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Conformational effects and level mixing in a doubly hydrogen-bonded 1 : 1 dimer of acetic acid and 3-fluorobenzoic acid

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Abstract

Vibronically resolved $S_1 \leftrightarrow S_0$ electronic spectra of a doubly hydrogen-bonded mixed dimer between acetic acid and 3-fluorobenzoic acid have been investigated by measuring laser-induced fluorescence excitation and dispersed fluorescence spectra in a cold supersonic jet expansion. Two isomeric species of the dimer have been identified, and the measurements show that their vibronic spectral patterns are significantly different. One of the isomers experiences distortion of dimer geometry upon $S_1 \leftarrow S_0$ excitation along the vibrational coordinate of a low-frequency hydrogen bond mode. Assignments of the vibronic spectral bands are suggested by correlating the observed band positions with the DFT-predicted normal mode vibrational frequencies. The methyl group of the acetic acid moiety has been found to be responsible to lower the IVR threshold of the electronically excited 3-fluorobenzoic acid moiety to a significant extent. The spectral features reveal that the vibrational relaxation rate of the ring-breathing mode on S_1 surface is possibly different in two conformers. The mechanism of the rotor effects, in terms of coupling of the large-amplitude rotor motion with the low-frequency hydrogen bond vibrations, has been discussed.

Keywords: Doubly hydrogen bonded cycle interface, conformational effects, level mixing, supramolecular aggregates, dimers.

1. Introduction

Doubly hydrogen-bonded cyclic interface represents a key structural feature found in many biological and synthetic supramolecular aggregates. Watson–Crick base pairs are the paradigms of such molecular assemblies, and the dimers of carboxylic acids are their simplest structural and spectroscopic analogues. A lot of attention has been paid to such systems in recent years, as it has been demonstrated in a number of experiments that such hydrogen-bonded linkages could play an important role in electron transfers in molecular biology [1–3].

Energetically the hydrogen bonds in carboxylic acid dimers are quite similar to those found in the dimers of much simpler systems like water and phenol [4]. However, the features of the gas-phase infrared absorption spectra corresponding to one quantum excitation of the O–H stretching vibration of these dimers show that the dynamical consequences of

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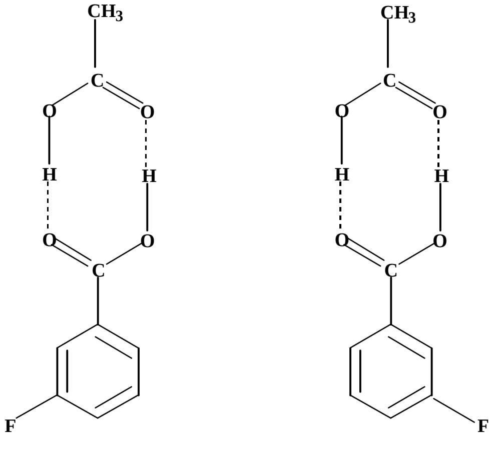
*Author for correspondence. Present address: Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032 such double hydrogen bonds are generically different from the others [5, 6]. In a normal situation, the hydrogen-bonded O–H bond in a molecule exhibits red-shift and enhanced intensity for one quantum excitation of the bond stretching vibration compared to a free O–H bond. Such behaviour has been nicely demonstrated in the case of phenol dimer by Mikami and coworkers at the Tohoku University in Japan [4]. On the other hand, Zwier and coworkers at the Purdue University have shown, by the use of IR-UV double resonance spectroscopy, that the one quantum excitation the O–H stretching vibration in benzoic acid dimer is unusually broad (~ 500 cm^{-1}), largely red-shifted (2500–3250 cm^{-1}) and exhibits many substructures over the broad profile [6]. The breadth and substructures are the indications of the complex dynamics of the vibrationally excited O–H stretching mode due to anharmonic coupling with the other modes of the carboxyl group. Recently we have shown that upon $S_1 \leftarrow S_0$ electronic excitation of benzoic acid dimer the intermolecular vibrations of the cyclic hydrogen bond frame of the dimer undergo extensive mixing with the intramolecular modes of the monomer moieties [7]. We have argued that such mode mixing is responsible for low threshold of vibrational relaxation [8], which is typical in many of such systems [9].

