Hydrogen Bonding in Water Complexes. Structures of 2-Pyridone–H_2O and 2-Pyridone–$(H_2O)_2$ in Their S_0 and S_1 Electronic States

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Abstract: Rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of the mono- and disolvated water complexes of 2-pyridone (2PY) have been obtained. Structures of 2PY–H_2O in its S_0 and S_1 electronic states have been determined from inertial parameters derived by fitting spectra of the protonated species, seven deuterated species, and the ^{18}O-labeled water species. The water molecule forms two planar, nonlinear hydrogen bonds with the amine hydrogen and the carbonyl oxygen of 2PY, in both states. In the ground state, the structure of 2PY is found to change significantly with complexation. These changes are consistent with an increase in the zwitterionic character of 2PY on solvation by water, which decreases on $S_1 \leftarrow S_0$ excitation. 2PY–$(H_2O)_2$ also is planar in both states with respect to the heavy atoms. It exhibits three hydrogen bonds; a linear bond between a water molecule and the amine hydrogen, a linear bond between a second water and the carbonyl oxygen, and a nonlinear bond between the two water molecules themselves. An apparent nonplanarity of the hydrogen bond "bridging" the two water molecules gives rise to separate conformers of 2PY–$(H_2O)_2$. The structural and dynamical properties of these complex structures are discussed.

Introduction

The structural characteristics of small hydrogen-bonded complexes have been the subject of extensive spectroscopic study in recent years.[1] Much of the structural data has been obtained using high-resolution microwave and infrared spectroscopy. The simplicity of these small complexes can be misleading in that although the spectroscopy itself is straightforward, large-amplitude motions resulting from weak hydrogen bonds and tunneling motions between isoenergetic conformations can greatly complicate interpretations of the spectra. Additionally, structural analysis often is restricted by the limited number of observed transitions resulting from the widely spaced rotational energy levels found for small complexes. The H_2O dimer, with one hydrogen bond holding the two water monomers together, is a notable example of a simple system whose tunneling motions produce complicated spectra.[2] However, when H_2O is complexed with N_2O[3] or $(H_2O)_2$ is complexed with CO_2,[4] the feasibility of many of the tunneling motions is diminished as a result of the formation of secondary intermolecular bonds. The added rigidity produced by these bonds simplifies the richer spectra of the larger complexes and their interpretation.

Here, we focus on complexes in which the hydrogen bonds formed with one and two water molecules are strong enough that large-amplitude motions are, in part, restricted by a rigid framework. In this case, the hydrogen-bonded structures are the mono- and disolvated water complexes of 2-pyridone (2PY), the keto form of 2-hydroxypyridine (2HP). The hydrogen-bonding interactions of the peptide functional group of 2PY with one and two water molecules model interactions that play a central role in determining the secondary structures of proteins and nucleic acids. These weak interactions also play an important role in the intermolecular recognition processes that are crucial to most biological systems.

Our study of the monohydrated complex of 2PY, 2PY–H_2O, begins with the establishment of an effective structure calculated from the rotational constants derived from fits of its fully resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum. We find that two hydrogen bonds exist in 2PY–H_2O, a donor O···H–N bond and an acceptor O–H···O bond. The water molecule in 2PY–H_2O thus behaves as both an acid and a base; *i.e.*, it exhibits amphoteric properties. To probe further the structure of the complex, we then observed and assigned the $S_1 \leftarrow S_0$ origin bands of eight isotopically labeled derivatives, including seven deuterated species and the ^{18}O-labeled water species. We derive from these spectra the atomic coordinates of the amine hydrogen, the hydrogen-bonded water hydrogen, the non-hydrogen-bonded water hydrogen, and the water oxygen in both electronic states. We determine the sensitivity of these coordinates to both in-plane and out-of-plane vibrational motions. We find that all three hydrogen atoms are relatively rigidly held in place with respect to in-plane distortions but exhibit larger amplitude out-of-plane motions. We also find that the solute distorts significantly toward a zwitterionic structure when the hydrogen bonds with the solvent are formed.

The high-resolution $S_1 \leftarrow S_0$ fluorescence excitation spectrum of the dihydrated complex 2PY–$(H_2O)_2$ also has been observed. Although isotopic labeling experiments were not performed on this species, the data derived from our analysis of its spectrum are consistent with a structure in which three hydrogen bonds exist; one linking a water molecule to the N—H group, a second linking the second water molecule to the C=O group, and a third connecting the two water molecules together. The first two bonds are planar; the third apparently is nonplanar. Two closely spaced electronic origins are observed in the $S_1 \leftarrow S_0$ spectrum of 2PY–$(H_2O)_2$, suggesting that there are two slightly inequivalent conformations of this structure in the two electronic states. These two conformers apparently differ in the nature of the out-of-plane displacements of the two water molecules.

Experimental Section

2-Hydroxypyridine (2HP), the source of 2-pyridone (2PY), was purchased from Aldrich and used without further purification. In the low-resolution experiments, 2PY–water complexes were formed by seeding

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[●] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

(1) Cohen, R. C.; Saykally, R. J. *J. Phys. Chem.* **1992,** *96,* 1024.

(2) Fraser, G. T. *Int. Rev. Phys. Chem.* **1991,** *10,* 189 and references therein.

(3) Zolandz, D.; Yaron, D.; Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1992,** *97,* 2861.

(4) Peterson, K. I.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1991,** *94,* 106.

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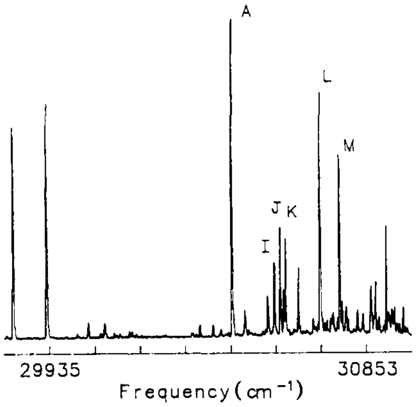

Figure 1. Low-resolution $S_1 \leftarrow S_0$ fluorescence excitation spectrum of 2-pyridone–water in a supersonic jet. The two bands at 29 832 and 29 927 cm^{-1} are the electronic origins of the 2-pyridone (2PY) monomer. Bands A, I, J, and K are vibronic bands of the monohydrated complex of 2-pyridone, 2PY–H_2O. Band L is the electronic origin of the dihydrated complex of 2-pyridone, 2PY–$(H_2O)_2$. Band M is a vibronic band of the 2-pyridone dimer, $(2PY)_2$.

small amounts of water vapor and 2HP into 3–5 atm of helium and expanding the mixture into a vacuum chamber through a 1-mm-orifice pulsed valve (General Valve Series 9) operating at 10 Hz. The concentrations of water vapor and 2HP were controlled by varying the temperature of the respective samples. The water sample was cooled using liquid nitrogen while the 2HP sample was heated to *ca.* 400 K. The complexes were excited by a frequency-doubled dye laser pumped by a Nd^{3+}:YAG laser, also operating at 10 Hz. The spectral resolution of the dye laser is 0.6 cm^{-1}. The signal was detected by a photomultiplier tube (PMT) and processed by a boxcar integrator; a MASSCOMP MCS561 data acquisition system was used to record the data. Relative frequency calibration was performed using a solid etalon (FSR = 1.0 cm^{-1} at the fundamental of the dye).

High-resolution data were obtained using our molecular beam CW laser spectrometer, described elsewhere.[5] The expansion gas was a mixture of water vapor, from a room temperature sample, and about 1 atm of helium. The estimated H_2O vapor concentration in the carrier gas in both the jet and beam experiments is 0.5–1.0%. The 2HP sample was heated to *ca.* 500 K, seeded into the gas mixture, expanded through a 240-μm quartz nozzle, skimmed once, and probed 10-cm downstream of the nozzle by a single-frequency tunable UV laser. Fluorescence was collected using spatially selective optics, detected by a PMT and photon counting system, and processed by the MASSCOMP data acquisition system. Under these operating conditions, the largely Doppler-limited spectral resolution was about 20 MHz in the UV. Relative frequency calibration was performed using a near-confocal interferometer having a mode-matched free spectral range of 299.7520 ± 0.0005 MHz. The absolute transition frequencies in both the low- and high-resolution spectra were determined by comparison to the I_2 absorption spectrum and are accurate to ±30 MHz.

Deuterated 2PY–H_2O complexes were formed by adding a mixture of H_2O/D_2O to the expansion gas. Facile exchange of deuterium with 2PY and H_2O produces complexes with varying degrees of deuteration. The degree of deuteration of 2PY–H_2O was controlled, to some extent, by varying the relative concentration of H_2O and D_2O. The 2PY–^{18}O-labeled water complex was formed by introducing 30% ^{18}O-enriched water (ICON Services Inc.) into the expansion gas.

