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Impact of Methyl Rotor in the Excited State Level Mixing of Doubly Hydrogen-Bonded Complexes of 2-Pyridone

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We have presented in this paper the laser-induced fluorescence excitation and resolved fluorescence spectra of five 1:1 hydrogen-bonded complexes of 2-pyridone (2PY) with formic acid (FA), acetic acid (AA), propanoic acid (PA), formamide (FM), and acetamide (AM). The resolved fluorescence spectra, measured following excitation to different single vibronic levels of the dimers indicate that the intermolecular hydrogen bond vibrations undergo mixing with a number of intramolecular modes of the 2PY moiety in the excited state. A comparison of the emission spectral features of these dimers clearly indicates that the methyl groups belonging to the AA and AM moieties spectacularly accelerate the vibrational energy redistribution (IVR) in the 2PY moiety. On the other hand, although the molecular size of PA is bigger than AA, the spectral features of the 2PY−PA dimer bear signatures of a slower IVR rate compared to those of 2PY−AA. We propose that hyperconjugation of the methyl group with the cyclic hydrogen-bonded network involving AA and AM is responsible for the observed phenomenon.

1. Introduction

It is known from many experimental and theoretical investigations of the past three decades that intramolecular vibrational energy redistribution (IVR) in an aromatic chromophore can be accelerated by a methyl group.[1−22] In most of those studies, the methyl group is attached directly to an aromatic site of the molecules considered. On the other hand, we demonstrated recently that in a dimeric molecular complex, the accelerating affect of the methyl group belonging to one molecular moiety can even be conveyed to the aromatic chromophore of an other moiety through a hydrogen-bonded network of two carboxylic acid groups.[23] The phenomenon was demonstrated by showing comparisons of evolution of the emission spectra following excitations to different vibronic levels in S_1 of the benzoic acid (BA) moiety of two mixed dimers of BA with acetic acid (AA) and formic acid (FA). In both dimeric systems, the Franck−Condon levels correspond to various ring modes of the BA moiety. However, the dynamics of the prepared levels of the two complexes were shown to be different. For example, when excited to the benzenoid $6a^1$ level of the BA moiety, the dimer with formic acid shows only sharp vibronic bands in the emission spectrum, but the bands in the emission spectrum of the BA−AA dimer is dramatically broadened.

To explore whether the phenomenon mentioned above is a general behavior of molecular complexes bound by double hydrogen bonds, we present in this paper a comparison of the emission spectra of five 1:1 complexes of 2-pyridone (2PY) with FA, AA, propanoic acid (PA), formamide (FM), and acetamide (AM) (Figure 1). In the first three cases, the molecular size, vibrational level density with increasing energy and the overall molecular flexibility increase from FA to PA through AA. On the other hand, the methyl rotor in the PA moiety of the 2PY−PA dimer is isolated from the hydrogen-bonded network by a methylene (−CH_2−) spacer. In effect, the electronic influence of the methyl group cannot be transmitted directly to the cyclic hydrogen-bonded interface. Thus, a comparison of the emission spectral behavior of 2PY−PA with those of 2PY−AA and 2PY−FA would allow us to estimate the relative importance of direct electronic interaction of the methyl group with the hydrogen-bonded interface for occurrence of the IVR acceleration process. In the 2PY−FM and 2PY−AM dimers, the functional groups involved in the hydrogen-bonded network are different from the first three cases. The studies with these systems indicate that IVR acceleration by a methyl group mediated by the hydrogen-bonded network does not depend on specific functional groups involved in hydrogen bonding.