In this paper, we report the conformational effects and hydrogen bond-induced level mixing in a mixed dimer between acetic acid and 3-fluorobenzoic acid (AA···3-FBA). The consequences of conformational differences on excited state dynamics in a doubly hydrogen-bonded dimeric system have been demonstrated recently by our group using the homodimer of 3-fluorobenzoic acid as the molecular model [10]. However, the present system is structurally more compact and can have only two distinct planar conformations for internal rotation about the C–C bond between the phenyl and carboxyl groups (Fig. 1). Furthermore, unlike the two identical and relatively more polarizable molecular moieties in 3-FBA$_2$, the methyl group of the acetic acid moiety in AA···3-FBA is expected to have little electronic influence when the FBA moiety is in electronically excited $pp*$ state. The rotor group of the acetic acid moiety may undergo nearly free large-amplitude internal rotation (rotor motion), and the significance of such motion in chemical dynamics has been discussed in numerous publications in the past two decades [11–15]. AA···3-FBA is also an attractive sys-



Conformer I Conformer II

FIG. 1. Optimized (DFT/B3LYP/6-311G**) structures of the two conformational isomers of the mixed dimer AA…3-FBA.

tem to investigate whether the degree of the long-range rotor-induced level mixing in the aromatic moiety is different in the two conformational isomers.

2. Experiment

The experimental set-up used to measure the laser-induced fluorescence excitation and dispersed fluorescence spectra of jet-cooled AA···3-FBA has been previously described [16, 17]. Briefly, to record the FE and DF spectra, a vapour mixture consisting of 3-fluorobenzoic acid, acetic acid and helium at a total pressure of 2 atm was expanded into vacuum through a pulsed nozzle (general valve) of orifice diameter 0.5 mm to generate the hydrogen-bonded dimers. The helium gas was passed successively through two cells containing acetic acid at a temperature of 0°C and 3-fluorobenzoic acid at 110°C. The dimers were excited by a tunable UV laser obtained as the doubled output of a dye laser (Sirah and Plasma Technik, model: Cobra Stretch), which is pumped by the second harmonic of an Nd: YAG laser (Spectra Physics, Model: INDI). For dispersed fluorescence measurement, a 0.75 m monochromator (Spex, Model 750 M) with a grating of groove density 2400/mm was used. Typical monochromator resolution of the spectra presented here is 7 cm^{-1}. To measure a fluorescence excitation spectrum, the total fluorescence is detected using a Hamamatsu R928 photomultiplier tube and the output signal of the photomultiplier is processed by a boxcar averager (SRS 250). To detect the dispersed fluorescence, a double-staged Peltier-cooled ICCD detector (Jobin Yvon, Model No. 3000V) was used.

The samples, 3-fluorobenzoic acid and acetic acid, were procured from Lancaster and purified further by vacuum distillation.

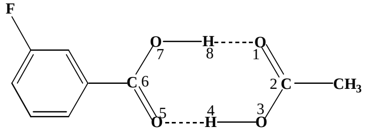
3. Result and discussion

3.1 *Theoretical*

The ground state structures and energies of two isomers of the AA…3-FBA were calculated by fully optimizing the geometries at the MP2/6-31G** level of theory. The optimized structures of the two conformers are shown in Fig. 1, and the predicted binding energies of the *syn* and *anti* forms are 16.41 and 16.36 kcal/mol, respectively. The values are similar to the binding energy estimated for benzoic acid dimer (16.2 kcal/mol) in the gas phase by use of temperature dependent infrared spectroscopy [18]. This indicates that the binding energy is primarily determined by hydrogen bonding interactions. A few of the key geometrical parameters of the cyclic hydrogen-bonded interface of the dimer are presented in Table I. It shows that the bond parameters in both the isomeric species are the same. However, on hydrogen bond formation, O–H bond lengths of AA and 3-FBA are increased by 0.027 and 0.023 Å, respectively, compared to the values of the free acids. Similarly, the C=O bond lengths of the two acids are increased by 0.019 and 0.014 Å, and the ∠O–C–O bond angles are increased by 1.6 and 1.7 degree, respectively. On the other hand, the ∠C–O–H angle is increased to the same extent in both the acids by as large as 4.0 degrees.

The frequencies of the normal vibrational modes in the ground state of the two isomeric forms of the dimer have been calculated by use of the DFT method using the Becke3LYP functional and 6-311G** basis set on all atoms. The predicted frequencies of a select few

Table I
DFT/B3LYP/6-311G-predicted geometrical parameters of the hydrogen-bonded cyclic interface of the dimer and comparison of these parameters with those in the free monomer moieties**