Results and Interpretation

The fluorescence excitation spectrum of 2PY–water in a supersonic free jet is shown in Figure 1. The two lowest frequency bands at 29 832 and 29 927 cm^{-1} are the electronic origins of two conformers of the 2PY monomer, planar and structurally identical in the S_0 state but differing in the degree of nonplanarity at the nitrogen atom in the S_1 state.[6]

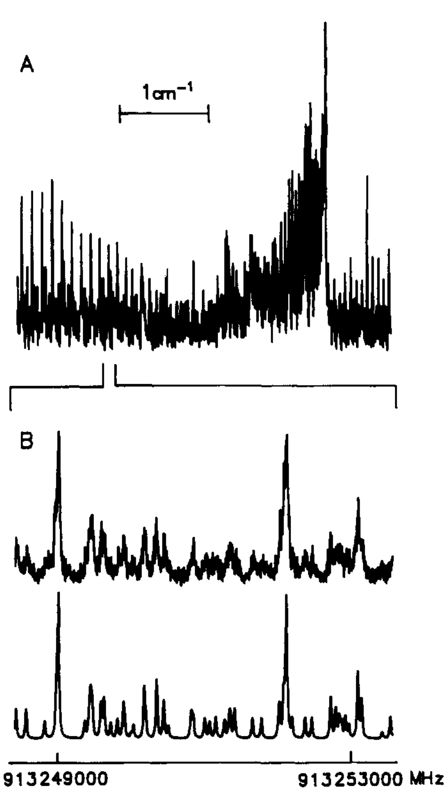

Figure 2. Rotationally resolved fluorescence excitation spectrum of the 2PY–H_2O origin band, band A in Figure 1. Panel B shows a portion of the observed spectrum at full experimental resolution, compared to the corresponding simulated spectrum.

The next strong band, at 30 465 cm^{-1}, is the electronic origin of the single-water complex, 2PY–H_2O, which we call band A. At higher frequency, we find a group of three bands (I, J, and K) that are vibronic bands of 2PY–H_2O. At still higher frequency, there is a group of several bands that include the electronic origin of the double-water complex, 2PY–$(H_2O)_2$ (band L at 30 720 cm^{-1}), and the electronic origin of the 2PY dimer, $(2PY)_2$ (band M at 30 776 cm^{-1}).[7] The frequencies of the monomer and water complex bands are in reasonable agreement with those measured in the previous MPI experiments of Nimlos *et al.*[8]

At higher water concentrations, the 2PY–$(H_2O)_2$ vibronic bands increase in intensity relative to those of 2PY–H_2O. No new bands appear with increasing water concentration. Higher order clusters [2PY–$(H_2O)_n$, $n > 2$] may be too unstable to form in the jet or may exist in so many conformations that no resolved transitions are observed. Comparing the fluorescence excitation spectrum of 2PY–water with the spectrum of 2PY [6,7] shows significant decreases in dimer band intensities relative to the intensities of the monomer bands. Addition of water vapor to the 2HP sample apparently disrupts the equilibrium between the monomer and dimer of 2PY in the jet.

A. 2-Pyridone-H_2O. We have obtained rotationally resolved spectra of four strong bands lying between 30 465 and 30 720 cm^{-1}, bands A, I, J, and L. Described here are the results for the three recorded bands of 2PY–H_2O, bands A, I, and J. Figure 2A shows the high-resolution spectrum of the electronic origin of the $S_1 \leftarrow S_0$ transition of 2PY–H_2O, band A. This band is a *b*-type band; *i.e.*, the $S_1 \leftarrow S_0$ transition moment (TM) lies parallel

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[5] Majewski, W. A.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1989**, *90*, 1362.

[6] Held, A.; Champagne, B. B.; Pratt, D. W. *J. Chem. Phys.* **1991**, *95*, 8732. An error appears in this paper; the correct frequencies of the monomer origin bands are 29 832.301 (A), 29 874.308 (A′), 29 927.394 (B), and 29 955.832 cm^{-1} (B′).

[7] Held, A.; Pratt, D. W. *J. Am. Chem. Soc.* **1990**, *112*, 8629.

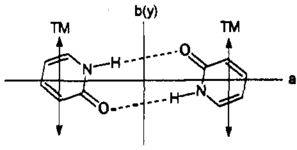
[8] Nimlos, M. R.; Kelley, D. F.; Bernstein, E. R. *J. Phys. Chem.* **1989**, *93*, 643.

Table I. Inertial Parameters of All Analyzed Bands in the $S_1 \leftarrow S_0$ Fluorescence Excitation Spectrum of 2-Pyridone–H_2O

band energy[a]	S_0		S_1		$S_1 - S_0$	
A, 30 464.599 cm^{-1}	A''	3996.5[b]	A'	3933.4[b]	ΔA	−63.1[b]
	B''	1394.1[b]	B'	1348.2[b]	ΔB	−45.9[b]
	C''	1034.8[b]	C'	1006.4[b]	ΔC	−28.4[b]
	κ''	−0.757	κ'	−0.766	$\Delta\kappa$	−0.009
	$\Delta I''$	−0.59[c]	$\Delta I'$	−1.18[c]	$\Delta\Delta I$	−0.58[c]
I, 30 605.795 cm^{-1}	A''	3996.4	A'	3927.6	ΔA	−68.8
	B''	1394.2	B'	1347.6	ΔB	−46.6
	C''	1034.8	C'	1008.6	ΔC	−26.2
	κ''	−0.757	κ'	−0.768	$\Delta\kappa$	−0.011
	$\Delta I''$	−0.56	$\Delta I'$	−2.63	$\Delta\Delta I$	−2.06
J, 30 620.247 cm^{-1}	A''	3996.4	A'	3923.8	ΔA	−72.6
	B''	1394.0	B'	1339.9	ΔB	−54.1
	C''	1034.7	C'	1001.9	ΔC	−32.7
	κ''	−0.757	κ'	−0.769	$\Delta\kappa$	−0.012
	$\Delta I''$	−0.54	$\Delta I'$	−1.56	$\Delta\Delta I$	−1.02

[a] ±0.002 cm^{-1}. [b] Rotational constants, ±0.1 MHz ($\Delta A = A' - A''$, *etc.*). [c] Inertial defects, ±0.03 amu Å^2.

to the *b* inertial axis. The corresponding band in the $S_2 \Leftarrow S_0$ spectrum of the symmetry-equivalent C_{2h} dimer, $(2PY)_2$, also is *b*-axis polarized (≥95%).[7,9] An *approximate* geometry of the single water complex may be deduced by comparing these two observations, if we assume that complex formation does not affect significantly the orientation of the TM in the inertial frame of the 2PY substrate. Thus, since 2PY–H_2O and $(2PY)_2$ have similarly oriented TM's, the 2PY–H_2O complex must have a geometry that conserves the inertial axis orientation of the $(2PY)_2$ dimer (**I**) with respect to the 2PY subunit of the complex (**II**). This result suggests (but does not prove) that in 2PY–H_2O the water molecule forms two hydrogen bonds with the amine hydrogen and carbonyl oxygen of 2PY, in both electronic states.



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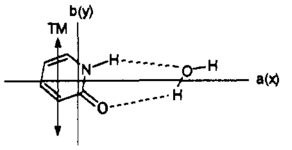


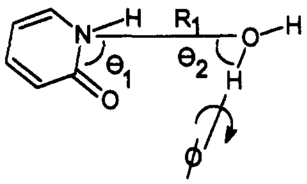
II

With structure II in hand, we next used its approximate geometry to estimate the rotational constants of 2PY–H_2O in both electronic states. We then fit the $S_1 \Leftarrow S_0$ spectra in the usual way.[10] Employing rigid rotor models for both states, we obtained fits of all three bands (A, I, and J). A portion of Figure 2A, at full experimental resolution along with the corresponding calculated simulation, is shown in Figure 2B to demonstrate the quality of the fit of band A. The fits of bands I and J are of similar quality. Each band (A, I, and J) contains over 3000 lines, and each was fit with a standard deviation of about 7 MHz. Individual lines exhibit Voigt line-shape profiles, with a Gaussian contribution (principally due to Doppler broadening) of 20 ± 2 MHz and a Lorentzian contribution (due to fluorescence decay) of 18 ± 2 MHz. This homogeneous width corresponds to a fluorescence lifetime of about 9 ns. This frequency-determined lifetime is the same, within experimental error, as the lifetimes of 2PY and $(2PY)_2$.[6,7]

Table I lists the derived rotational constants of the six vibronic levels involved in bands A, I, and J. Immediately apparent is the fact that the three sets of rotational constants for the S_0 levels are the same, within experimental error (±0.1 MHz). From this we conclude that bands A, I, and J all originate in the same vibronic level, the zero-point vibrational level of S_0. Also apparent is the fact that the three sets of S_1 rotational constants are both different from each other and different from those of the S_0 zero-point level. From this we conclude that the three upper state levels have equilibrium geometries that are different and that these geometries are different from that of the S_0 zero-point level. Notably, the inertial defects (ΔI) of all vibronic levels are both small and negative, indicating a planar (heavy-atom) complex geometry in both electronic states.

