Spectroscopy and Structure of 2-Hydroxyquinoline

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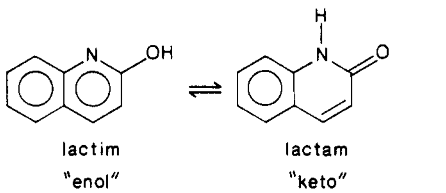
The two-photon time-of-flight mass spectroscopy (TOFMS), fluorescence excitation spectrum, and dispersed emission spectra of 2-hydroxyquinoline are reported. Absorption and emission spectra from both the lactim (2-hydroxyquinoline) and the lactam (2(1*H*)-quinolone) tautomers are observed. The origins for the lactam and lactim forms are 29 112 and 31 349 cm^{-1}, respectively. No evidence of excited-state proton transfer in the lactim with up to 2800 cm^{-1} of excess vibrational energy can be found.

Introduction

2-Hydroxyquinoline (2-HQ) is known to exist as two tautomeric forms which are nearly equal in energy. These tautomers are referred to as the lactim and lactam (or enol and keto) forms



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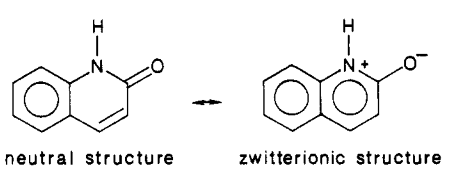
and are interconverted by simple hydrogen atom transfer between the oxygen of the O–H group and the ring nitrogen. The spectroscopy of 2-HQ is of interest because of this tautomerization. Similar proton-transfer processes which are important in many biochemical systems[1] may be modeled and elucidated by studying the comparable process in 2-HQ: a complete characterization of the dynamics and energetics of tautomerization in 2-HQ would therefore not only shed light on the 2-HQ system but would serve as a general guide for the understanding of other systems.

A different set of energetics governing the equilibrium of eq 1 is expected in the ground and electronically excited states; however, little experimental data are available on the energetics, structure, or spectroscopy of the tautomeric forms of 2-HQ. Gas-phase calorimetric measurements[2] show that the lactim form is more stable than the lactam by 0.3 kcal/mol; however, the solvated lactam form is stabilized by a zwitterionic resonance structure. In this zwitterion, the nitrogen would carry a positive charge and the singly bonded oxygen would carry a negative charge as depicted in eq 2. Polar solvents should stabilize this

2–HQ lactam



(2)

zwitterionic resonance form and decrease the energy of the lactam relative to the lactim tautomer. In water, the lactam form is thought to be more stable[3,4] by about 5 kcal/mol. The latter can only be represented as the aromatic naphthalene-like structure and thus has no other resonance structures available to it.

The extent to which the two structures in eq 2 are mixed can be shown by examining the molecular structure of the lactam tautomer. For example, if the zwitterionic structure were predominate, one would expect that the C–C and C–N bond lengths would be roughly those of the aromatic pyridine[5] (1.39 and 1.34 Å, respectively). All bond angles would then be about 120°. If the neutral structure were more important, bonds with lengths similar to single C–C bonds (1.50 Å), double C–C bonds (1.33 Å), aromatic C–C bonds (1.39 Å), and single C–N bonds (1.45 Å) would be expected. One might also expect the bond angles to deviate slightly from 120°. Although no molecular structures are available for the tautomers of 2-HQ, the bond lengths of the lactam form have been calculated by semiempirical methods.[6] These results show that all the bond lengths in the benzenoid ring are roughly those of an aromatic ring (1.39 Å); however, in the heterocyclic ring the bonds drawn as single C–N bonds, single C–C bonds, and double C–C bonds have distances of about 1.39, 1.46, and 1.36 Å, respectively. The values are halfway between those expected for the neutral and zwitterion structures. Similar results are calculated for hydroxypyridine, for which ab initio[7] and experimental[8] structures are available. Thus, the electronic structure of the lactam tautomer contains significant contributions from both the neutral and the zwitterion forms shown in eq 2: the aromatic π cloud is delocalized over the oxygen atom as well as the two rings.