Geometrical Parameters	Carboxyl group of acetic acid moiety	Carboxyl group of 3-FBA moiety	H-bonded interface of the *syn* conformer	H-bonded interface of the *anti* conformer
H_8–O_7	–	0.971	0.998	0.998
H_4–O_3	0.971	–	0.994	0.994
C_6–O_7	–	1.359	1.327	1.327
C_2–O_3	1.362	–	1.328	1.328
C_2–O_1	1.218	–	1.237	1.237
C_6–O_5	–	1.221	1.235	1.235
C_6–O_7–H_8	–	105.2	109.2	109.2
C_2–O_3–H_4	105.2	–	109.2	109.2
O_1–C_2–O_3	122.7	–	124.4	124.3
O_5–C_6–O_7	–	122.7	124.3	124.4

modes of the dimer are presented in Table II along with the experimentally observed frequencies in the DF spectra recorded following excitations of the electronic origin bands of the two isomers. The assignments of the measured spectral bands are suggested by correlating the numbers with the theoretically predicted vibrational frequencies, the nature and symmetry of the modes as observed by visualization of the atomic displacement vectors and deviation of the frequencies from those of the benzoic acid. All calculations were carried out using the Gaussian 98 suite of programs [19].

3.2. *Experimental*

3.2.1. *Fluorescence excitation spectrum*

The laser-induced fluorescence excitation (FE) spectra for $S_1 \leftarrow S_0$ electronic transition of the dimer AA···3-FBA, measured in a supersonic free jet expansion of helium, is presented in Fig. 2 (upper trace). The homodimer of 3-FBA also absorbs in the same spectral range. As a result, the upper spectrum, being non-mass-selective, contains a number of bands which originates due to absorption of the homodimer. Such transitions are denoted by asterisks and to clarify this point further the FE spectrum of $(3\text{-FBA})_2$ is presented here (lower trace). The common bands between the two spectra are indicated by vertical dotted lines. The most intense band at the longest wavelength (285.502 nm) in Fig. 2(a), which is absent in Fig. 2(b), has been assigned to the transition from the zero-point level of S_0 to the zero-point level of S_1 (0^0_0) of the mixed dimer. It is worth to mention here that the monomers of benzoic acid and 3-fluorobenzoic acid do not fluoresce, and acetic acid monomer does not absorb in this spectral region. Therefore, the spectra are not contaminated by monomer transitions. Some weaker features in the longer wavelength, the intensity of which increases with increase in vapour pressure of acetic acid, could be due to higher clusters. However, near the origin transition of the dimers the spectra are not congested by the higher clusters.

Table II
Observed vibronic frequencies and suggested assignments in the $S_0 \leftarrow S_1$ dispersed fluorescence spectra measured following excitations of the 0_0^0 bands of the two isomers of the mixed dimer AA….3-FBA. Theoretically predicted (DFT/B3LYP/6-311G) normal mode frequency of two isomers are also given here for comparison**

Dimer I				Dimer II				Assignments
Freq. (cm^{-1})	Rel. freq. (cm^{-1})	Rel. int.	Theory (cm^{-1})	Freq. (cm^{-1})	Rel. freq.	Rel. int.	Theory	
35026	0	100		35050	0	100		Origin
34950	76	11	71					Rocking of 3-FBA at the H-bonded interface
34860	166	5	130	34885	165	4	130	IP H-bond stretching
				34809	241	2	247	IP COOH bend and sliding at the H-bonded interface
34633	393	20	390	34672	378	8	377	IP Ring dfmn + H-bond IP stretching (Q1)
34614	406	12	407	34630	420	29	418	IP ring dfmn + H-bond IP stretching (Q2)
34518	508	5	502	34542	508	8	502	COOH in-plane bend + COOH internal angle dfmn + ring dfmn (A)
34477	549	17	550	34496	554	2	554	COOH in-plane bend + COOH internal angle dfmn + ring dfmn (B)
34363	663	3	660	34390	660	3	660	Ring dfmn + COOH scissoring (R)
34267	759	18	751	34291	759	11	752	IP COOH scissoring (different phase) + IP ring bending (P1)
33099	927	9	925	34130	920	7	926	C–O–H bending + ring dfmn (P2)
34022	1004	30	1000	34046	1004	32	1000	Aromatic ring dfmn (Benzene mode 12)
33801	1224	25	1212	33815	1235	12	1220	C-F str. + ring dfmn
33754	1272	6	1266	33762	1288	13	1270	COOH dfmn + IP fanning of ring C–H bonds
33723	1314	10	1309	33743	1307	17	1290	C–O–H bend + Ph–COOH stretch + Benzene mode 3 type ring dfmn
33626	1400	14		33666	1384	2		12 + Q1
33584	1442	2		33626	1424	11		12 + Q2
				33540	1510	2		12 + A
33475	1551	3						12 + B
33362	1664	3		33390	1660	2		12 + R
33263	1763	3		33290	1760	2		12 + P1
33095	1931	3		33125	1924	1.5		12 + P2

IP = in-plane; str. = Stretching; dfmn = deformation.