2. Experiment

The details of experimental setup used to record the fluorescence excitation (FE) and dispersed fluorescence (DF) spectra have been described before.[24,25] Briefly, the helium gas at a pressure of 2 atm was passed first through a cell containing carboxylic acids or amides, and subsequently through another glass cell containing 2-pyridone maintained at 100 °C. The glass cell containing carboxylic acids was cooled to 0 °C, and when amides were used the cell was heated to 50 °C. The final gas

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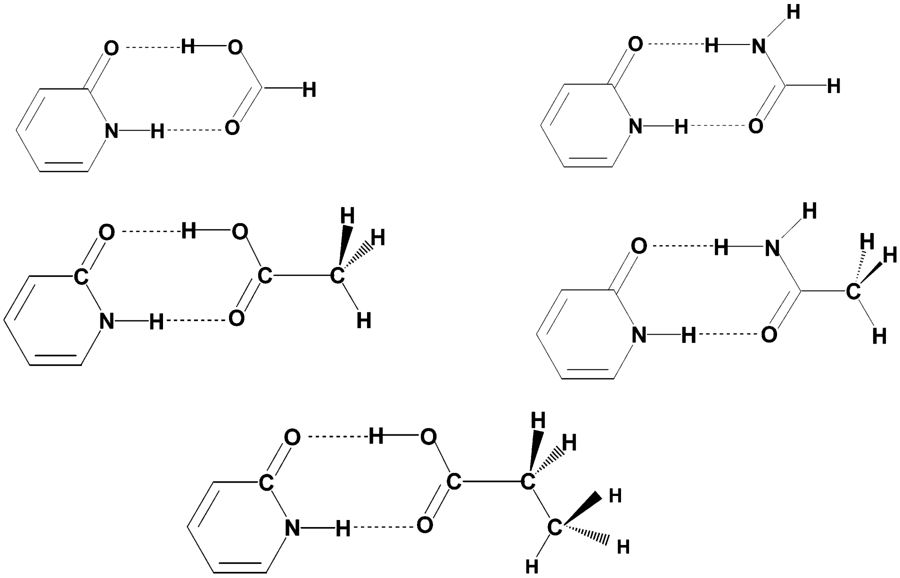

Figure 1. Structures of the doubly hydrogen-bonded dimers of 2-pyridone with (a) formic acid, (b) acetic acid, (c) propanoic acid, (d) formamide, and (e) acetamide.

mixture was expanded into vacuum through a pulsed nozzle (General Valve) of orifice diameter 0.5 mm. The expansion-generated clusters were excited by the frequency-doubled output of a tunable dye laser (Sirah and Plasma Technik, model Cobra Stretch), which was pumped by the second harmonic ($\lambda = 532$ nm) of a Nd:YAG laser (Spectra Physics, model INDI). The laser beam (line width ~0.5 cm^{-1}) intersects the free jet perpendicularly at about 12 mm downstream of the nozzle orifice, and the emission is collected from the intersection point in a direction perpendicular to both the laser and free jet. For measurements of a FE spectrum, total fluorescence was detected by a Hamamatsu R928 photomultiplier tube. The output signals of the PMT were processed by a boxcar averager (model RS250, Stanford Research Corporation). The averaged output of the boxcar was stored in a computer using a home-built data acquisition system. To measure the DF spectra we have used a 0.75 m monochromator (Spex, model 750 M) equipped with a grating of groove density 2400/mm and a double staged Peltier cooled ICCD (Jovin Yvon, Model No. 3000V) detector. The spectra presented in this paper were recorded with a monochromator of resolution 6 cm^{-1}.

3. Results and Discussion

(i) FE Spectra. The FE spectra for $S_1 \leftarrow S_0$ excitations of the mixed dimers are presented in Figure 2 . We have noticed that the relative intensities of the bands in each spectrum are practically insensitive to the changes of carrier gas pressure of the nozzle as well as the sample concentrations in the pre-expansion gas mixture. This indicates that the bands displayed in these spectra are due to mixed dimers, and there is no contribution from higher sized clusters to these spectral features.