The above additional resonance delocalization results in a π–π* transition of the lactam tautomer that is lower in energy than the comparable transition of the lactim tautomer. This conclusion follows from a very simple particle in a box model of the π electrons in an aromatic system; that is, the larger the box, the lower and more closely spaced are the energy levels. Similar arguments can be made for 2-hydroxypyridine for which the π–π*

TABLE I: $\pi\pi$* Origins of Substituted Naphthalenes and Related Molecules

molecule	energy, cm^{-1}	wavelength, nm	ref
naphthalene	32019	312.31	12
1-methylnaphthalene	31773	314.73	13
2-methylnaphthalene	31705	315.41	13
1-fluoronaphthalene	31622	316.23	14
2-fluoronaphthalene	31514	317.31	14
1-chloronaphthalene	31421	318.25	14
2-chloronaphthalene	31572	316.73	14
1-bromonaphthalene	31347	319.09	14
2-bromonaphthalene	31150	321.02	14
1-naphthol	31457	317.89	15
2-naphthol	30587	326.93	16
	30905	323.57	16
isoquinoline	31929	313.19	17, 18
quinoline	32192	310.63	17
7-hydroxyquinoline	30520	327.65	19
	30853	324.11	19
2-hydroxyquinoline	29112	343.50	this work
	31342	319.06	this work

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transitions are observed[2,9,10] at ca. 279 and 337 nm for the lactim and lactam forms, respectively. The origins of the two 2-HQ transitions should not be split by as much as in 2-hydropyridine, since the additional delocalization should have less of an effect in the two-ring system than in the one-ring system. This was shown experimentally by Cook et al.,[3,11] who measured the ring aromaticity of both tautomers of 2-hydroxypyridine and 2-HQ. They showed that the difference in aromaticity of the two tautomers was greater for 2-hydroxypyridine than for 2-HQ.

We can further anticipate the energies of π–π^* transitions for the tautomers of 2-HQ. For the lactim form, the transition energy should be near the value for other substituted naphthalenes. Table I collects the π–π^* transition energies[12–19] for several of these molecules. From an average of these values, one would expect the origin of the lactim $S_1 \leftarrow S_0$ transition to occur around 31 000 cm^{-1}. As discussed above, one would then expect that the origin of the comparable π–π^* lactam transition to fall at a lower energy. Furthermore, the splitting between these origins of 2-HQ should be less than it is for 2-hydroxypyridine (5000 cm^{-1}): we can therefore expect the lactam transition to have an energy greater than 26 000 cm^{-1}. This ordering of the transition energies is further confirmed by general trends in excited-state acidities: aromatic ring nitrogens are typically more basic in the π–π^* excited state than in the ground state, and the reverse is true for aromatic alcohols.[20] This results in relative stabilization of the excited-state lactam, reducing the energy of the $S_1 \leftarrow S_0$ lactam transition.

The particular vibronic features expected to be active in the π–π^* transition can also be anticipated on the basis of these resonance structures. Since both tautomers contain significant contributions from naphthalene-like resonance forms, one would expect the vibronic features to be grossly similar to those found in naphthalene or 2-naphthol; that is, intensity in vibrational modes with frequencies of about 400, 700, and 1300 cm^{-1} should be observed.[12,13,16] The lactam spectrum should be more complicated than that of the lactim tautomer, due to contributions from the nonaromatic structure in eq 2. The lactam zwitterion resonance is expected to contribute more in S_1 than in S_0.[21] Therefore, a relatively large geometry change for the lactam can be expected in the $S_1 \leftarrow S_0$ transition which will result in increased vibronic activity.