The two above-mentioned vibronic bands (I and J) terminate in S_1 vibrational levels having low frequencies (141 and 156 cm^{-1}, respectively). We believe that these are primarily intermolecular hydrogen bond vibrations. Six such modes exist; they include modes with significant in-plane and out-of-plane vibrational character. The differences in the rotational constants of the 141-cm^{-1} vibrational level and the zero-point level in the S_1 state are relatively small, making an in-plane mode an unlikely assignment. But the $|\Delta I|$ value of the 141-cm^{-1} level is significantly larger than that of the zero-point level, suggesting that the former involves large-amplitude out-of-plane motion (*e.g.*, a torsion). The $|\Delta I|$ value of the 156-cm^{-1} vibrational level is only slightly larger than that of the zero-point level, but the rotational constants of the former are significantly smaller than those of the latter. Thus, the most likely assignment of the 156-cm^{-1} level is an in-plane vibrational mode (*e.g.*, hydrogen bond stretch). These frequencies compare favorably with those calculated for the corresponding intermolecular vibrations of the formamide–water complex.[11]

Next, we calculated the effective structures of 2PY–H_2O in the zero-point levels of its S_0 and S_1 electronic states. Bond angles and distances in the pyridone ring were fixed at the values determined for α-pyridone by Penfold[12] using X-ray crystallography. The bond angle and distances in H_2O were fixed at the experimentally determined values for free water.[13] The remaining four geometrical parameters in 2PY–H_2O are the heavy atom separation R_1(N–H···O), the two in-plane angles θ_1 and θ_2, and the out-of-plane tilt angle ϕ (see III). The out-of-plane tilt angle was fixed by assuming that the non-hydrogen-bonded hydrogen is the sole contributor to the inertial defect. The value of ΔI = −0.56 amu Å^2 corresponds to a tilt angle of 37°. The remaining three variables were varied until the calculated rotational constants converged to within 1% of the experimental values. From these data, we then derive the heavy-atom separations R_1(N–H···O) = 2.86 Å and R_2(O···H–O) = 2.77 ± 0.03 Å, the hydrogen bond lengths r_1[(N)H···O] = 1.96 Å and r_2[O···H(O)] = 1.97 ± 0.03 Å, and the hydrogen bond angles $\angle_1$(N–H···O) = 146.2° and $\angle_2$(O···H–O) = 139.6 ± 1° in the ground state of 2PY–H_2O. These parameters clearly show that in 2PY–H_2O the water molecule forms two nonlinear hydrogen bonds with the amine hydrogen and carbonyl oxygen of 2PY. The hydrogen bond lengths are slightly longer than the *ab initio* values of Field and Hillier[14] (r_1 = 1.80 Å and r_2 = 1.79 Å), but the angles are in reasonably good agreement ($\angle_1$ = 146.5° and $\angle_2$ = 147.5°). On electronic excitation to the S_1 state of 2PY–H_2O, R_1(N–H···O) increases to 2.97 Å and R_2(O···H–O) increases to 2.91 ± 0.03



III

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(9) Held, A.; Pratt, D. W. *J. Chem. Phys.* **1992**, *96*, 4869.

(10) Champagne, B. B.; Pfanstiel, J. F.; Plusquellic, D. F.; Pratt, D. W.; van Herpen, W. M.; Meerts, W. L. *J. Phys. Chem.* **1990**, *94*, 6.

(11) Wang, X. C.; Nichols, J.; Feyereisen, M.; Gutowski, M.; Boatz, J.; Haymet, A. D. J.; Simons, J. *J. Phys. Chem.* **1991**, *95*, 10419.

(12) Penfold, B. R. *Acta Crystallogr.* **1953**, *6*, 591.

(13) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(14) Field, M. J.; Hillier, I. H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 617.

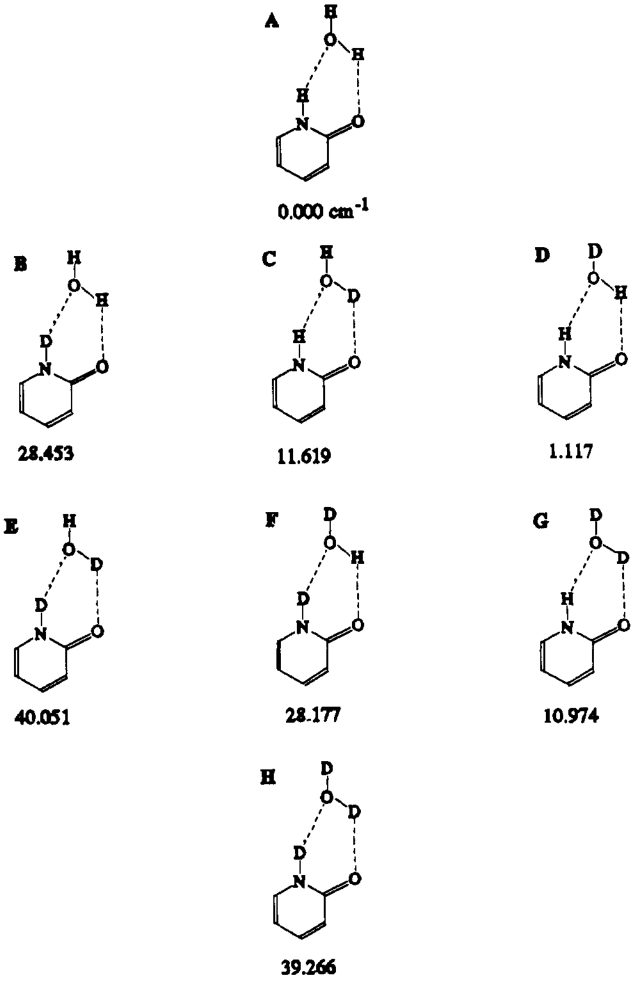

Figure 3. Isotopomers resulting when 2PY is mixed with an H_2O/D_2O-seeded expansion gas. Shown below each structure are the relative blue shifts, in cm^{-1}, of each origin band with respect to the protonated 2PY–H_2O origin band.

Table II. Inertial Parameters of All Analyzed Isotopomer Bands in the $S_1 \leftarrow S_0$ Fluorescence Excitation Spectrum of 2-Pyridone–H_2O/D_2O (A–H) and 2-Pyridone–$H_2{}^{18}O$ (A′)

band energy[a]	S_0 (calc)		S_0 (expt)		$S_1 - S_0$ (expt)	
A, 30 464.599 cm^{-1}	A''	3996.8[b]	A''	3996.5[b]	ΔA	−63.1[b]
	B''	1394.5[b]	B''	1394.1[b]	ΔB	−45.9[b]
	C''	1034.8[b]	C''	1034.8[b]	ΔC	−28.4[b]
	κ''	−0.757	κ''	−0.757	$\Delta\kappa$	−0.009
	$\Delta I''$	−0.47[c]	$\Delta I''$	−0.60[c]	$\Delta\Delta I$	−1.18[c]
A′, A + 0.458 cm^{-1}	A''	3969.9	A''	3970.7	ΔA	−59.5
	B''	1324.9	B''	1325.4	ΔB	−44.9
	C''	994.3	C''	994.8	ΔC	−28.0
	κ''	−0.778	κ''	−0.778	$\Delta\kappa$	−0.009
	$\Delta I''$	−0.47	$\Delta I''$	−0.55	$\Delta\Delta I$	−0.58
B, A + 28.453 cm^{-1}	A''	3959.6	A''	3958.4	ΔA	−56.7
	B''	1389.2	B''	1389.2	ΔB	−45.9
	C''	1029.4	C''	1029.4	ΔC	−27.9
	κ''	−0.754	κ''	−0.754	$\Delta\kappa$	−0.010
	$\Delta I''$	−0.47	$\Delta I''$	−0.51	$\Delta\Delta I$	−1.12
C, A + 11.619 cm^{-1}	A''	3995.4	A''	3995.8	ΔA	−61.6
	B''	1365.9	B''	1365.9	ΔB	−46.0
	C''	1018.9	C''	1019.2	ΔC	−28.6
	κ''	−0.767	κ''	−0.767	$\Delta\kappa$	−0.009
	$\Delta I''$	−0.47	$\Delta I''$	−0.59	$\Delta\Delta I$	−1.17
D, A + 1.117 cm^{-1}	A''	3978.6	A''	3979.1	ΔA	−64.5
	B''	1336.7	B''	1338.0	ΔB	−43.4
	C''	1002.3	C''	1002.9	ΔC	−27.2
	κ''	−0.775	κ''	−0.775	$\Delta\kappa$	−0.008
	$\Delta I''$	−0.88	$\Delta I''$	−0.78	$\Delta\Delta I$	1.49
E, A + 40.051 cm^{-1}	A''	3957.9	A''	3957.5	ΔA	−55.5
	B''	1361.2	B''	1361.4	ΔB	−45.9
	C''	1013.8	C''	1014.2	ΔC	−28.0
	κ''	−0.764	κ''	−0.764	$\Delta\kappa$	−0.010
	$\Delta I''$	−0.47	$\Delta I''$	−0.62	$\Delta\Delta I$	−1.23
F, A + 28.177 cm^{-1}	A''	3942.7	A''	3928.2	ΔA	−56.9
	B''	1332.1	B''	1309.4	ΔB	−42.7
	C''	997.4	C''	984.9	ΔC	−26.6
	κ''	−0.773	κ''	−0.780	$\Delta\kappa$	−0.008
	$\Delta I''$	−0.88	$\Delta I''$	−1.49	$\Delta\Delta I$	−2.16
G, A + 10.974 cm^{-1}	A''	3976.7	A''	3976.5	ΔA	−63.7
	B''	1311.2	B''	1312.4	ΔB	−43.3
	C''	987.6	C''	988.5	ΔC	−27.2
	κ''	−0.783	κ''	−0.783	$\Delta\kappa$	−0.008
	$\Delta I''$	−0.88	$\Delta I''$	−0.91	$\Delta\Delta I$	−1.62
H, A + 39.266 cm^{-1}	A''	3940.5	A''	3939.4	ΔA	−58.1
	B''	1306.9	B''	1308.2	ΔB	−43.2
	C''	983.1	C''	983.9	ΔC	−26.7
	κ''	−0.781	κ''	−0.781	$\Delta\kappa$	−0.008
	$\Delta I''$	−0.89	$\Delta I''$	−0.97	$\Delta\Delta I$	−1.74

[a] ±0.002 cm^{-1}. [b] Rotational constants, ±0.1 MHz. [c] Inertial defects, ±0.03 amu Å^2.