The 0_0^0 origin bands of these dimers display large blue shifts compared to that of the 2PY monomer, and these shifts for 2PY−FA, 2PY−AA, 2PY−PA, 2PY−FM, and 2PY−AM dimers are 1232, 1134, 1120, 755, and 707 cm^{-1}, respectively, from the "A" origin band of the 2PY monomer.[26] In this spectral region, the vibronic bands of the monomer are extremely weak compared to the dimer bands, and we could not detect any band that belongs to the monomer spectrum. Furthermore, below 200 cm^{-1}, each dimer spectrum shows several prominent low-frequency bands, whereas the lowest frequency vibronic transition in the FE spectrum of the 2PY monomer[26] appears at 217 cm^{-1}. Therefore, the low-frequency vibronic features in the dimer spectra can be assigned to intermolecular modes, and these assignments have been found to be consistent with the DF spectra measured following excitations of these bands. The frequencies as well as relative intensities of these features look different in the five spectra. The differences could arise for two reasons. A very obvious one is the differences in molecular weights of the carboxylic acids and amide moieties. The second

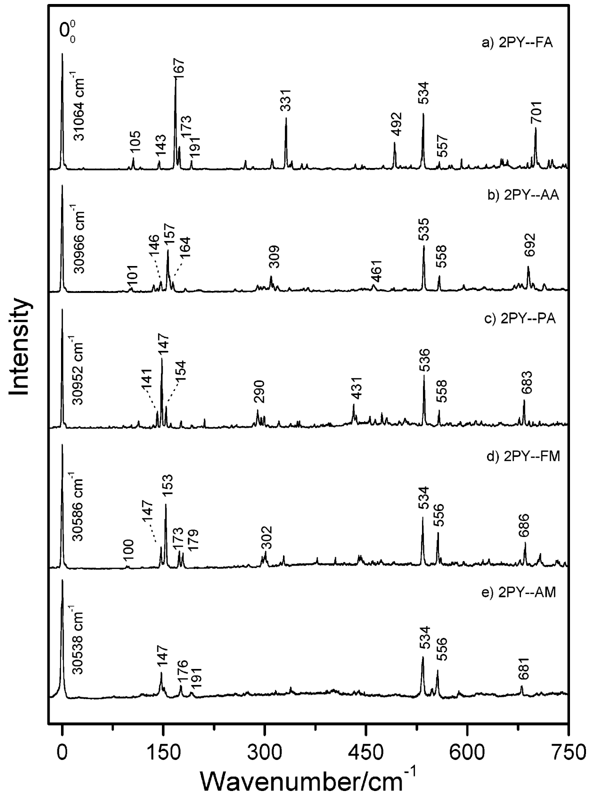

Figure 2. First 750 cm^{-1} of the fluorescence excitation spectra for $S_1 \leftarrow S_0$ electronic transitions of (a) 2PY−FA, (b) 2PY−AA, (c) 2PY−PA, (d) 2PY−FM, and (e) 2PY−AM, mixed dimers in a supersonic free jet expansion. The horizontal scale corresponds to vibronic energy of the dimers with respect to the 0_0^0 transition frequencies.

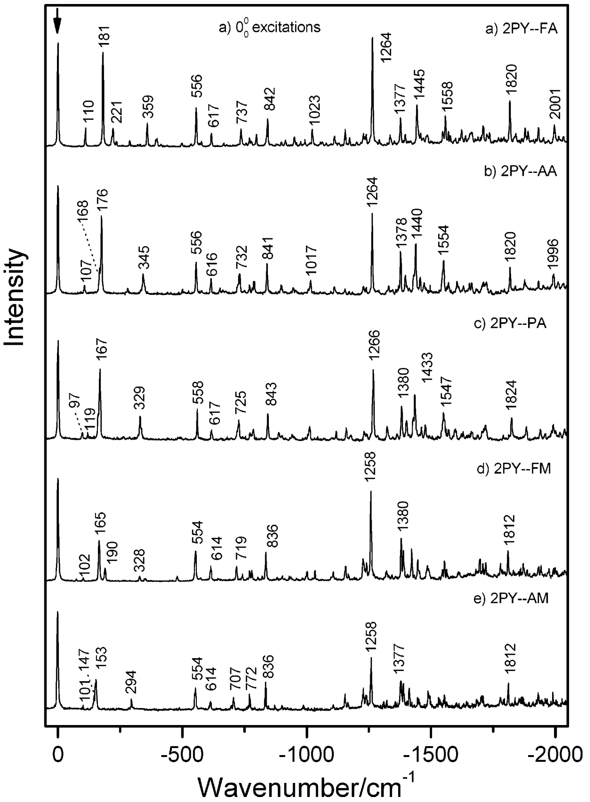

Figure 3. Dispersed fluorescence spectra of the five dimers measured following excitations of their $S_1 \leftarrow S_0$ electronic origin (0_0^0) bands. The horizontal scale corresponds to displacements of the emission spectral bands in cm^{-1} unit from the corresponding excitation frequency.

