c and d) are strikingly different from the emission of the two 0–0 bands. Interestingly, a new emission built on a false origin located at 639 cm^{-1} from the L$_a$ transition origin becomes visible. The relative intensity of this emission depends on the excitation wavelength and its contribution to total emission increases when exciting the 0–0+57 and 0–0+73 cm^{-1} bands. The maximum of this emission is red shifted by about 1800 cm^{-1} and correlates well with the CT emission observed in non-polar solvents [23].

The red-shifted emission is already observed in addition to the structured LE emission when exciting the vibration less level. It is therefore attributed to the origin of another state, the origin of which is about 640 cm^{-1} below the L$_a$ state. This state has been assigned to the CT state. After curve-crossing from the LE to the CT state, intramolecular vibrational redistribution (IVR) takes place within the CT state, which results in a broad and slightly red-shifted redistributed emission. The corresponding transition does not appear in the excitation spectrum due to its forbidden character. This behaviour is well known in the case of charge transfer in jet-cooled complexes. The optically excited state is usually the locally excited state which evolves to the charge-transfer state from which redistributed emission takes place.

Excitation of low-frequency modes facilitates the coupling between LE and CT states. Therefore, the 639 cm^{-1} band appears weakly when exciting the two transition origins and more strongly when exciting higher energy vibronic bands (0–0+57 and 73 cm^{-1} bands). This indicates that the initially excited level couples through these low-frequency modes to iso-energetic modes in the CT manifold.

The 639 cm^{-1} band assigned to the origin of the CT emission is more prominent in the emission from the origin transition of conformer II than Conformer I. Similarly, the emission resulting from the excitation of the 0–0+75 cm^{-1} band shows more redistributed emission assigned to emission from the CT state than that resulting from the excitation of the 0–0+57 cm^{-1} band. It may be concluded from these observations that the extent of coupling of L$_a$ state with the CT state in conformer II is more than conformer I.

Charge transfer is facilitated in AMBME relative to the parent molecule AMBE, for which no charge transfer state has been evidenced in jet-cooled conditions [29]. However, the fluorescence arising from the CT state shows very limited red-shift when compared to DMABN or 4-N,N-dimethyl amino benzoic acid methyl ester (DMABE) [2]. This is probably due to the presence of methyl in ortho position in AMBME, which has +I electron donating effect. Similar behaviour has been observed in DMABN derivatives [2]. For example, the ring methylated DMABN derivative shows a higher intensity CT emission than DMABN itself, but its CT emission is blue shifted relative to DMABN.

One reason for that might be the molecule is already twisted in the ground state because of the presence of the methyl group. As a result, the difference in equilibrium geometry between the TICT and the S$_0$ state would not be that large; the emission does not take place towards the repulsive part of the S$_0$ energy surface, which explains the limited red shift. However, theoretical calculations show that the twist angle, even if not zero, is quite small (about 4–5°). This geometrical parameter alone cannot explain the limited red shift of the CT emission. Another rea-
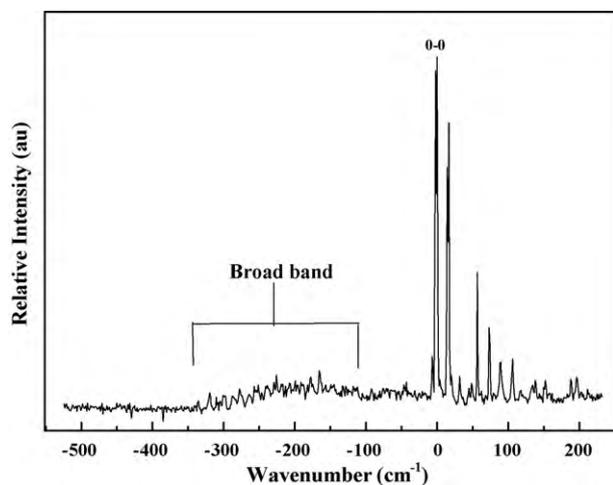
Fig. 4. LIF excitation spectrum of the AMBME:ACN complex. The zero of the scale is taken at the transition origin of Conformer I at 34251 cm^{-1}.

son is obviously the fact that the CT and LE states are close in energy.