Å. The out-of-plane tilt angle ϕ was held fixed at the ground-state value. The hydrogen bond lengths and angles for the S_1 state are r_1[(N)H···O] = 2.06 Å, $\angle_1$(N–H···O) = 146.7°, r_2[O···H(O)] = 2.05 Å, and $\angle_2$(O···H–O) = 147.2°. The increase in both hydrogen bond lengths on electronic excitation suggests that both hydrogen bond strengths decrease in the S_1 state, relative to the S_0 state. This is consistent with the vibronic activity in the $S_1 \leftarrow S_0$ spectrum and the large blue shift of the origin band of the complex relative to the origin bands of the bare molecule.

To probe the structure of 2PY–H_2O further, the isotopic substitution technique[15] was used to determine the positions of key hydrogen atoms in the complex. When 2HP is mixed with an H_2O/D_2O seeded expansion gas, facile exchange occurs between the two hydrogen atoms of H_2O, the two deuterium atoms of D_2O, and the amine hydrogen atom of 2PY. Eight isotopomers result, as shown in Figure 3.

We have recorded rotationally resolved spectra of the electronic origins of all eight of these isotopomers (bands A–H). There is a shift in the position of one origin with respect to another owing to isotopically induced changes in the zero-point energies of the two electronic states. But all origin bands of the eight isotopomers of 2PY–H_2O/D_2O lie within a 50-cm^{-1} range. Therefore, the individually resolved spectra could be recorded by overlapping ~7-cm^{-1} scans of the laser over the full range, using an isotopically mixed sample. Eight bands were observed, each containing more than 3000 lines. The band types and linewidths exhibited by the deuterium-substituted molecules are the same as those of the protonated species. We then analyzed each of the bands separately and obtained the rotational constants of each isotopomer in its S_0 and S_1 states. The standard deviations of the fits all were less than 7 MHz. The derived values of the band origins and rotational constants are listed in Table II.

Examining the data in this table, we see that single or multiple deuterium substitution produces significant changes in the rotational constants of the S_0 and S_1 states. However, the changes in these constants that occur on $S_1 \leftarrow S_0$ excitation differ very little from one isotopomer to another. This suggests that isotopic substitution has little or no effect on the electronic and geometric structure of the complex.

To assign the seven deuterated species, we compared the experimental S_0 rotational constants with those calculated using the effective structure described above, replacing one or more hydrogen atoms with a deuterium atom. With one exception (see Table II), an unambiguous assignment followed; there is excellent agreement (±1 MHz) between the two sets of constants for all isotopomers except F. We then compared the band origin frequencies of the different isotopomers. The deuterated complex origins all are blue shifted with respect to the protonated complex

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(15) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*, 3rd ed.; Wiley-Interscience: New York, 1984.

origin. This result is consistent with the larger hydrogen bond strengths in the S_0 state.

Nimlos *et al.*[8] found that the three $S_1 \Leftarrow S_0$ d_1 origins of 2PY–H_2O/D_2O were blue shifted by 0, 12, and 27 cm^{-1} relative to the origin of 2PY–H_2O. We find that the smallest shift (1.1 cm^{-1}) is for the O···H–O–D species D, that the next largest shift (11.6 cm^{-1}) is for the O···D–O species C, and that the largest shift (28.5 cm^{-1}) is for the N–D···O species B. These results are reasonable, since the $S_1 \Leftarrow S_0$ excitation of 2PY–H_2O is essentially localized on the 2PY ring. For comparison, replacement of the amine hydrogen by deuterium produces blue shifts of 28.4 and 42.0 cm^{-1} in 2PY[6] and 10.8 cm^{-1} in the energy-delocalized dimer $(2PY)_2$-d_1.[9]

Multiple deuterium substitution of 2PY–H_2O leads to largely additive shifts, even for isotopomer F. Nimlos *et al.*[8] found that the three d_2 origins of 2PY–H_2O/D_2O are blue shifted by 8, 26, and 36 cm^{-1} and that the single d_3 origin is blue shifted by 36 cm^{-1}. We find slightly different values for these shifts (11.0, 28.2, 40.1, and 39.3 cm^{-1}, respectively) and assign them to isotopomers G, F, E, and H, respectively. The calculated values of these shifts, assuming additivity, are 12.7, 29.6, 40.1, and 41.2 cm^{-1}, respectively. Thus, those isotopomers in which the non-hydrogen-bonded hydrogen is replaced by deuterium (F, G, and H) exhibit shifts that are up to 2 cm^{-1} less than expected. For comparison, replacement of the two amine hydrogens in $(2PY)_2$ by deuterium produces a blue shift of 10.1 cm^{-1},[9] also less than expected.

Two other trends in the data reported in Table II are worthy of note. First, isotopomers A, B, C, and E all exhibit nearly identical inertial defects in the ground state, with $\Delta I''$ values lying between −0.51 and −0.62 amu Å^2. In contrast, isotopomers D, F, G, and H exhibit substantially larger $\Delta I''$ values, ranging from −0.78 to −1.49 amu Å^2. This parameter clearly distinguishes those isotopomers with an exocyclic hydrogen atom (A, B, *etc.*) from those with an exocyclic deuterium atom (D, F, *etc.*). Second, isotopomers A, C, D, and G exhibit $|\Delta A|$ values greater than 60 MHz, whereas isotopomers B, E, F, and H exhibit $|\Delta A|$ values less than 60 MHz. Thus, this parameter distinguishes the isotopomers with an N–H bond from those with an N–D bond. The largest difference in $|\Delta A|$ values is between isotopomers D and E; D has one deuterium in the exocyclic position whereas E has two deuterium atoms in the endocyclic positions.

Next, we used the observed rotational constants and their dependence on both the position and number of deuterium substitution(s) to determine the center-of-mass coordinates of the three affected hydrogen atoms, with the aid of Kraitchman's equations.[15] These atoms are labeled 1, 2, and 3 corresponding to the amine hydrogen, the hydrogen-bonded water hydrogen, and the non-hydrogen-bonded water hydrogen, respectively. The atomic coordinates of each atom were determined independently using four different sets of isotopic species, once the calculated coordinates were transformed into a common principal axis system (that of the all-protonated species).[16] The results of this analysis are given in Table III.

Table III. Center-of-Mass Coordinates of the Substituted Hydrogen Atoms of 2-Pyridone–H_2O in Its S_0 and S_1 States[a,b]

species	S_0 coordinates (Å)			S_1 coordinates (Å)		
	$\lvert x\rvert$	$\lvert y\rvert$	$\lvert z\rvert$	$\lvert x\rvert$	$\lvert y\rvert$	$\lvert z\rvert$
			Hydrogen Atom 1			
A[2PYH(HOH)]	1.15	1.13	*i*	1.18	1.04	*i*
B[2PYD(HOH)]	(0.02)	(0.02)		(0.02)	(0.02)	
C[2PYH(DOH)]	1.13	1.11	*i*	1.16	*i**	*i*
E[2PYD(DOH)]	(0.02)	(0.02)		(0.02)		
D[2PYH(HOD)]	2.83	1.19	0.62	2.89	1.10	0.61
F[2PYD(HOD)]	(0.01)	(0.03)	(0.07)	(0.01)	(0.04)	(0.06)
G[2PYH(DOD)]	1.14	1.11	0.2	1.16	1.02	0.2
H[2PYD(DOD)]	(0.02)	(0.02)	(0.1)	(0.02)	(0.03)	(0.1)
			Hydrogen Atom 2			
A[2PYH(HOH)]	2.74	0.17	*i*	2.84	*i*	*i*
C[2PYH(DOH)]	(0.01)	(0.12)		(0.01)		
B[2PYD(HOH)]	2.73	*i**	*i*	2.83	*i*	*i*
E[2PYD(DOH)]	(0.02)			(0.01)		
D[2PYH(HOD)]	2.74	0.16	0.27	2.83	*i*	0.28
G[2PYH(DOD)]	(0.01)	(0.16)	(0.10)	(0.01)		(0.10)
F[2PYD(HOD)]	0.84	*i*	*i*	0.93	*i*	*i*
H[2PYD(DOD)]	(0.03)			(0.03)		
			Hydrogen Atom 3			
A[2PYH(HOH)]	3.89	0.70	0.31	3.92	0.70	0.40
D[2PYH(HOD)]	(0.01)	(0.03)	(0.06)	(0.01)	(0.03)	(0.05)
B[2PYD(HOH)]	4.66	0.77	*i*	4.72	0.77	*i*
F[2PYD(HOD)]	(0.02)	(0.03)		(0.02)	(0.04)	
C[2PYH(DOH)]	3.89	0.70	*i*	3.92	*i*	*i*
G[2PYH(DOD)]	(0.01)	(0.12)		(0.01)		
E[2PYD(DOH)]	3.89	0.72	0.43	3.91	0.74	0.52
H[2PYD(DOD)]	(0.01)	(0.03)	(0.16)	(0.01)	(0.03)	(0.10)