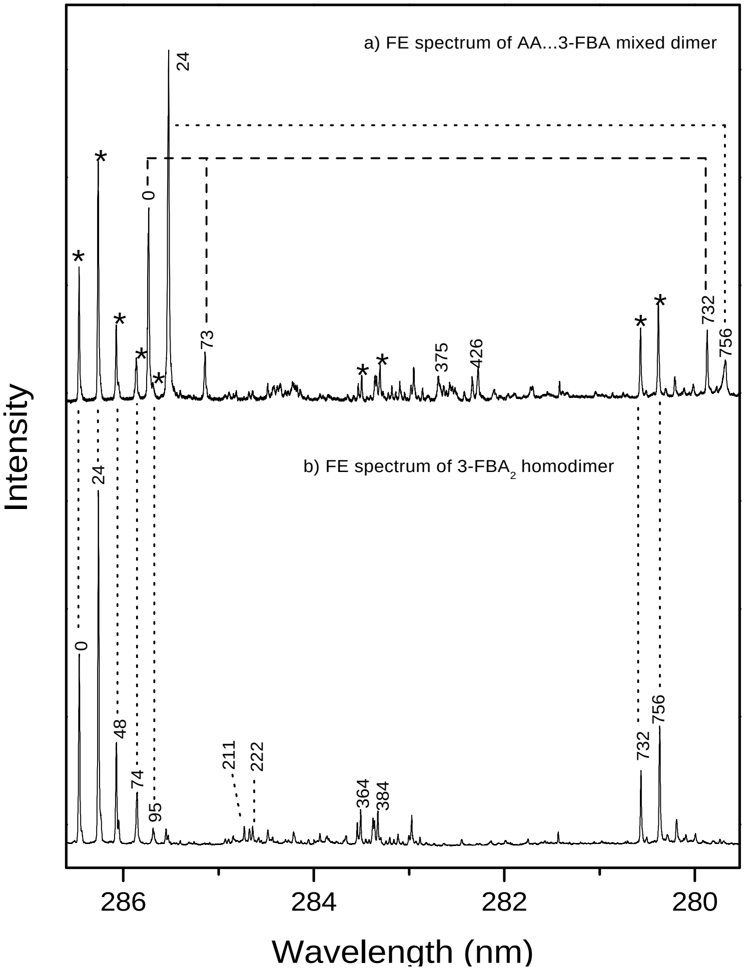


FIG. 2. Comparison of the fluorescence excitation spectra for $S_1 \leftarrow S_0$ electronic excitations of the (a) mixed dimer AA···3-FBA and (b) homodimer (3-FBA)$_2$. The homodimer bands in (a) are labeled by asterisks. The band-labeled 24 has been assigned as 0_0^0 transition of a second conformational species of the dimer.

A number of earlier investigations with isotopically substituted dimers of benzoic acid have concluded that the electronic excitations in such species are localized primarily on only one of the moieties [20, 21]. The consequence of such excitation localization is that the inter-ring excitation exchange or exciton splitting of the 0_0^0 band is very small. In the case of the benzoic acid homodimer, such splitting was estimated to be as small as 0.3 cm^{-1} [20]. Therefore, the role of the AA moiety in our present system of AA···3-FBA, and of the second moiety in the case of the homodimer [(3-FBA)$_2$], which is not excited by one-photon absorption, is like that of solvent molecules.

It is denoted in the figure that the 0_0^0 band of AA···3-FBA is 90 cm^{-1} blue-shifted compared to that of the homodimer (3-FBA)$_2$. On the other hand, we have noticed that in the case of a mixed dimer between formic acid and 3-fluorobenzoic acid (FA···3-FBA) the 0_0^0 band is 20 cm^{-1} red-shifted from the homodimer origin [22]. The nature of these spectral shifts can be interpreted, in localized electronic excitation picture, considering the proton-donating tendencies of the unexcited acid moiety. In water, the $\text{p}K_a$ values of FA, AA, and 3-FBA are 3.75, 4.75 and 3.86, respectively [23]. If we assume that the proton-donating tendency in isolated molecular dimer follows the trend of the condensed-phase $\text{p}K_a$ values, the $S_1 \leftarrow S_0$ transition energy of the solute (3-FBA) should exhibit the largest red-shift in the case of FA···3-FBA and the least for AA···3-FBA, and this is consistent with the observations.