A further complication to the spectrum of 2-HQ may result from excited-state dynamics. As mentioned earlier, tautomerization in 2-HQ is accomplished by a simple proton transfer. In particular, the first excited state (S_1) of the lactim form may tautomerize to the more energetically stable S_1 state of the lactam form. Figure 1 is a schematic representation of the potential energy curves which could be involved in excited-state proton transfer (ESPT). The ESPT process could evolve as follows. The lactim form is photoexcited from the ground electronic state (S_0) to the π–π^* state (S_1). If enough energy can be localized in the reaction coordinate such that proton barrier crossing or tunneling can occur, the lactam tautomer will be formed in the S_1 excited state. The lactam tautomer could then relax to its ground state

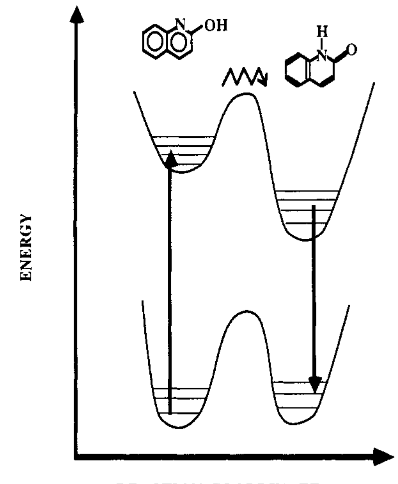

Figure 1. Schematic representation of a possible excited-state proton-transfer (ESPT) process in 2-HQ. The arrow on the left shows excitation from the S_0 state to the S_1 state of the lactim tautomer. The origin of this absorption is at 31 349 cm^{-1}. Excited-state intramolecular proton transfer may occur, forming the lactam tautomer. Conclusive evidence for ESPT would be $S_0 \leftarrow S_1$ emission from the lactam. This transition is represented by the arrow on the right of the figure. The most intense feature of the lactam emission would occur at about 29 100 cm^{-1}.

by radiationless or radiative processes. Such emission would be characterized by a considerable Stokes shift and perhaps the vibronic signature of the lactam tautomer. Little experimental information is available on the potential energy surface of the ESPT reaction. The likelihood of lactim to lactam excited-state proton transfer must therefore be estimated from the available experimental and theoretical results concerning 2-hydroxypyridine. Ab initio calculations[7] have determined that the barrier to proton transfer in ground-state 2-hydroxypyridine is about 50 kcal/mol. One would expect a similar barrier in 2-HQ, and therefore proton transfer should not occur in the ground state near room temperature. Nonetheless, tunneling through the excited-state barrier may be sufficiently facile to allow proton transfer.

In this paper we report the use of high-resolution spectroscopy to identify the vibronic features of the first π–π^* transition in 2-HQ. The absorption and emission spectra obtained by seeding 2-HQ in a supersonic jet expansion are reported and discussed. We identify the spectra of the two tautomers shown in eq 1 and explore the possibility of ESPT for the bare molecule.

Experimental Procedures

The experimental apparatus used in this study has been discussed in detail elsewhere.[22] Briefly, rotationally and vibrationally cold 2-HQ molecules are produced in a seeded supersonic expansion from a high-pressure region (30 psig) to a high-vacuum region (10^{-6} Torr). The expansion gas is He. The cold, isolated 2-HQ molecules are then studied by two-color time-of-flight mass spectroscopy (TOFMS), fluorescence excitation (FE), and dispersed emission (DE) spectroscopies.

In the two-color TOFMS experiments, the expansion is generated through a pulsed nozzle. Samples of 2-HQ are placed inside the head of the nozzle which is heated to 70 °C. The molecular beam is crossed at right angles by the output of two Nd^{3+}:YAG pumped dye lasers. The pump laser is scanned through the vibronic transitions of 2-HQ while the fixed-frequency ionization laser ionizes a 2-HQ from the excited π–π^* electronic state. Resultant ions are detected by a time-of-flight mass spectrometer. Pump and ionization laser energies are 29 000–32 000 and 45 400 cm^{-1}, respectively. When the pump laser is in resonance with a vibronic transition of 2-HQ, a signal is detected in the 146 amu mass channel.