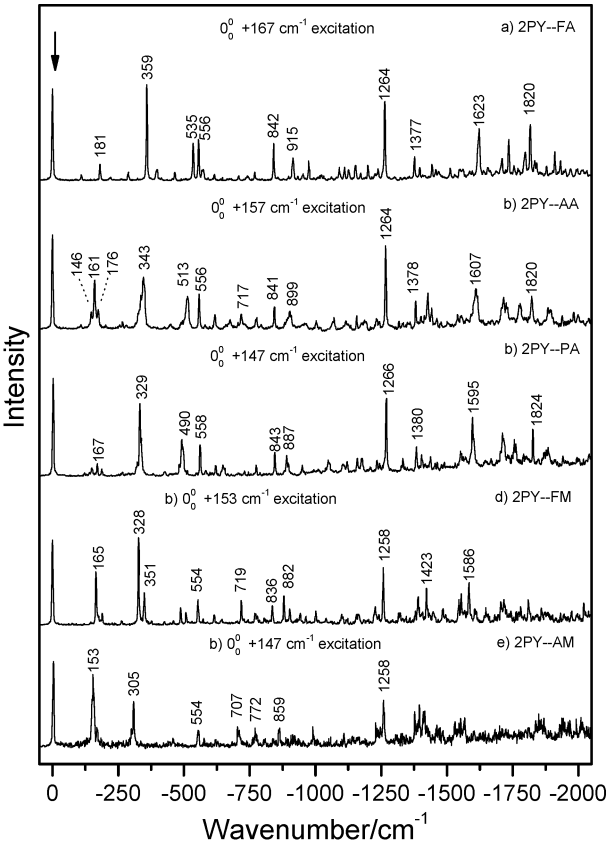

Figure 4. Dispersed fluorescence spectra recorded following excitations of the most intense intermolecular vibronic bands of all the dimers. The horizontal scale corresponds to displacements of the emission spectral bands in cm^{-1} unit from the corresponding excitation frequency.

reason, which is more subtle, is due to differences in coupling of the low-frequency modes associated with AA, AM, and PA moieties with the intermolecular hydrogen bond modes of the dimers. Such coupling should be absent in the dimers with FA and FM. The signature of such coupling should be manifested in the DF spectra, and below we present such spectra measured following excitations to different vibronic levels of the dimers.

(ii) DF Spectra. The spectra measured following excitation of their 0_0^0 origin bands of all the dimers are presented in Figure 3. The vibronic features look somewhat similar to those in the FE spectra. Thus, the bands of frequencies more than 550 cm^{-1} look similar in all the spectra, but the low-frequency features ($<$500 cm^{-1}) are significantly different. In the first case, the bands are mostly due to intramolecular modes of the 2PY moiety, the frequencies of which appear to be affected very little by the second moiety. Recently, we reported the detailed assignments of the spectra of 2PY−FA and 2PY−FM mixed dimers.[27,28] The low-frequency bands were assigned to different intermolecular modes and the observed frequencies match quite satisfactorily with those predicted by the DFT/B3LYP/6-311++G** level of theory. The assignments of the other spectra will be reported elsewhere.