The methyl internal rotation might also facilitate the LE to CT coupling, by increasing the density of states. Indeed, the rate for IVR in the S$_1$ state is accelerated by one order of magnitude when going from *para* difluorobenzene to *para* fluorotoluene [36]. Despite IVR being already active at an excess energy of ~640 cm^{-1}, it is usually not complete at this excess energy if no methyl rotor is present [37].

3.3. Studies of clusters with usual solvents

Spectroscopic measurements in jet-cooled isolated conditions enable us to investigate the CT characteristics of this bare molecule, but the intermolecular factor, *i.e.* solute–solvent interaction, is still an important factor for ICT reaction. To investigate the microscopic solvation effect on ICT process we have carried out laser-induced fluorescence excitation and dispersed fluorescence study of the clusters of AMBME with usual polar solvents. We have selected acetonitrile, methanol and water as solvents for this study for the sake of comparison with our previous work done in the condensed phase [23].

3.3.1. AMBME–ACN clusters

The LIF spectrum of AMBME in presence of ACN (Fig. 4) shows a broad and structureless band, which is red-shifted from the 0–0 transition of the bare chromophore. Such a broad excitation band in the low-frequency region might be due to the formation of different sizes of AMBME–ACN clusters. However, the intensity dependence as a function of the ACN concentration shows that this absorption is due to a 1:1 complex and is intrinsically broad in nature. As seen in Fig. 5a, the broad-band emission spectra recorded after exciting the complex at the maximum of the broad excitation band clearly shows red-shifted emission relative to that of the bare molecule, recorded under the same broad band conditions (Fig. 5b). The maximum of the emission is shifted by 3000 cm^{-1} from the excitation, which indicates stabilization of the charge-transfer state of the AMBME/ACN clusters relative to the bare molecule.

3.3.2. AMBME–methanol cluster

Fig. 6 shows the LIF spectra of AMBME/methanol solvated clusters at different methanol concentrations. With increased methanol concentration, the 0–0 band of the bare molecule is quenched and several new bands appear at the low-energy side of the 0–0 transition of the bare molecule. These bands can be separated in two classes. The first one includes a strong band located at −35 cm^{-1},
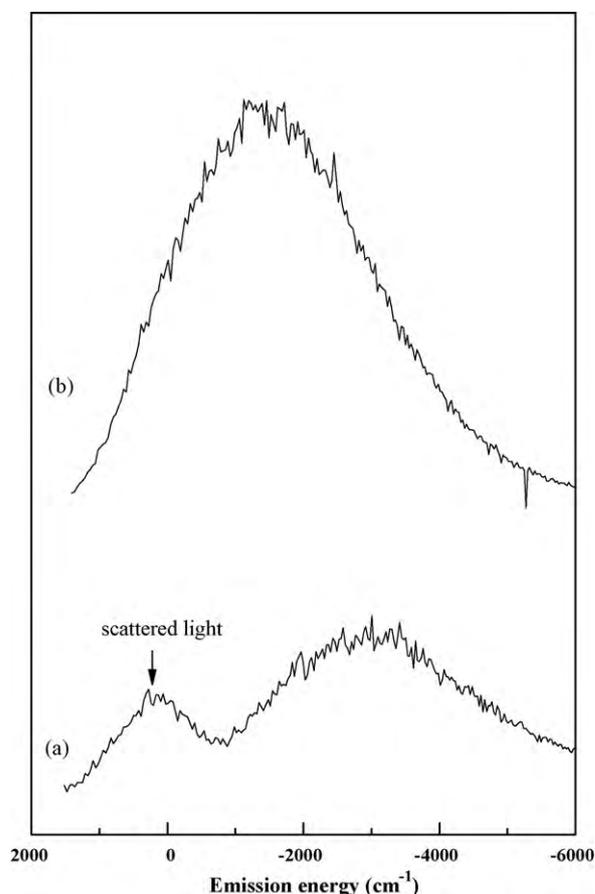