In the FE and DE experiments, the sample is placed in a CW nozzle and heated to 200 °C. A single laser beam crosses the

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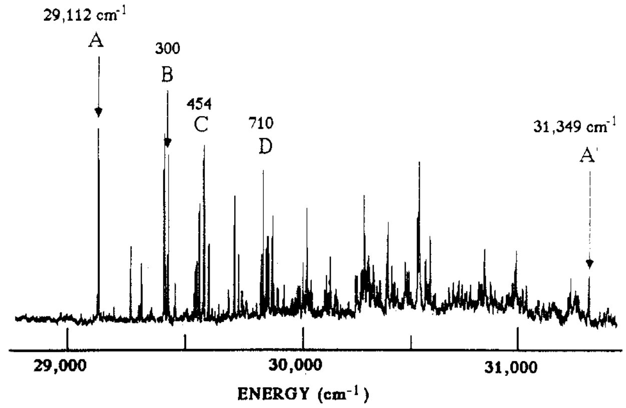

Figure 2. Two-color TOFMS spectrum of 2-HQ taken with a low-temperature (70 °C) pulsed nozzle. Peak A is identified as the origin for the lactam tautomer and has an energy of 29 112 cm^{-1}. The origin of the lactim tautomer is the peak (A′) at 31 349 cm^{-1}. Notice that the intensity of A′ is about a fourth of the intensity of A. The energies (in cm^{-1}) of peaks B, C, and D relative to A are shown.

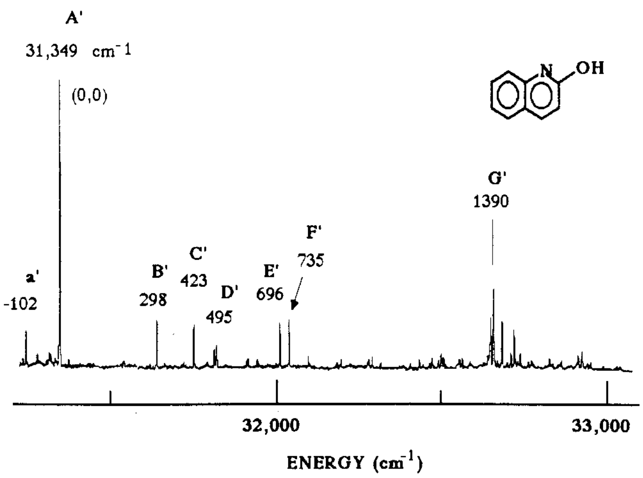

Figure 3. FE spectrum of the high-energy region of the 2-HQ $S_1 \leftarrow S_0$ transition taken with a high-temperature (200 °C) CW nozzle. Peak A′ is the origin of the lactim tautomer and is about 10 times as intense as the origin of the lactam tautomer (see Figure 2 for comparison). The energies (in cm^{-1}) of peaks a′, B′, C′, D′, E′, F′, and G′ relative to A′ are shown.

molecular jet at right angles, and the emission is monitored at right angles to both beams. The total emission intensity is monitored as the laser wavelength is scanned in the FE experiments. In the DE experiments, the laser is tuned to a specific vibronic feature and the emission intensity is monitored as a function of wavelength, analyzed by a 1-m monochromator with a 1200 grooves/mm grating.

Results

The results of the experiments discussed above indicate that the spectra of two distinct species are seen in the supersonic expansion. This will be shown by comparing the TOFMS results to the FE results and by analyzing the vibronic structure of the DE spectra.

The TOFMS of the m/z 146 amu mass channel is presented in Figure 2. Since the ions in this experiments are mass selected, all of the features in this spectrum must be associated with tautomers of 2-HQ. The intensity of the feature at 29 112 cm^{-1} is about 4 times that of the feature at 31 349 cm^{-1}. Figure 3 shows the FE spectrum in the 31 000–33 000-cm^{-1} region. We note that the 29 112-cm^{-1} line is an order of magnitude less intense than the 31 344-cm^{-1} line in the FE spectrum. Figure 3 shows that several features in the FE spectrum appear to be related to the feature at 31 349 cm^{-1} with regard to both intensity and energy spacings. This relation will be explored in the context of the DE spectra.