Figure 4 shows the DF spectra recorded following excitations of the most intense intermolecular vibronic bands of the five dimers, which appear near 150 cm^{-1} energy of the 0_0^0 origin bands. This band has been assigned earlier to intermolecular stretching (ν) type at the hydrogen-bonded interface.[25,28] An important feature of these spectra is appearance of a large number of prominent $\nu_0^1 n_1^0$ type cross-sequence transitions in addition to the expected ν_1^1 type sequence transition, where n corresponds to any mode other than ν. For example, in the case of 2PY−FM complex,[28] the fluorescence spectrum measured following excitation of the 0_0^0 + 153 cm^{-1} band shows sequence transition at 165 cm^{-1} displacement. In addition, prominent cross-sequence transitions appear corresponding to the intramolecular vibrational modes of frequencies 554, 836, and 1258 cm^{-1} of the 2PY moiety, and the same spectral pattern is repeated in case of other dimeric species. This indicates that in the excited state, the hydrogen bond modes undergo extensive mixing[29] with the intramolecular modes of the 2PY moiety. The most likely reason for occurrence of this phenomenon is the distortion of the geometry of 2PY moiety as well as the cyclic hydrogen-bonded interface on $S_1 \leftarrow S_0$ electronic excitation, and the normal mode description in terms of internal coordinates are not same in the two electronic states. In other words, some modes in the S_1 state can be described in terms of (linear combination) ground state normal modes. Distortion in geometry in the excited electronic state has been inferred recently for the 2PY monomer[30] as well as hydrogen-bonded complex of 2PY with water.[31]

In Figure 5 we have presented the DF spectra measured by exciting the dimers to $6a^1$ vibronic level (~535 cm^{-1} above the 0_0^0 band, Figure 2) of their 2PY moiety. The most important feature of these spectra is appearance of dramatically different spectral bandwidths of the 2PY−AA and 2PY−AM dimers compared to that of 2PY−FA and 2PY−FM. The fwhm in case of 2PY−AA is nearly 30 cm^{-1}, whereas the same for 2PY−FA complex is only 6 cm^{-1}, which is determined by resolution of the monochromator. On the other hand, the emission bands of the 2PY−PA dimer are distinctly sharper (fwhm ~ 13 cm^{-1}) compared to those of the 2PY−AA and 2PY−AM dimers. This spectral broadening is a clear manifestation of excited state IVR and absence of such feature in the

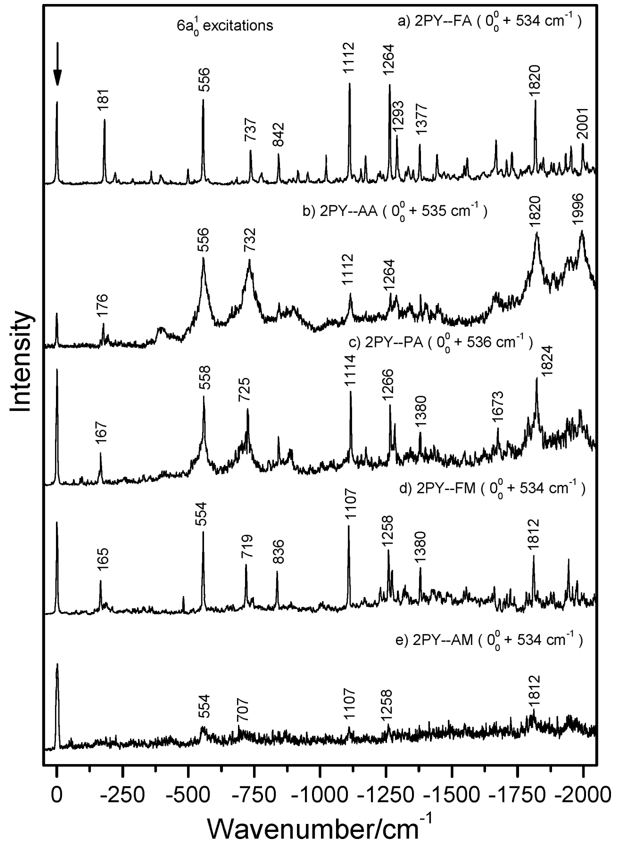

Figure 5. Dispersed fluorescence spectra of the five dimers recorded following excitations to 6a$_0^1$ level of the 2PY moiety. The horizontal scale corresponds to displacements of the emission spectral bands in cm^{-1} unit from the corresponding excitation frequency.

emission spectra of 2PY−FA and 2PY−FM indicates that the methyl group in the former two cases is responsible for occurrence of the observed differences. Appearance of relatively sharper bands in the emission spectrum of 2PY−PA indicates that the ethyl group of PA is less effective compared to the methyl group of AA in promoting the process responsible for the spectral broadening, although, the size of 2PY−PA complex is largest and it is likely to have the largest density of states at the excited levels with similar energies among the five cases.