The assignments of the vibronic bands in the homodimer spectrum have been discussed in one of our previous reports [10]. Therefore, we discuss here only the features of the mixed dimer. The prominent low-frequency bands over the electronic origin (0_0^0) appear at 24 and 73 cm^{-1}, and the intensity pattern of these bands gives the feeling that they belong to a vibronic progression. However, by use of dispersed fluorescence spectroscopy we show below that the 24 cm^{-1} band is actually the 0_0^0 transition of the second conformational species of the dimer. The assignment of the 73 cm^{-1} band has been settled (see below) as one of the large amplitude hydrogen bond vibrations of the dimer and the corresponding ground state frequency of the mode is 76 cm^{-1} (Fig. 3). Visualization of the atom displacement vectors indicates that it corresponds to a kind of in-plane cogwheel type of motion of the two molecular moieties across the hydrogen-bonded interface. Interestingly, in the excitation spectrum only one isomer exhibits this large amplitude vibration. This indicates that the geometry distortion along this vibrational coordinate, as a result of electronic excitation, occurs only in one isomer.

A second notable point is the intensity difference between the origin transitions of the two isomers. Theoretical calculation shows that the binding energies, and hence the ground state stabilities of both the isomers are the same, and this implies that their population ratio in the ground electronic state is also the same. Therefore, the intensities of the origin transitions of two isomers are mainly determined by their Franck–Condon factors. Larger inten-

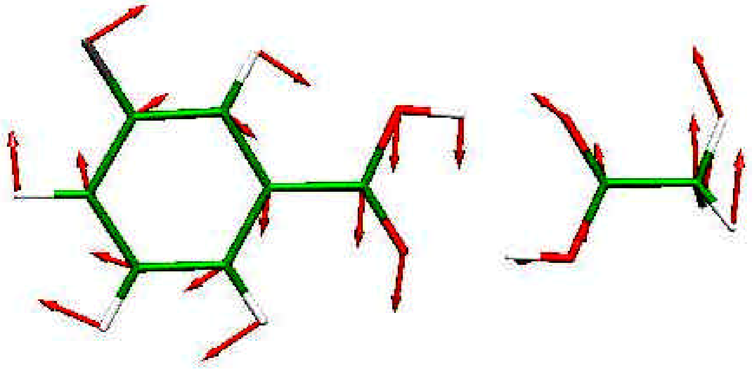


FIG. 3. The DFT-predicted mode pattern of the rocking motion of the 3-FBA moiety at the hydrogen-bonded interface. The conformer-I undergoes geometry distortion along this vibrational coordinate on $S_1 \leftarrow S_0$ electronic excitation.

sity of the second origin (24 cm^{-1}) implies that the S_1 geometry of this isomeric specie is more similar to its S_0 geometry compared to that of the other isomer. This interpretation is also consistent with the building up of the progression of the low-frequency mode, mentioned above.

Other prominent vibronic features in the mixed as well as the homodimer spectra appear around 400 and 730 cm^{-1}. The former correspond mainly to the in-plane phenyl ring deformation but the latter is due to ring-breathing vibration. It is interesting to note that the intensity of the ring-breathing vibronic transition for the second isomer (756 cm^{-1}) band is relativly weaker and the bandwidth is larger than the band of the first isomer (732 cm^{-1}). Our dispersed fluorescence measurement indicates that the vibrational redistribution following excitation to this vibronic energy range is quite extensive. The line shape pattern and intensity reversal compared to the origin transitions indicate that the vibrational relaxation rate of the second isomer is faster from this level.

3.2.2. *Dispersed fluorescence spectra*

The dispersed fluorescence spectra measured following excitations of the first three bands (0, 24 and 73 cm^{-1}) of the mixed dimer are presented in Fig. 4. The vibronic spectral pattern in the first two spectra (Fig. 4(a) and (b)) look almost identical and this indicates that emission in both the cases occurs from the same level of the S_1 surface, and this is possible only if both the bands correspond to 0_0^0 transitions of the two isomeric species. Two notable differences in the two spectra are with respect to the presence of the weak 76 cm^{-1} band only in Fig. 4(a) and the features around 400 cm^{-1}. The DFT-predicted 76 cm^{-1} vibration has already been described and is shown in Fig. 3. The bands near 400 cm^{-1} correspond to vibrations that involve both the in-plane deformation (benzene 6*a* type) of the phenyl ring of the 3-FBA moiety and the intermolecular hydrogen bond vibrations (mostly stretching type). DFT calculation shows that frequencies of the two modes in this region are extremely sensitive to the identity of the isomeric species. In conformer-I, the predicted frequencies, 390 and 407 cm^{-1} (Fig. 5(a) and (b)), are in excellent agreement with the observed bands at 393 and 406 cm^{-1} in the DF spectrum in Fig. 4(a). Similarly, for the conformer-II, the predicted frequencies 377 and 418 cm^{-1} (Fig. 6(a) and (b)) agree nicely with the observed bands at 378 and 420 cm^{-1} in the DF spectrum of Fig. 4(b). Such agreements between the theory and experiment for the conformation-sensitive vibrations aid to making absolute assignment of the measured spectra to specific conformational isomers. Thus, we assign the band labeled 0 in the excitation spectrum (Fig. 2(a)) to the electronic origin of conformer-I, and the band labeled 24 to the origin of conformer-II. The assignments of the other vibrations in the two dispersed fluorescence spectra have been presented in Table II.