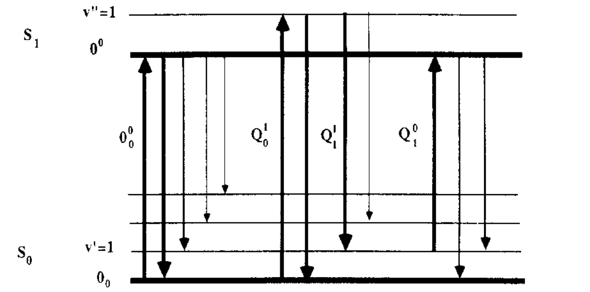

Figure 4. Schematic representation of the DE spectrum which results when the origin is pumped (0_0^0), when an excited vibronic state is pumped (Q_1^0), and when a vibrationally hot molecule is pumped (Q_1^0). The DE transitions are represented by downward arrows to the right of the excitation transitions (the upward arrows). In the absense of large changes in equilibrium geometries, the $\Delta V = 0$ transition in each DE spectrum should be quite intense. For the 0_0^0 excitation the 0_0^0 emission is intense, and for the Q_0^1 excitation the Q_1^1 emission is intense. The energies at 0_0^0 and Q_1^1 should be approximately equal. When the hot molecule is excited, the 0_0^0 transition should be observed in the DE spectrum which is at a higher energy than the excitation energy.

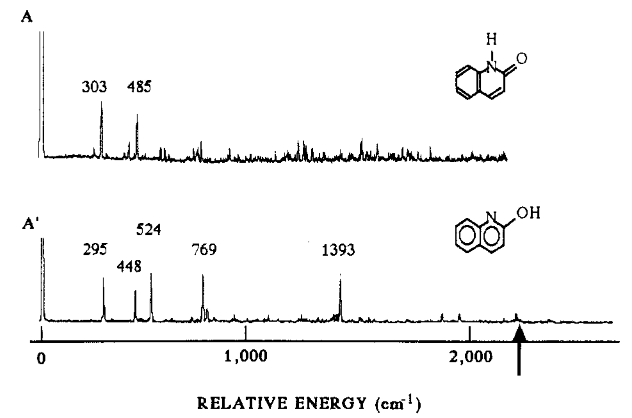

Figure 5. DE spectra which result when peaks A and A′ (see Figures 2 and 3) are excited. The energies (in cm^{-1}) of the peaks relative to the excitation energy are shown. The top spectrum is the emission of the lactam form, and the bottom spectrum is the emission of the lactim form. In the bottom spectrum, the arrow points to the energy (29 112 cm^{-1}) of peak A. Notice that the two spectra are qualitatively different.

Figure 4 illustrates the utility and importance of the DE spectra for identifying the 2-HQ tautomers. The diagram schematically displays the DE transitions in 2-HQ. The horizontal lines on the bottom of the figure represent the vibrational levels of the ground electronic state (S_0), while the lines on the top of the figure represent the vibrational levels of the S_1 excited state. The origin of the excitation spectrum is the the 0_0^0 transition. The DE transitions from this electronically excited state are shown as the downward arrows. The highest energy DE feature following 0_0^0 excitation will correspond to 0_0^0 emission whose intensity may be enhanced due to the presence of scattered laser light. The energy spacings between this transition and the other transitions in the DE spectrum will be indicative of the vibrational energy level spacings in the ground state. In the center position of Figure 4 the DE spectrum following Q_0^1 excitation is illustrated. The DE transitions shown to the right of the Q_0^1 feature include the resonant transition and the Q_1^1 transition. If the equilibrium geometries and vibrational frequencies of the S_0 and S_1 states are quite similar, the Q_1^1 transitions will be an intense feature in the spectrum and will occur at nearly the same energy as the 0_0^0. Therefore, the DE spectra which result from exciting vibrations in S_1 should have strong features (sequence bands) nearly corresponding in energy to the $S_1 \leftarrow S_0$ 0_0^0 transition. Finally, if a vibrationally excited molecule is pumped from the S_0 state to the S_1 state (Q_1^0), emission may occur at higher energy than the resonant transition. This situation ("hot bands") is shown on the right-hand side of Figure 4.