A second feature is the prevalence of cross-sequence transitions involving both the low-frequency hydrogen bond modes and higher frequency intramolecular modes of 2PY moiety. For example, in case of 2PY-FM complex, the vibronic band at 554 cm^{-1} displacement can be assigned as $6a_1^1$ sequence transition, and 165 cm^{-1} band as $6a_0^1\nu_1^0$ cross-sequence transition, where ν denotes the intermolecular stretching mode. The other cross-sequence bands at 719, 836, 1107, 1258, and 1380 cm^{-1} can be corresponded to $6a_0^1n_1^0$ type transitions, where n denotes the intramolecular modes of the 2PY moiety. The assignments of these bands have been discussed in recent publications from our group.[28]

We propose the following mechanism for the observed process. In Figures 4 and 5, the cross-sequence vibronic features reveal that as on $S_1 \leftarrow S_0$ electronic excitation the intramolecular modes of 2PY moiety are mixed with the low-frequency hydrogen bond modes of the dimeric interface. Thus, the second moiety of the dimer is electronically coupled with the 2PY system. In other words, the electronic conjugation of 2PY ring is extended over all the atoms of the hydrogen-bonded interface. Because the methyl groups in the 2PY−AA and 2PY−AM dimers are directly linked with the carbon atom belonging to the cyclic hydrogen-bonded network, they could be electronically coupled with the latter via hyperconjugative mechanism. The mechanism has been invoked in many cases earlier to explain the internal rotational barrier of the methyl group attached with other chromophores.[13] However, such hyperconjugation of the terminal methyl group in the PA moiety of 2PY−PA is suppressed because of the intervening methylene spacer.

It is of course worth mentioning that the emission spectra of the 2PY−AA or 2PY−AM dimers do not display any vibronic feature that can be assigned directly to torsion or any other mode of the methyl group. This indicates that the relative orientation of the methyl group with respect to the hydrogen-bonded interface is the same in both S_0 and S_1 electronic states, and the rotor modes are not directly excited at the Franck−Condon levels. However, the rotor modes can contribute to IVR acceleration via second and higher tiers of mixed levels;[18] i.e., the background levels to which the excitation energy from the Franck−Condon levels flows are modified by the methyl group directly attached with the hydrogen-bonded interface. Recently, we reported the occurrence of efficient IVR acceleration by the methyl group in the excited electronic state of *p*-vinyltoluene (pVT) cooled in a supersonic jet expansion.[22] The role of the methyl group in the process was demonstrated by showing comparison of emission spectra of the molecule with those of vinylbenzene and *p*-fluorovinylbenzene. The DF spectra of pVT, measured following excitations of different vibronic bands, do not show direct signatures of coupling of the rotor mode with other modes at the Franck−Condon levels in the excited state. However, its role in the emission line-broadening process was shown to be unambiguous. Thus it was invoked that the rotor mode must have been involved in the IVR process via the higher tiers of mixed levels.

4. Summary

In summary, the results demonstrated in this paper and in earlier publications from our group[23,32] indicate that hydrogen bond mediated IVR acceleration by a methyl group in the excited electronic state of an aromatic chromophore is a general molecular phenomenon. On the basis of the observed differences in emission spectral features between the 2PY mixed dimers of acetic acid and propanoic acid, we infer that hyperconjugation of the methyl group with the hydrogen-bonded interface is the most likely mechanism for coupling between the two groups. To our knowledge, such an effect in the ground electronic state has not been investigated yet and it is highly desirable to initiate experimental studies in this direction.

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