Fig. 5. Broad-band emission spectra of (a) AMBME:ACN complex excited at the maximum of the broad absorption at −220 cm^{-1} from the AMBME 0–0 transition. (b) AMBME excited in its 0–0 transition, recorded in the same experimental conditions. The zero of the scale is taken at the excitation wavelength.
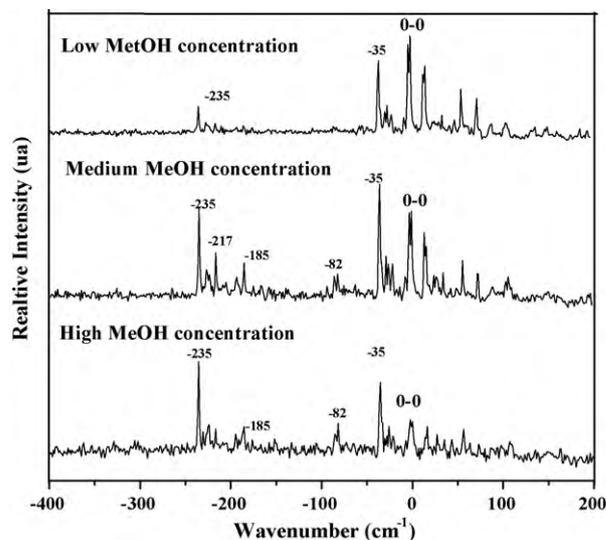

Fig. 6. LIF excitation spectra of AMBME:methanol clusters obtained at different methanol concentration. The zero of the scale is taken at the transition origin at 34251 cm^{-1}.

followed by several bands of much weaker intensity. The red shift of this class of band is limited. The second bunch of bands shows a much more pronounced red shift and starts at −235 cm^{-1} from the transition origin. The intensity of the −235 cm^{-1} band increases much more rapidly with increased methanol concentration than
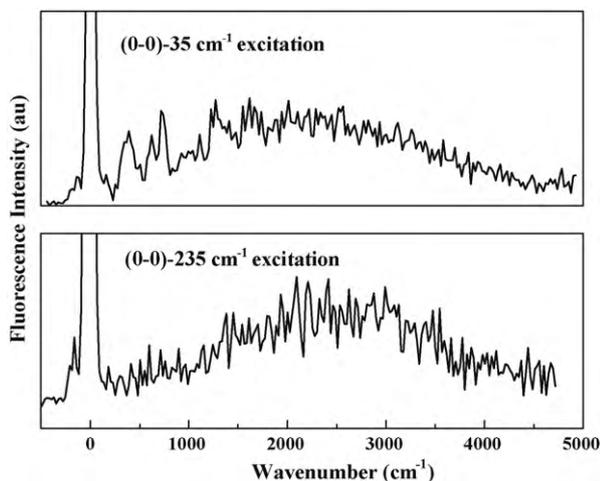
Fig. 7. Dispersed fluorescence spectra of AMBME:methanol clusters of different size. Top trace: 1:1 cluster. Bottom trace: 1:2 cluster. These spectra are shown without elimination of scattered light. The zero of the scale is taken at the excitation wavelength.

Fig. 8. LIF spectra of the AMBME:water clusters obtained at different water concentration. The zero of the scale is taken at the transition origin of Conformer I at 34251 cm^{-1}.

that of the other bands. This indicates that the −235 cm^{-1} band is due to the formation of a large cluster of AMBME with methanol. Dependency of cluster band intensity on increasing methanol concentration indicates that the −35 cm^{-1} band corresponds to a 1:1 cluster and the −235 cm^{-1} band probably corresponds to 1:2 cluster. As seen in Fig. 7, the dispersed fluorescence spectra resulting from the excitation of the −35 cm^{-1} and −235 cm^{-1} bands are different in nature. The 1:1 complex shows very limited red-shift in absorption (−35 cm^{-1}) and resonant emission, which means that the excited state is similar to that involved in the bare molecule (L_a). In contrast, the −235 cm^{-1} band assigned to the 1:2 complex is much more shifted in absorption, its excitation results to the disappearance of the resonance emission. The DF spectrum recorded by setting the excitation wavelength at −235 cm^{-1} is red shifted and structure less, in contrast with the resonant emission observed after excitation of the −35 cm^{-1} band. Only a broad emission showing limited red-shift (2500 cm^{-1}) is observed. This case can be compared to what has been observed in the monohydrate of 4-N,N-dimethylaminobenzoate. Indeed, double resonance experiments have shown that the first excited state of the monohydrate does not change in nature relative to the bare molecule and remains of local character, while the di-hydrate shows CT emission [38]. The case presented here is slightly different as CT emission is already observed in the bare molecule. However, it is not favoured by adding one water molecule only. This is probably related to specific solvation, as observed in 4-N,N-dimethylaminobenzoate di-hydrates [39]. Indeed, only those of the complexes which show solvation on the amino site undergo ICT reaction. The same explanation could hold here for explaining the differences between 1:1 and 1:2 clusters.