On the other hand, the emission spectral pattern in Fig. 4(c) looks different from the other two. The band at the excitation position (shown by an inverted arrow) is weaker, and the strongest band in the spectrum appears at a displacement of 76 cm^{-1}. This band behaves as a sequence origin, i.e. all the other bands in this spectrum can be assigned as the built-up over the vibronic spectrum in Fig. 4(a). Some of the major features are indicated by the inclined dotted lines. This confirms that the 73 cm^{-1} band in the excitation spectrum is the vibronic transition corresponding to the hydrogen bond mode of conformer-I.

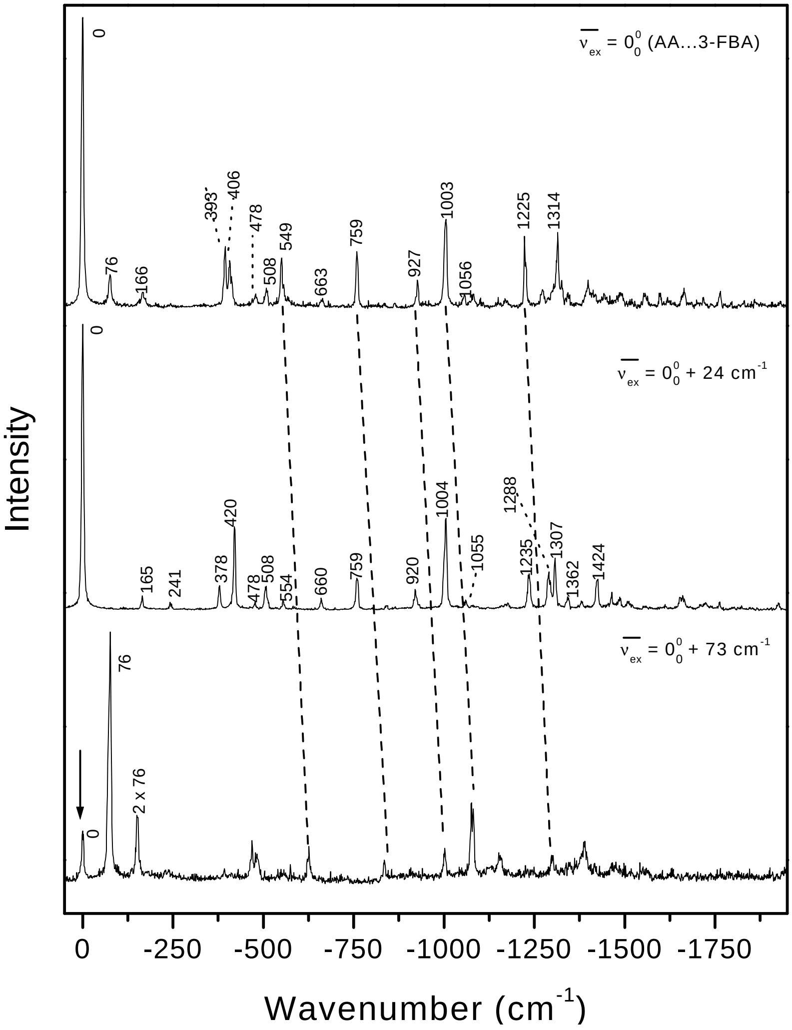


FIG. 4. Comparison of the dispersed fluorescence spectra of the (a) 0, (b) 24 and (c) 73 cm^{-1} bands of the mixed dimers.

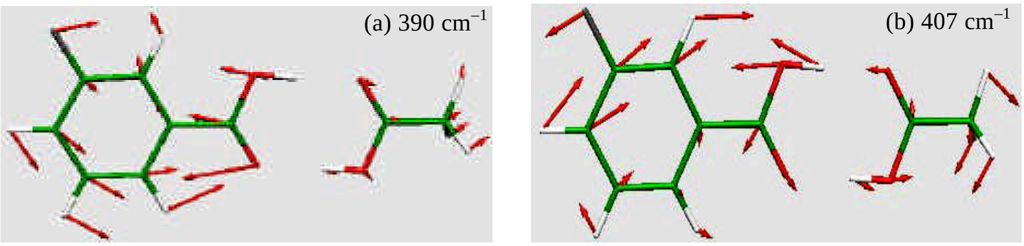


FIG. 5. The normal mode description of a vibrational mode in the two isomers of the dimer. This mode is sensitive to conformation and has been used as pointers for absolute assignments of the measured spectra.