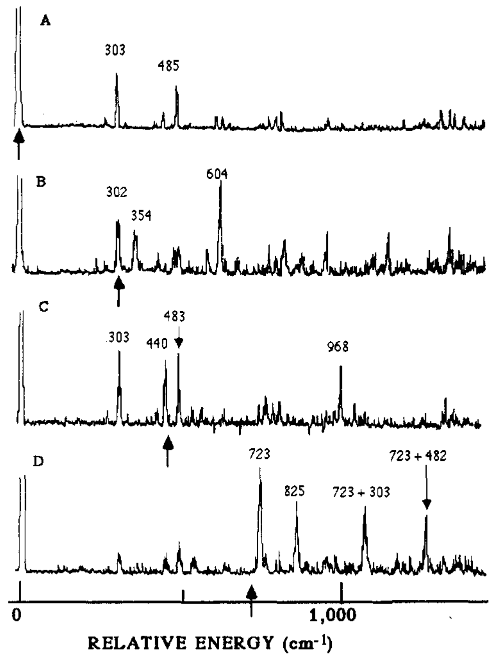

Figure 6. DE spectra of the lactam tautomer which result when peaks A–D of Figure 2 are excited. The energies of the peaks relative to the excitation energies are shown. The upward pointing arrows indicate the energy 29 112 cm^{-1} of the 0_0^0 lactam transition (see Figure 4). Since in each spectrum the arrow is near an intense peak, this must be the energy of the origin of the lactam.

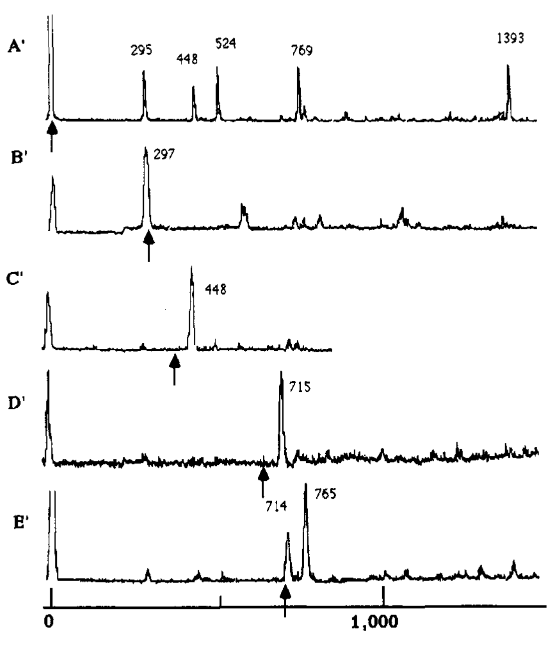

Figure 7. DE spectra of the lactim tautomer which result when peaks A′–E′ of Figure 3 are excited. The energies of the peaks relative to the excitation energies are shown. The arrows show the energy (31 349 cm^{-1}) of the 0_0^0 lactim transition (see Figure 4). In each spectra this arrow is near an intense feature which suggests that this is the energy of the origin of the lactim.

The DE spectra which result from exciting peaks A and A′ in Figures 2 and 3, respectively, are shown in Figure 5. In each spectrum, the energies (in cm^{-1}) of the peaks relative to the resonant transition are also shown. Below the bottom (A′) spectrum, an arrow points to the absolute energy 29 112 cm^{-1}: one would expect to see an intense feature (0_0^0 sequence band) at this energy if A′ were a vibronic feature built on the origin A. Since the A and A′ spectra are very different and since no such intense feature appears at this energy, we conclude that the peaks A and A′ must arise from different tautomers of 2-HQ. Furthermore,

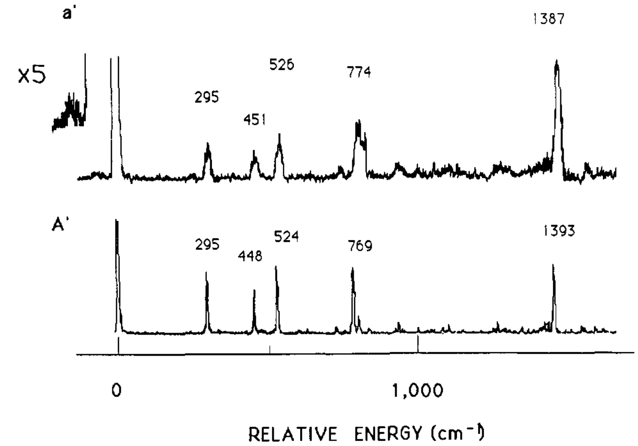

Figure 8. Comparison of the DE spectra which result when peak a′ (top) and peak A′ (bottom) are excited (see Figure 3). The spectra are nearly identical except that in the spectrum on the top a feature is found at higher energy than the excitation energy. (This feature is magnified to the left.) This suggests that peak a′ is a "hot band" built on peak A (see Figure 4).