[a] The symbol *i* denotes coordinates that are calculated to be imaginary using Kraitchman's equations. [b] The symbol *i** denotes coordinates that are calculated to be imaginary using Rudolph's transformation.

The key assumption made in this method of determining atomic coordinates is that there is no change in the vibrationally averaged position of an atom when it is replaced by an isotope of different mass. Tests of this assumption should be performed when the substituted atoms are light and/or can undergo large-amplitude motions that differ significantly between the reference and the substituted species. One such test is whether or not independent determinations of a coordinate give identical results. For example, in our recent study of $(2PY)_2$,[9] it was found that the three sets of amine hydrogen coordinates that were determined by comparing the rotational constants of the three differently deuterium-labeled isotopomers did not agree, within the experimental error of the individual measurements. We concluded from this observation that there are changes in the vibrationally averaged positions of the two hydrogen-bonded amine hydrogens when H is replaced by D in $(2PY)_2$. These changes, in turn, produce changes in the effective geometry of the dimer, along both in-plane and out-of-plane coordinates (the Ubbelohde effect).[17] But in 2PY–H_2O, we see from the data in Table III that all isotopic comparisons for a given hydrogen atom yield the same center-of-mass coordinates, in cases where there is more than one independent determination. The only exception to this finding are the coordinates derived from comparisons involving isotopomer F. We conclude from this observation that Kraitchman's equations are valid for 2PY–H_2O. There is no change, within experimental error, in the vibrationally averaged positions of the substituted atoms in all isotopomers except F. We note, however, that the test for 2PY–H_2O is less sensitive than the test for $(2PY)_2$ with respect to this issue. This is because the hydrogen bonds in 2PY–H_2O are weaker than those in $(2PY)_2$ and because, if shifts in the atomic positions do occur, the effect on the rotational constants would be smaller in 2PY–H_2O than in $(2PY)_2$ owing to the smaller moment arm of H_2O.

A second factor limiting the accuracy of the derived coordinates of the substituted atoms in 2PY–H_2O is that many of these atoms lie close to an inertial axis or plane in the reference structure. The changes in the moments of inertia produced by isotopic substitution of these atoms are therefore small along the coordinate(s) corresponding to that axis or plane. This can lead to significant errors in the values of the derived coordinates. If these atoms also exhibit large-amplitude motion, this also can lead to imaginary coordinates (denoted by "*i*" in Table III) *via* the Kraitchman analysis. Examination of Table III shows that the *z* (out-of-plane) coordinates of the hydrogen atoms are particularly susceptible to these effects. And, in still other cases, imaginary

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(16) Rudolph, H. D. *J. Mol. Spectrosc.* **1981**, *89*, 430.

(17) Robertson, J. M.; Ubbelohde, A. R. *Proc. R. Soc. London, Ser. A* **1939**, *170*, 222. Ubbelohde, A. R.; Gallagher, K. J. *Acta Crystallogr.* **1955**, *8*, 71. Gallagher, K. J. In *Hydrogen Bonding*; Hadži, D., Ed.; Pergamon: Belfast, 1959.

Table IV. Average Center-of-Mass Coordinates of the Substituted Hydrogen Atoms and the Water Oxygen of 2-Pyridone–H_2O in Its S_0 and S_1 States

	S_0 coordinates (Å)			S_1 coordinates (Å)		
species	$\|x\|$	$\|y\|$	$\|z\|$	$\|x\|$	$\|y\|$	$\|z\|$
hydrogen 1	1.14	1.12	0.2	1.17	1.03	0.2
hydrogen 2	2.74	0.17	0.3	2.83		0.3
hydrogen 3	3.89	0.71	0.4	3.92	0.74	0.5
oxygen (H_2O)[a]	3.09	0.68	0.0	3.17	0.65	0.0

[a] Errors in the x and y coordinates of the oxygen atom are ±0.01 and ±0.02 Å, respectively.

coordinates are produced *via* the Rudolph transformation[16] (denoted by "i^*" in Table III). An example of this behavior is seen in the transformation of the second set of isotopomers, used to calculate the S_1 y coordinate of hydrogen atom 1, into the reference 2PY–H_2O frame.

Despite these constraints, we see from the limited data in Table III that all three substituted hydrogen atoms exhibit vibrationally averaged positions that are significantly out-of-plane. These displacements are small and have relatively large error bars. But the displacements are statistically significant. They also increase monotonically from the amine hydrogen (~0.2 Å) to the hydrogen-bonded water hydrogen (~0.3 Å) to the non-hydrogen-bonded water hydrogen (~0.4–0.5 Å), a trend that is consistent with the observed inertial defects and their sensitivity to deuterium substitution. Thus, one possible explanation for these displacements is that the out-of-plane vibrational amplitudes of the three hydrogen atoms increase as one moves away from the rigid 2PY ring, their equilibrium positions being planar. Alternatively, there may be small barriers along the out-of-plane coordinates that destabilize the completely planar configurations.

All coordinates calculated using the rotational constants of isotopomer F are in poor agreement with those calculated using the constants of the remaining species (*cf.*, Table III). This is not a surprising result given the "anomalous" nature of the rotational constants of isotopomer F, but we have no explanation for it. One possibility is that the band assignment is wrong; for example, band F could be a hot band. Other, more complicated scenarios may be imagined. But given the excellent agreement of the other measurements, we disregard the data for isotopomer F here and compute the average values of the S_0 and S_1 coordinates of the three hydrogen atoms from the remaining three independent determinations. These are listed in Table IV.

To complete our study of 2PY–H_2O, we performed experiments on a water sample labeled with ^{18}O. Examining a mixture of 2HP, $H_2{}^{16}O$, and $H_2{}^{18}O$ (30%), we found in the fully resolved spectrum of 2PY–H_2O a weak band blue shifted by 0.458 cm^{-1} with an intensity that was 30% of that of band A. We assigned this band, band A′, as the $S_1 \Leftarrow S_0$ electronic origin of 2PY–$H_2{}^{18}O$. Its S_0 rotational constants (Table II) were then compared to those calculated using the effective structure, replacing the ^{16}O atom with the ^{18}O atom. Excellent agreement was obtained, confirming the assignment. We then compared the experimental rotational constants of 2PY–$H_2{}^{16}O$ and 2PY–$H_2{}^{18}O$ to determine the center-of-mass coordinates of the oxygen atom, in both electronic states. These values also are listed in Table IV. Notably, the water oxygen atom in 2PY–H_2O exhibits no significant out-of-plane displacement.

B. 2-Pyridone-$(H_2O)_2$. The rotationally resolved spectrum of the origin band (band L) of 2PY–$(H_2O)_2$ is shown in Figure 4. This spectrum was recorded under the same expansion conditions used for the spectra of 2PY–H_2O. The two apparent band heads in the R-branch portion of the spectrum of 2PY–$(H_2O)_2$ are the result of two individual overlapping bands, 1 and 2, separated by 0.377 cm^{-1}. Each band contains over 3000 lines. All lines in the spectrum of 2PY–$(H_2O)_2$ exhibit widths (FWHM) of 35 ± 3 MHz. These line widths are significantly broader than those found for 2PY–H_2O. We were unable to fit these lineshapes to a unique Voigt profile, owing to spectral congestion. But if this width is homogeneous, it corresponds to a fluorescence lifetime that is approximately 4 ns shorter than that of 2PY–H_2O. The shorter singlet lifetime of 2PY–$(H_2O)_2$ relative to that of 2PY–H_2O may result from a higher state density associated with an increase in low-frequency intermolecular vibrations leading to faster internal conversion.