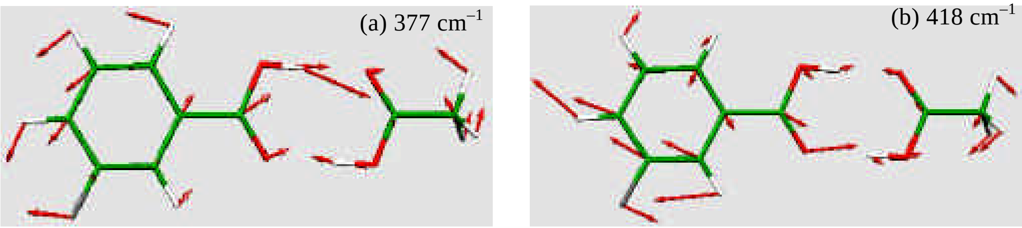


FIG. 6. The normal mode description of a second vibrational mode in the same spectral region for two isomers of the dimer. This mode is also found to be sensitive to conformation.

The DF spectra measured by exciting the two lowest frequency ring vibronic bands of the dimer (0_0^0 + 376 and 0_0^0 + 396 cm^{-1}) are presented in Fig. 7. The bands in both the spectra look unusually broad, given that the excess vibronic energy of the excited levels in the S_1 surface is reasonably low. In contrast, the emission spectrum of the formic acid···3-

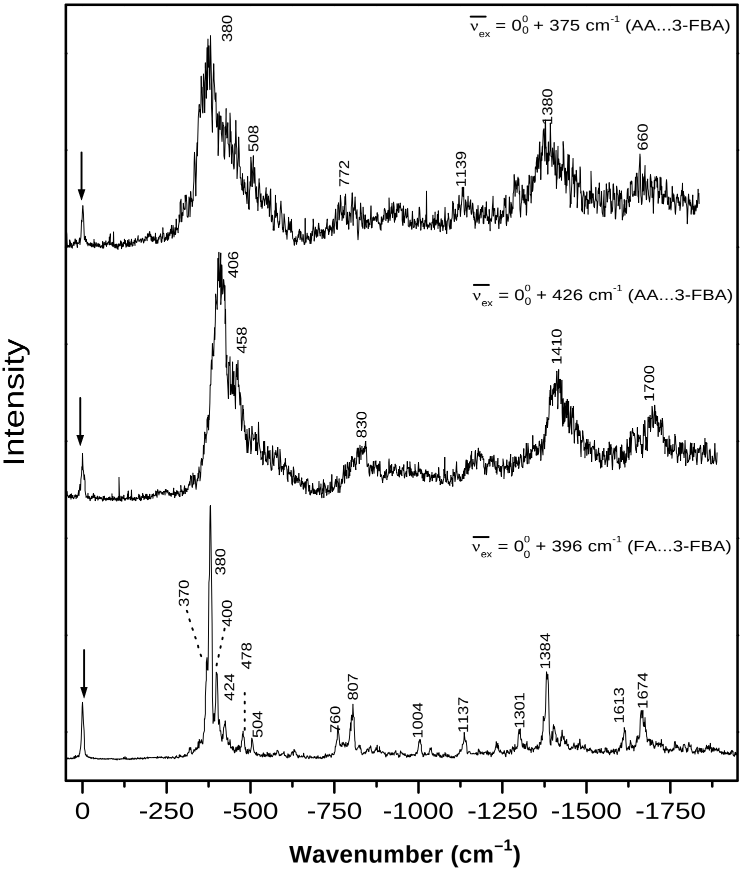


FIG. 7. Comparison of the dispersed fluorescence spectra for excitations with similar excess vibronic energy of the (a, b) AA···3-FBA mixed dimer with that of (c) FA···3-FBA dimer.

fluorobenzoic acid mixed dimer (FA···3-FBA), measured by exciting with similar excess vibronic energy (375 cm^{-1}) in the S_1 surface, looks very different (lower trace). Unlike the broad features in the first two spectra, the latter exhibits only sharp features. The spectral broadening in the first two cases is the typical signature of vibrational redistribution from the levels excited. The spectral contrasts of the two dimeric species indicate that the large-amplitude internal motions of methyl group of the acetic moiety in AA···3-FBA is responsible for the vibrational level mixing in the aromatic chromophore. The results also demonstrate that the doubly hydrogen-bonded interface in the dimeric system behaves as an efficient conduit to propagate the rotor effects. Such behavior of the rotor group and hydrogen-bonded interface has been demonstrated in other systems as well [8, 15].