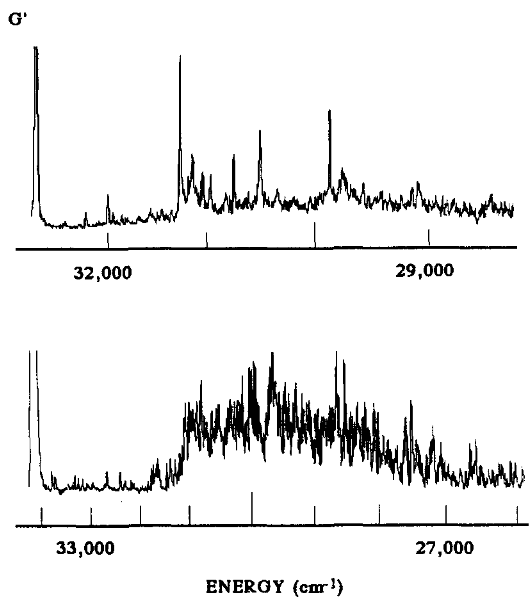

Figure 9. DE spectra which result when two high-energy features of the lactim absorption spectrum are pumped. The top and bottom spectra show the emission which results when features with 1390-cm^{-1} (peak G′ in Figure 3) and 2816-cm^{-1} excess vibrational energy are pumped. No clear onset of intense emission near 29 112 cm^{-1}, which would suggest ESPT, can be observed (see Figure 1).

the DE spectra resulting from the excitation of various features in the excitation spectra show that peaks A and A′ are separate origins. Figure 6 compares the DE which results when peaks A through D of Figure 2 are excited. The dark arrow below each spectrum indicates the absolute energy of 29 112 cm^{-1}. Since all the spectra have an intense feature near this energy, 29 112 cm^{-1} must be the 0_0^0 for this tautomer. In like manner, the DE spectra displayed in Figure 7 point to peak A′ at 31 349 cm^{-1} as an origin. Moreover, when peak a′ (Figure 3) is pumped, some of the emission appears at a higher energy than the resonant transition (see Figure 8). Therefore, peak a′ must arise from vibrationally excited molecules; that is, peak a′ is a hot band associated with the origin transition A′. Additional DE spectra, obtained by exciting higher energy vibronic features of the 31 349-cm^{-1} origin, are shown in Figure 9. These will be discussed below with regard to ESPT.

Discussion

The high-energy portion of the FE spectrum of 2-HQ (shown in Figure 3) can be assigned by comparison to the spectra of other

TABLE II: Vibrational Frequencies (in cm^{-1}) of 2-Naphthol and 2-Hydroxyquinoline

ground state			excited state		
2-naphthol[a]			2-naphthol[a]		
syn	anti	2-HQ	syn	anti	2-HQ
	286	295		286	298
422	424		397	395	423
461	460	448	451	451	486
523	523	524	491	496	495
587		622	498		590
771	773	769	720	719	696
					725

[a] Reference 16.

substituted naphthalenes. Since the electronic structure of the lactim form is similar to these molecules, its $\pi-\pi^*$ origin should have roughly the same energy as those presented in Table I. Therefore, the peak at 31 349 cm^{-1} is assigned as the origin of the lactim $\pi-\pi^*$, $S_1 \leftarrow S_0$ transition. Similarly, the vibronic features in the absorption and emission spectra of the lactim tautomer should be fairly similar to those seen for 2-naphthol.[16] The strong vibronic features in the 2-naphthol spectra are presented in Table II along with the vibronic intervals found for the lactim tautomer. The agreement between these three sets of numbers is good, confirming the assignment. Based on this assignment, the vibrational modes observed in these spectra are undoubtedly ring vibrations.