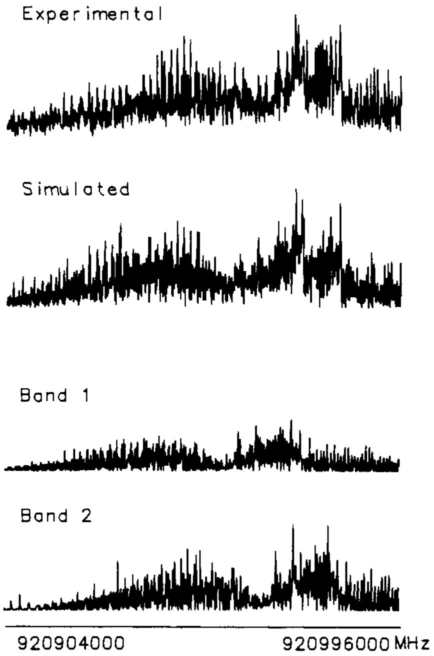
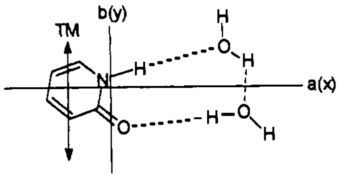


Figure 4. Rotationally resolved fluorescence excitation spectrum of the 2PY–$(H_2O)_2$ origin band, band L in Figure 1. The second panel shows the simulated fit to the spectrum. The band is a superposition of two closely overlapping bands, as shown in the bottom two panels.

The strategy used to fit each of the two 2PY–$(H_2O)_2$ bands was the same as that described earlier. Starting with the rotational constants of an *ab initio* geometry of 2PY–$(H_2O)_2$,[14] each spectrum was fit to a rigid rotor Hamiltonian with a standard deviation of less than 6 MHz. The derived rotational constants for bands 1 and 2, for both electronic states, are listed in Table V. The overall fit is compared to the experimental data in Figure 4a and b. Simulated spectra of the two separate bands are shown in Figure 4c and d. Notably, band 1 is roughly 1.5 times less intense than band 2.

Bands 1 and 2 are polarized entirely (≥95%) along the b-axis. Recalling the all b-type polarizations of 2PY–H_2O and $(2PY)_2$ and assuming that the orientation of the transition moment in 2PY is again unaffected by complex formation, we conclude that 2PY–$(H_2O)_2$ has the geometry shown below (**IV**). Three hydrogen bonds exist in 2PY–$(H_2O)_2$; one linking a water molecule to the N—H group, a second linking the second water molecule to the C=O group, and a third connecting the two water molecules together. Comparing this structure to that of 2PY–H_2O, we see that adding a second water molecule to the cluster requires that the first water be reoriented with respect to its original position. The geometry of the water dimer in 2PY–$(H_2O)_2$ is very different from that found in $(H_2O)_2$.[2]



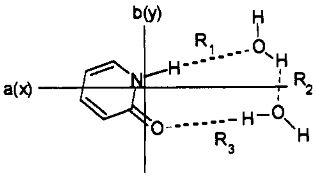
IV

Table V. Inertial Parameters of the Origin Bands in the $S_1 \leftarrow S_0$ Fluorescence Excitation Spectrum of 2-Pyridone–$(H_2O)_2$

band energy[a]	S_0		$S_1 - S_0$	
band 1, 30 719.841 cm^{-1}	A''	2580.8[b]	ΔA	15.2[b]
	B''	895.7[b]	ΔB	−38.0[b]
	C''	668.8[b]	ΔC	−19.7[b]
	κ''	−0.763	$\Delta\kappa$	−0.023
	$\Delta I''$	−4.36[c]	$\Delta\Delta I$	−0.89
band 2, 30 720.217 cm^{-1}	A''	2584.8	ΔA	14.9
	B''	894.3	ΔB	−37.8
	C''	667.8	ΔC	−19.6
	κ''	−0.764	$\Delta\kappa$	−0.024
	$\Delta I''$	−3.81	$\Delta\Delta I$	−0.91

[a] ±0.002 cm^{-1}. [b] Rotational constants, ±0.1 MHz. [c] Inertial defects, ±0.03 amu Å^2.

We next determined an effective structure of 2PY–$(H_2O)_2$ in both electronic states using the measured rotational constants. In these calculations, the bond distances and angles for the pyridone ring and the two water molecules were fixed and assumed to be unaffected by complex formation. We also assumed that the two hydrogen bonds to 2PY are linear. This reduces the problem of structure determination to a problem in three variables; the three heavy-atom separations R_1(N—H···O), R_2(O—H···O), and R_3 ((C=O)···H—O) (see V). These separations were adjusted until the calculated rotational constants matched the (average values of the) experimental rotational constants in Table V, yielding R_1 = 2.85 Å, R_2 = 2.67 Å, and R_3 = 2.78 ± 0.02 Å for the ground state of 2PY–$(H_2O)_2$. On excitation of 2PY–$(H_2O)_2$ to its S_1 state, R_1 and R_3 increase by 0.14 and 0.11 Å, respectively, while R_2 decreases by 0.07 A. It should be observed, from V, that the decrease in R_2 on excitation is derived almost exclusively from the increase in the A inertial constant, while the increases in R_1 and R_3 are nearly exclusively derived from changes in the B and C inertial constants. Isotopic substitution experiments to refine the structure of 2PY–$(H_2O)_2$ were not performed, owing to the anticipated difficulty of analyzing the 64 spectra of the 32 isotopomers that would be produced in a simple H_2O/D_2O/rare gas expansion.



V

Some additional information about the structure of 2PY–$(H_2O)_2$ can, however, be gleaned from the observed rotational constants (Table V). The inertial defects of 2PY–$(H_2O)_2$ are, for example, substantially larger in magnitude than those of 2PY–H_2O (*cf.*, Table I). Small, negative inertial defects result from large-amplitude out-of-plane vibrations and/or nonplanar equilibrium structures. The increase in $|\Delta I|$ that is observed on $S_1 \Leftarrow S_0$ excitation of 2PY–H_2O most likely results from increased vibrational amplitudes along out-of-plane coordinates, owing to a weakening of the intermolecular hydrogen bonds. A similar effect is observed in 2PY–$(H_2O)_2$. But the S_0 and S_1 inertial defects of 2PY–$(H_2O)_2$ are substantially larger in magnitude than those of 2PY–H_2O. While we cannot rule out increased vibrational amplitudes as the only source of these differences, we believe that a major contributor to the larger inertial defects of 2PY–$(H_2O)_2$ is nonplanar equilibrium hydrogen atom positions. Three other planar molecules with out-of-plane hydrogen atoms are 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), and 2,3-dimethylnaphthalene (2,3DMN). These have inertial defects of −3.3, −3.4, and −6.6 amu Å^2, respectively, in their S_0 states.[18] 1MN and 2MN each have two out-of-plane hydrogens, while 2,3DMN has four. On the basis of a comparison of these values with those for 2PY–$(H_2O)_2$, we believe that in 2PY–$(H_2O)_2$ the two water oxygen atoms are coplanar with respect to the 2PY ring and that at least two of the four water hydrogen atoms are displaced out-of-plane in the equilibrium structure.

Finally, we note that the rotational constants of the two vibronic levels associated with band 1 and those associated with band 2 are significantly different. Recall that the intensities of bands 1 and 2 also are different. These observations suggest that there are two stable, slightly inequivalent conformations of 2PY–$(H_2O)_2$ in the two electronic states. These conformations are believed to differ in the nature of the out-of-plane displacements of the hydrogen atoms of the two water molecules, primarily because they exhibit different inertial defects (*cf.*, Table V). We elaborate on this idea below.

Discussion

We have found that when 2PY is solvated by a single water molecule in the gas phase, two hydrogen bonds are formed, one in which the water molecule accepts electrons from the carbonyl group of 2PY and one in which the water molecule donates electrons to the amine group of 2PY. The solvent thus acts simultaneously as an acid and a base, a rare occurrence in cluster chemistry.

We also have calculated the effective structures of 2PY–H_2O in its S_0 and S_1 electronic states from the observed rotational constants. Assuming that the structures of 2PY and H_2O are unaffected by hydrogen bond formation, we find that the hydrogen bond lengths r_1[(N)H···O] and r_2[O···H(O)] are 1.96 and 1.97 ± 0.03 Å, respectively, in the ground state of 2PY–H_2O. These values compare favorably with those exhibited by a wide variety of biological structures in the condensed phase[19] and by formamide–water in the gas phase.[20] On electronic excitation to the S_1 state of 2PY–H_2O, r_1 increases by 0.11 ± 0.03 Å and r_2 increases by 0.14 ± 0.03 Å relative to the case of the S_0 state. Apparently, then, both hydrogen bond strengths decrease when the photon is absorbed.

Two other conclusions may be drawn from the data obtained in these experiments. The first conclusion is that the structure of the water molecule is relatively unaffected by hydrogen bond formation with 2PY. Water itself has O–H bond distances of 0.96 Å and a bond angle of 104.5°.[13] The O–H bond distances of the water molecule in S_0 2PY–H_2O, calculated from the vibrationally averaged coordinates listed in Table IV and shown in Figure 5, are 0.97 ± 0.02 Å and 0.90 ± 0.04 Å for the "inner" and "outer" OH bonds, respectively. Given the significant out-of-plane vibrational displacements that are observed, especially for the exocyclic hydrogen atom, these values appear unchanged from the value of 0.96 Å for water itself. Two values of the water bond angle in S_0 2PY–H_2O are obtained from our analysis, 101.9 ± 0.5°, if the two water hydrogens are displaced on the same side of the heavy-atom plane, and 116.5 ± 0.5°, if the two hydrogens are displaced on opposite sides of this plane. Again, these values suggest that, given the motion that is occurring, the water molecule itself is not distorted significantly from its equilibrium geometry when the hydrogen bonds to 2PY are formed.