An interesting point of the vibronic features of spectra of the dimer presented above is that the transitions involving the methyl group do not gain Franck–Condon intensity in either the FE or DF spectra. Burneau *et al.* [24] have reported recently that the DFT-predicted frequency for the internal rotational motion of the free acetic acid monomer is 73 cm^{-1}. In the doubly hydrogen-bonded acetic acid dimer, the frequency is decreased to 52 cm^{-1}. However, in the present AA···3-FBA dimeric system no band around 50 cm^{-1} has been identified in the DF spectra of the S_1 origins (Fig. 4 (a, b)) in either of the two isomers. One obvious reason is that the 0–1 vibronic transition involving this mode is forbidden due to spin conservation. However, the absence of any sequence transition involving this mode in the measured spectra indicates that the background levels to which the excitation energy flows from the optically active levels are significantly coupled with the rotor mode. Such coupling becomes efficient because of comparable energies of the rotor and inter-moiety hydrogen bond vibrations.

The mechanism of the observed spectral behaviour can be understood in the following way. The hydrogen bond pattern in the cyclic interface of the dimer (Fig. 1) shows that a carboxyl group behaves both as a hydrogen-bond donor and as an acceptor. It is known that on $S_1 \leftarrow S_0$ electronic excitation, the acidic character of aromatic carboxylic acids is reduced, i.e. the hydrogen bond donor property is decreased. On the other hand, the basic character, i.e. the tendency to accept the hydrogen bond at the oxygen atom of the C=O sub-group is enhanced [25]. As a result, one of the two H-bonds of the cyclic interface, for which the BA moiety is the H donor, is weakened, but the other, for which it is H acceptor, is strengthened. This leads to distortion of the geometry of the cyclic H-bonded interface of the dimer in the S_1 surface [20], and also possibly causes some redistribution of the partial charges on H and O atoms of the carboxyl group of the AA moiety. Some torsional adjustment of the rotor group must be required in this new environment and this induces coupling of the rotor mode with the other hydrogen bond modes.

Excitation of the $0_0^0 + 737$ cm^{-1} band of the dimer generates only broad and red-shifted emission spectrum, and the measured spectra (not shown here) look almost the same for both the isomeric species. Thus, the dispersed fluorescence measurements do not indicate whether the IVR rate in the two isomers are the same or different at this vibronic level. A time-resolved study would be extremely helpful to resolve this issue. However, as pointed out earlier, the peak height of this band with respect to the electronic origin (0_0^0) is smaller in the case of the conformer-II than to conformer-I. Furthermore, the band in the former is broader than the latter. The line shapes of the bands in a frequency-resolved spectrum may appear different because of trivial reasons like overlapping of the two bands. However, in the present case, a simultaneous intensity-decrease and broadening of bandwidth indicate that most probable reason for these spectral changes is dynamic rather than structural.

4. Conclusion

Two isomeric species of the 1 : 1 mixed dimer between acetic acid and 3-fluorobenzoic acid have been identified in a supersonic jet expansion by the use of laser-induced fluorescence excitation and dispersed fluorescence spectroscopy. The spectral features indicate that the $S_1 \leftarrow S_0$ electronic excitation induces the geometry distortion of one of the isomeric species along the coordinate of an intermolecular hydrogen bond vibration. The ground-state frequency for the mode is 76 cm^{-1}, and with the aid of DFT calculation, we have assigned the mode to in-plane rocking vibration of the 3-FBA moiety at the cyclic hydrogen-bonded interface. The calculations predict that the hydrogen bond energies of both the isomers in the ground electronic state are the same. The 0_0^0 transitions of the two isomers appear different in the FE spectrum because of differences in the Franck–Condon factors of the two transitions. Assignments of the vibronic bands in the dispersed fluorescence spectra for a particular conformer are suggested by correlating the observed frequencies with the predicted normal mode frequencies. The spectral features indicate that the dimer exhibits very low threshold of IVR on the S_1 surface. A comparative study with a 1 : 1 dimer between formic acid and 3-fluorobenzoic acid reveals that the methyl group of the acetic acid moiety is responsible for acceleration of level mixing. Such effect of the methyl group, over a long range, is mediated by the doubly hydrogen-bonded dimer interface.

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