3.3.3. AMBME–water cluster

The LIF spectra of AMBME/water clusters are shown in Fig. 8. Here also numerous bands due to cluster formation appear at the low-energy side of the 0–0 transition of the bare molecule; the strongly red-shifted band at −210 cm^{-1} becomes much more prominent when increasing the water partial pressure. It may indicate that the −210 cm^{-1} corresponds to a 1:2 cluster; the other bands at −7 and −23 cm^{-1} correspond to 1:1 clusters of AMBME–water. As observed for methanol, excitation of the bands near the bare molecule transition origin (not shown) results to resonance fluorescence. In contrast, a broad red-shifted CT emission is observed when exciting the AMBME–water cluster band
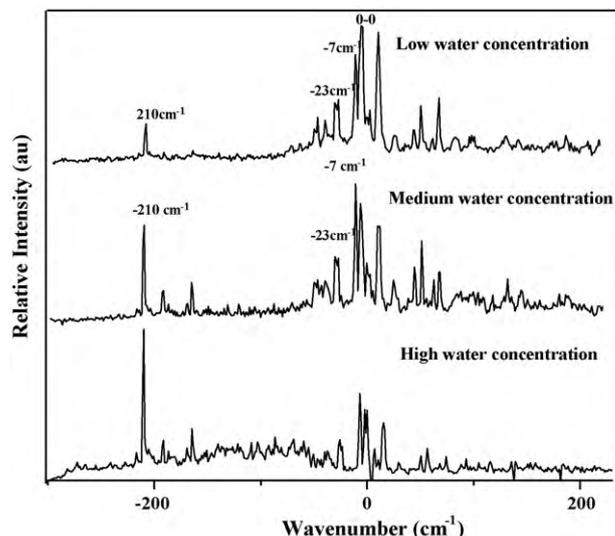
at −210 cm^{-1} from the bare molecule origin. As observed in the methanol complexes, CT is favoured by solvation by more than one water molecule. IR–UV fluorescence dip experiments on the monohydrate of the similar molecule 4-amino-benzonitrile have shown that one of the observed complexes involves a hydrogen bond from the amino group to water [40], and the others a hydrogen bond from water to the CN substituent. Analogous structures are also likely for the AMBME hydrate; in this type of structure the lone pair of the amino group is free and can be involved in the CT process, which is inherently of $n\pi^*$ character.

4. Summary and conclusion

AMBME and its solvated clusters with ACN, water and methanol have been studied in supersonic jet conditions. Laser-induced fluorescence excitation and dispersed fluorescence studies evidence the existence of two almost iso-energetic ground-state conformers of AMBME. Both of them show photo-induced charge transfer. Coupling between LE and CT states already happens for the excitation of the transition origin, which results to red-shifted broad CT emission. It is facilitated by the excitation of low-frequency modes. The red shift of the CT emission is limited, as already observed in solution. Modification of the donor–acceptor properties by the methyl group facilitates the CT process relative to the parent molecule 4-N,N-dimethylaminobenzoate because the presence of the methyl group increases the density of states, reverses the energy order between the L_a and L_b transitions relative to the parent molecule ABME, and induces a limited twist of the amino group.

Over all, the most interesting observation is that the weak primary amino donor molecule shows red-shifted emission by transfer of the nitrogen lone pair electron to the acceptor site in the isolated free jet. AMBME forms clusters with ACN, methanol and water which show solvent polarity dependent red-shifted CT emission.

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