The second conclusion is that there *is* a distortion of the 2PY solute molecule by the water solvent molecule when the two hydrogen bonds are formed, in the S_0 state. This conclusion is based on a comparison of the four sets of ground-state rotational constants of 2PY listed in Table VI. The first set of constants

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(18) Tan, X.-Q.; Majewski, W. A.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1991**, *94*, 7721. Tan, X.-Q.; Clouthier, D. J.; Judge, R. H.; Plusquellic, D. F.; Tomer, J. L.; Pratt, D. W. *J. Chem. Phys.* **1991**, *95*, 7862.

(19) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*, Springer-Verlag: Berlin, 1991.

(20) Lovas, F. J.; Suenram, R. D.; Fraser, G. T.; Gillies, C. W.; Zozom, J. *J. Chem. Phys.* **1988**, *88*, 722.

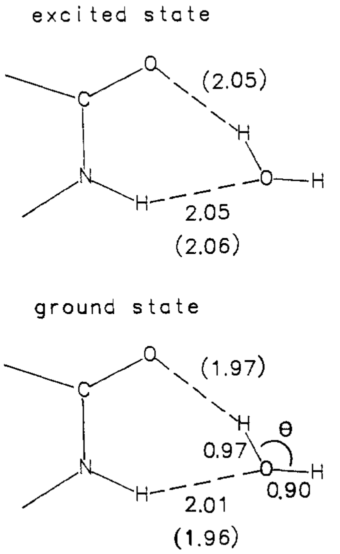


Figure 5. Hydrogen bond geometries in $2PY-H_2O$ in its S_0 and S_1 states. The hydrogen bond lengths shown were derived from the Kraitchman analysis; those in parentheses were derived from the effective structure of $2PY-H_2O$. A value of Θ = 101.9° was calculated assuming the same sign for the z coordinates of hydrogen atoms 2 and 3. A value of Θ = 116.5° was calculated assuming opposite signs for these coordinates. Fewer parameters are reported for the S_1 state because the S_1 coordinates of hydrogen atom 2 are not well determined.

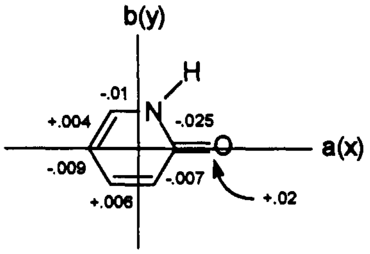
Table VI. Comparison of the Rotational Constants (in MHz) and Inertial Defects (in amu Å^2) of the Bare and Complexed 2-Pyridone in Its Electronic Ground State

constant	1, bare 2PY[a]	2, complexed 2PY[b]	3, complexed 2PY[c]	4, crystal 2PY[d]
A''	5643.9	5670.6	5675.9	5738.0
B''	2793.5	2774.4	2775.6	2802.8
C''	1868.8	1864.8	1864.8	1883.0
$\Delta I''$	−0.04	−0.10	−0.27	0.0

[a] Reference 6. [b] Assuming $z = 0$ for hydrogens 1, 2, and 3. [c] Assuming the nonzero z values for hydrogens 1, 2, and 3 given in Table IV. [d] Reference 12.

shown, set 1, are the rotational constants of the bare molecule.[6] Sets 2 and 3 are the rotational constants of a "complexed" 2PY, obtained by subtracting the inertial contributions of the two water hydrogens and the water oxygen from the rotational constants of $2PY-H_2O$.[21] Set 2 was calculated by assuming that the equilibrium positions of hydrogen atoms 1, 2, and 3 are planar (*i.e.*, have $z = 0$). Set 3 was calculated by assuming that the z coordinates of these atoms are those determined from the Kraitchman analysis (Table IV). The fourth set of constants in Table VI are those calculated from the crystal structure of 2PY.[12] The differences between the rotational constants in Sets 2 and 3 are small, as expected. But the rotational constants in sets 2 and 3 are *very* different from those in set 1. This shows that the *gas-phase* structure of 2PY changes significantly when it is complexed to a single water molecule, also in the gas phase. The rotational constants in sets 2 and 3 also are very different from those in set 4. This shows that the structure of 2PY hydrogen bonded to a single water molecule in the gas phase also is very different from that of 2PY in the crystal.

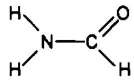
Comparing the first two sets of constants in Table VI, we see that when the water molecule is attached *via* two hydrogen bonds to 2-pyridone, the rotational constant A of the solute increases by 26.7 MHz, the constant B decreases by 19.1 MHz, and the constant C decreases by 4.0 MHz. Thus, primarily, the principal moment of inertia about the a-axis decreases, and the principal moment of inertia about the b-axis increases. Shown below (**VI**)



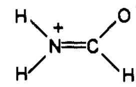
VI

is a sketch of the orientations of these axes in the principal coordinate system of the bare molecule, based on the geometry calculated by Field and Hillier.[14] Also shown in **VI** are the changes in bond lengths that occur when 2PY is complexed by H_2O according to the *ab initio* calculations.[14] The largest changes according to theory are in the C–O bond length, which increases by 0.02 Å, and in the C–N bond length, which decreases by 0.025 Å. Additionally, there is a decrease in the bond length alternation around the ring. Taken together, these changes clearly lead to an overall decrease in the moment about the a-axis and to an overall increase in the moment about the b-axis, with only a small change in the moment about the c-axis. These predicted changes are completely consistent with the experimentally derived changes in the rotational constants that are produced when the solvent is attached.[22]

The decrease in the C—N bond length and the increase in the C═O bond length with hydrogen bond formation to water clearly result from a polar solvent-induced increase in the importance of the ionic resonance form in the valence bond description of amide species



VII



VIII

While such a phenomenon has long been anticipated from a variety of theoretical calculations[14,23,24] and solid-state experiments,[19,25] we are unaware of a previous experimental demonstration of this effect in *isolated* molecules.

In the previous study of 2PY,[6] we found that the bare molecule exhibits two geometries in its S_1 state that have different nonplanar distortions at the nitrogen atom. Thus, the isolated molecule exhibits two $S_1 \leftarrow S_0$ origins, separated by 95 cm^{-1}. In contrast,

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(21) Some care should be exercised in calculations of this sort. Thus, the inertial contributions of the three water atoms to the total moments of inertia of the complex are simple functions of their masses and their positions with respect to the center-of-mass. Since we know the masses and coordinates of the three atoms, we can easily calculate their inertial contributions and subtract them from the total moments of inertia of the complex, to obtain the effective moments of the "complexed" 2PY. But once one atom is "removed", the resulting new inertial tensor must be diagonalized, and the remaining atomic coordinates must be transformed into the new principal axis frame before the next atom can be subtracted. In the present case, we obtained the necessary transformation matrices by comparing the moments of inertia of the complex and the complex minus a subtracted atom using Kraitchman's equations.[15] This procedure was repeated for each of the three water atoms to obtain the two sets of rotational constants of the "complexed" 2PY listed in Table VI.

(22) A reviewer has suggested that the differences in the rotational constants in the two systems might be due to additional nonrigidities in $2PY-H_2O$, so that the effective structure of the complexed 2PY might be different from the uncomplexed 2PY. While plausible, this suggestion seems unlikely, since rigid rotor models adequately account for the observed spectra. Additionally, unaccounted-for intermolecular vibrations between 2PY and H_2O would introduce larger changes in C than in A and B. Our analysis shows that the C rotational constant is the least affected by complexation.

(23) Wong, M.-W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992,** *114,* 1645.

(24) Guo, H.; Karplus, M. *J. Phys. Chem.* **1992,** *96,* 7273.

(25) Gili, G.; Belucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989,** *111,* 1023.

2PY–H_2O exhibits a single electronic origin in its $S_1 \Leftarrow S_0$ transition. The appearance of a single origin in 2PY–H_2O strongly suggests that hydrogen bond formation with H_2O forces the excited state into a planar configuration, a fact that is consistent with the increased importance of the ionic resonance structure **VIII**, even in the excited state.

Unlike the spectra of the two conformers of the 2PY monomer, the spectra of 2PY–H_2O and 2PY–$(H_2O)_2$ exhibit none of the anomalous rotational line intensities resulting from axis switching.[6] Axis switching, in the 2PY monomer, results from changes in the in-plane geometry of 2PY on electronic excitation. The geometry of 2PY changes in such a way as to produce a reorientation of the excited-state principal axes relative to the ground-state principal axes. The structural changes that cause axis switching to occur in the $S_1 \Leftarrow S_0$ excitation of the 2PY monomer also may occur in the complexed 2PY species. However, because the complexing molecule(s) lie far from the center-of-mass of the complex, significant rotation of the axes does not occur.