Since the high-energy absorption can be assigned to the lactim tautomer, we can then assign the low-energy absorption of 2-HQ to the lactam tautomer. As anticipated in the Introduction, the origin of the lactam $S_1 \leftarrow S_0$ transition is less than 5000 cm^{-1} to the red of lactim $S_1 \leftarrow S_0$ transition origin. The vibronic features of the lactam transition are much more complicated than those of the lactim. No attempt to assign these vibrations will be made here.

Having identified the two different tautomeric forms of the 2-HQ molecule, one may attempt to determine whether or not ESPT occurs from the excited S_1 state of the lactim form (0_0^0 at 31 349 cm^{-1}). We expect that the lactim to lactam ESPT process will be characterized by emission similar to that of the lactam (0_0^0 at 29 112 cm^{-1}). However, in general, any significantly red-shifted emission (see Figure 1) might also suggest the occurrence of an ESPT process. Unfortunately, intramolecular vibrational redistribution from highly excited vibronic features (31 349 cm^{-1} plus ca. 2000 cm^{-1}) of the lactim tautomer with no ESPT will also produce broad red-shifted emission. Thus, the observation of broad red-shifted emission after excitation at the lactim 0_0^0 + 2816 cm^{-1} (see Figure 9) is not a decisive indication of lactim to lactam ESPT. Figure 9 does show, however, that proton transfer does not take place upon excitation of the lactim ring modes within ca. 1400 cm^{-1} above the 31 349-cm^{-1} lactim 0_0^0.

Conclusion

Both the lactam and lactim tautomers of 2-HQ exist in the supersonic jet expansion. The energy of the origin of the $\pi-\pi^*$ lactam transition is 29 112 cm^{-1} and of the $\pi-\pi^*$ lactim transition is 31 349 cm^{-1}. No conclusive evidence could be found for excited-state proton transfer in the lactim tautomer with up to 2816-cm^{-1} excess vibrational energy.

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Fluorescence Quenching of a Cationic Porphyrin by Cationic and Anionic Aromatics. Formation of Ground-State Complexes

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Fluorescence of the 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] cation dimer ($(TMPyP^{4+})_2$) in water is quenched statically by 3,6-dimethylacridinium cation (PFl^+) via ground-state complex formation. The temperature dependence of the formation constants, which were determined from the linear Stern–Volmer plots (I_0/I vs [PFl]), indicates that the complexation of $(TMPyP^{4+})_2$ with PFl^+ is an enthalpy-dominating process. The ^1H NMR spectra suggest a face-to-face complex where the hydrophilic part of PFl is spatially directed to the aqueous bulk phase. The van der Waals interaction is assumed as the main binding force for the $(TMPyP^{4+})_2-PFl^+$ molecular complex. For the fluorescence quenching of $(TMPyP^{4+})_2$ by 9,10-anthraquinone-2-sulfonate (AQS^-), however, the relationship between I_0/I and the quencher concentration cannot be explained by the formation of the 1:1 complex of $(TMPyP^{4+})_2$ and AQS^-. The fluorescence lifetime of $(TMPyP^{4+})_2$ is not affected by AQS^-, indicating that no dynamic quenching occurs under the present conditions. The deviation from the simple Stern–Volmer relationship is interpreted as that the fluorescent association complexes of the cationic porphyrin and the anionic dye, $(TMPyP^{4+})_2-(AQS^-)_n$, are formed at lower AQS^- concentrations and the nonfluorescent π-complex, $(TMPyP^{4+})_2-(AQS^-)_{n+1}$, becomes predominant at higher AQS^- concentrations. ^1H NMR reveals the formation of a stacking-type π-complex of $(TMPyP^{4+})_2$ and AQS^-.

Introduction

Recently, a cationic porphyrin, 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium] cation ($TMPyP^{4+}$), became a topical porphyrin because of its ability to be bound with DNA and its related compounds.[1-4] Few fundamental studies on the molecular complex formation of this porphyrin, however, have been carried out. On the basis of the novel fluorescence behavior, we inferred previously that $TMPyP^{4+}$ in water exists as an aggregate form even at very low concen-

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