The effective structure calculated for 2PY–H_2O in this work was derived on the basis of the assumption that the geometry of 2PY in the gas-phase complex is the same as that of 2PY in the crystal. Clearly, as shown in Table VI, this is not the case. There are significant differences between the rotational constants of the two 2PY molecules in the two environments. This is not a surprising result, given that we now know that 2PY is distorted even when it is complexed to a single water molecule in the gas phase. But an important question remains; do the differences in the structures of 2PY in the gas phase and in the condensed phase introduce significant error into the calculated effective structure of the gas-phase complex? We can assess this error by adding the inertial contributions of the water molecule, using our experimentally determined coordinates, to the inertial tensor of "crystalline" 2PY and comparing the resulting inertial constants to the corresponding constants of 2PY–H_2O. Adding the inertial contributions of H_2O to crystalline 2PY was accomplished by reversing the procedure used earlier to subtract water's inertial contributions from the complex.[21] We find that the errors introduced into the 2PY–H_2O inertial constants using the crystalline 2PY geometry are 0.9, 0.4, and 0.5% for *A*, *B*, and *C*, respectively. These errors correspond to changes in the intermolecular separations of less than 0.02 Å. Therefore, the differences in the gas-phase and condensed-phase 2PY structures introduce negligible error into the effective gas-phase structure of 2PY–H_2O.

In gas-phase 2PY–$(H_2O)_2$, we found that three hydrogen bonds exist in the S_0 and S_1 states, one linking a water molecule to the N—H group, a second linking a second water molecule to the C═O group, and a third connecting the two water molecules together. The heavy-atom separations, calculated from the effective structure, are $R_1(\text{N—H}\cdots\text{O}) = 2.85$ Å, $R_2(\text{O—H}\cdots\text{O}) = 2.67$ Å, and $R_3[(\text{C═O})\cdots\text{H—O}] = 2.78 \pm 0.03$ Å for the ground state of 2PY–$(H_2O)_2$. On excitation of 2PY–$(H_2O)_2$ to its S_1 state, R_1 and R_3 increase by 0.14 and 0.11 Å while R_2 decreases by 0.07 Å. The heavy-atom separations R_1 and R_3 and the changes in these separations on excitation are the same, within error, as those for the corresponding distances in 2PY–H_2O. This fact, in addition to the observed small decrease in R_2, leads to the expectation that the origin of 2PY–$(H_2O)_2$ should be red shifted with respect to that of 2PY–H_2O. Instead, a blue shift of ~255 cm^{-1} is observed.

The above expectation is based on the assumption that a correlation exists between hydrogen bond strength and heavy-atom separation. But there are significant differences in the hydrogen bond geometries of 2PY–H_2O and 2PY–$(H_2O)_2$. In 2PY–H_2O, the hydrogen bond angles are ~145° with hydrogen bond lengths of ~2.00 Å. Our effective structure of 2PY–$(H_2O)_2$, while having similar heavy-atom separations, has essentially linear hydrogen bonds with significantly shorter hydrogen bond lengths of ~1.80 Å. We believe, on the basis of this comparison, that the hydrogen bonds in both S_0 and S_1 2PY–$(H_2O)_2$ are significantly stronger than the corresponding bonds in both S_0 and S_1 2PY–H_2O. Electronic excitation of 2PY–$(H_2O)_2$, while producing changes in R_1 and R_3 that are identical to those of the corresponding separations in 2PY–H_2O, produces larger decreases in the corresponding hydrogen bond strengths, which more than compensate for the increased O–H···O bond strength in S_1 2PY–$(H_2O)_2$. This explains why the $S_1 \Leftarrow S_0$ origin of 2PY–$(H_2O)_2$ is blue shifted relative to that of 2PY–H_2O.

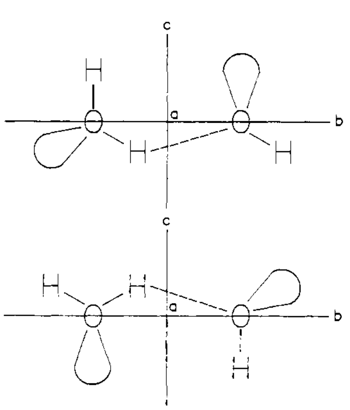

Figure 6. Out-of-plane hydrogen bond connecting the two water molecules in 2PY–$(H_2O)_2$. The view is along the *a* inertial axis, showing a projection of atomic positions in the *bc*-plane. The lone pairs shown are the nonbonding lone pairs of the two water oxygen atoms.

Complexation of 2PY with water produces blue shifts in the electronic origins of both 2PY–H_2O and 2PY–$(H_2O)_2$ relative to the monomer origins. The blue shifts together with the structural data presented here indicate that the intermolecular hydrogen bonds in the two complexes weaken on electronic excitation of 2PY to its S_1 state. Now, our analysis[6] of the rotational constants of the bare molecule in its S_1 state strongly suggests that there is a decrease in the π bond orders of the C–O, C_3–C_4, and C_5–C_6 bonds and an increase in the π bond order of the C_4–C_5 bond of 2PY on electronic excitation. The π bond order of the C_2–C_3 bond also increases, while that of the C_6–N bond decreases. As a result, the S_1 state of 2PY has a considerably more electron delocalized structure than the S_0 state. Concomitantly, there are significant decreases in the acidity of the amine hydrogen and in the basicity of the carbonyl oxygen that occur when the photon is absorbed. Weaker hydrogen bonds then form between S_1 2PY and H_2O than between S_0 2PY and H_2O, leading to a decreased importance of the zwitterionic resonance form and of π bond cooperativity effects[19] in the S_1 states of 2PY–H_2O and 2PY–$(H_2O)_2$. This explains why the $S_1 \Leftarrow S_0$ origins of these two complexes are blue shifted relative to the corresponding origin(s) of the bare molecule.

Finally, it will be recalled that two electronic origins are observed in the $S_1 \Leftarrow S_0$ spectrum of 2PY–$(H_2O)_2$, separated by 0.377 cm^{-1}. Consideration of the inertial defects exhibited by these two bands strongly suggests that at least two of the four water hydrogen atoms are displaced out-of-plane in the equilibrium structures and that the two bands are due to two slightly inequivalent conformations of 2PY–$(H_2O)_2$ in the two electronic states. A plausible geometry of 2PY–$(H_2O)_2$ that could give rise to two stable conformers is shown in Figure 6. Here, the three hydrogen atoms shown are the two exocyclic hydrogens of the two water molecules, and the hydrogen-bonded hydrogen between them. The view is along the *a* inertial axis (see V), showing a projection of the atomic positions in the *bc*-plane. As illustrated in Figure 6, inversion of the hydrogen-bonded hydrogen through the *ab*-plane also rotates the two exocyclic hydrogens with respect to the two hydrogen bonds linking the waters to 2PY. The small differences in the relative positions of the three hydrogen atoms in the two conformers are consistent with the small differences in the derived rotational constants, in both electronic states. And motion along this coordinate could give rise to unresolved splittings (~10 MHz) in their spectra, thereby providing an alternative explanation of the apparent increase in the line width of 2PY–$(H_2O)_2$ relative to 2PY–H_2O. Further probes of this motion in 2PY–$(H_2O)_2$ will require isotopic labeling experiments.

Summary

We have obtained the rotationally resolved fluorescence excitation spectra of 2PY–H_2O, of seven deuterated species of 2PY–H_2O, and of the ^{18}O-labeled water complex of 2PY–H_2O. A partial substitution structure derived from these data shows that the water molecule forms two planar, nonlinear hydrogen bonds with the amine hydrogen and the carbonyl oxygen of 2PY, in both states. Both hydrogen bond lengths increase on electronic excitation, suggesting a decrease in hydrogen bond strengths in the S_1 state relative to the S_0 state.

A complete substitution structure of the water molecule attached to 2PY was determined from the data. The structure of H_2O changes very little with complexation. But the data also show that the 2PY structure is modified significantly when the complex is formed. These changes are consistent with an increase in the zwitterionic character of 2PY on solvation by water, which decreases on $S_1 \Leftarrow S_0$ excitation.

Spectra of the dihydrated complex of 2PY also were obtained. 2PY–$(H_2O)_2$ also is planar with respect to the heavy atoms, in both states. It exhibits three hydrogen bonds, one between a water molecule and the amine hydrogen, one between a second water molecule and the carbonyl oxygen, and one between the two water molecules themselves. The hydrogen bonds in 2PY–$(H_2O)_2$ are stronger than the corresponding bonds in 2PY–H_2O. The increased hydrogen bond strengths are due, in part, to the increased linearity of the hydrogen bonds in 2PY–$(H_2O)_2$. The hydrogen bond formed between the two water molecules in 2PY–$(H_2O)_2$ is nonlinear and nonplanar. The nonplanarity of the "bridging hydrogen" gives rise to separate conformers that exhibit distinct $S_1 \Leftarrow S_0$ spectra.

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