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Ammonia as a Hydrogen Bond Donor and Acceptor in the Gas Phase. Structures of 2-Pyridone–NH_3 and 2-Pyridone–$(NH_3)_2$ in Their S_0 and S_1 Electronic States

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Abstract: Rotationally resolved $S_1 \leftarrow S_0$ electronic spectra of the hydrogen-bonded complexes of 2-pyridone (2PY) with one and two ammonia molecules have been observed. Both complexes, in both electronic states, exhibit behavior which indicates that the ammonia molecule acts as both an acid and a base. Evidence for this amphoteric behavior in the monosolvated complex (2PY–NH_3) is found in the derived, effective, hydrogen-bonded structure and in the barriers to internal rotation of the NH_3 group, $V_3(S_0) = 424.3$ cm^{-1} and $V_3(S_1) = 274.4$ cm^{-1}. The effective structure derived for the disolvated complex [2PY–$(NH_3)_2$] shows strong hydrogen bonding, similar to that found for the dihydrated complex (Held and Pratt, *J. Am. Chem. Soc.*, preceding paper in this issue). The donor and acceptor bonds in 2PY–$(NH_3)_2$ are strong enough to completely inhibit any internal rotation of the ammonia molecules. Like the dihydrated complex, 2PY–$(NH_3)_2$ exists in a number of different conformational forms. The structural and dynamical properties of these complexes are discussed.

Introduction

In order to understand the nature of biomolecular structures, one must begin with the subtle interactions that lead to hydrogen bonding. Intra- and intermolecular hydrogen bonds dictate the three-dimensional structures and reactivities of biological molecules. These relatively weak bonds can be broken and reformed with energies that lie within the range of thermal fluctuations found in living systems.[1] One example are the hydrogen bonds in complexes of 2-pyridone (2PY) with one and two water molecules, 2PY—H_2O and 2PY—$(H_2O)_2$. The H—N(R)—C(R)═O linkage in 2PY is a model for the *cis* peptide linkages in proteins and in the functional groups of nucleic acids. In a recent study,[2] we determined the equilibrium structures and hydrogen bond geometries of 2PY—H_2O and 2PY—$(H_2O)_2$ in their S_0 and S_1 electronic states from an analysis of their rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra in a molecular beam.

Motivated by these findings, we report here a study of the $S_1 \leftarrow S_0$ electronic spectra of the gas phase complexes of 2PY with one and two ammonia molecules. The rotational constants derived from fits of their fully resolved spectra have been used to determine the effective structures of 2PY–NH_3 and 2PY–$(NH_3)_2$ in their S_0 and S_1 electronic states. Additionally, the spectrum of 2PY–NH_3 exhibits torsion-rotation perturbations from which the barriers to hindered internal rotation of the attached NH_3 group in both electronic states have been determined. A comparison of these barriers with those in other systems shows that ammonia acts as *both* a hydrogen bond donor and a hydrogen bond acceptor in 2PY–NH_3. Perturbations of this type were not observed in 2PY–$(NH_3)_2$. However, the disolvated species exhibits conformational isomerism and motion along the isomerization coordinate in its fully resolved $S_1 \leftarrow S_0$ spectrum. These properties, together with those observed for the water complexes, provide new information about the interactions that are responsible for hydrogen bond formation in isolated molecules.

Experimental Section

Both low-resolution (~1 cm^{-1}) and high-resolution (~10^{-3} cm^{-1}) fluorescence excitation experiments were performed. 2-Pyridone (2PY) was purchased from Sigma and used without further purification. Anhydrous NH_3 was purchased from Matheson and premixed with He in a specially designed high pressure chamber. Typically, mixtures of 0.5% NH_3 in He were used. In the low-resolution supersonic jet experiment, 2PY was heated to *ca.* 400 K, seeded into 3–5 atm of the carrier gas mixture, and expanded into a vacuum chamber through a 1-mm-orifice pulsed valve (General Valve Series 9) operating at 10 Hz. The complexes were excited by a scanning, 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.[3] The expansion gas was a combination of NH_3 gas and He gas premixed in the same high-pressure chamber used in the low-resolution experiments. The mixtures were typically 0.5% NH_3 for the monosolvate experiments and up to 1.5% NH_3 for the dissolvate experiments. 2PY was heated to *ca.* 500 K, seeded into the NH_3/He gas mixture, expanded continuously through a 240-μm quartz nozzle, skimmed once, and probed 15-cm downstream of the nozzle by a single-frequency tunable UV laser operating at ~335 nm. Fluorescence, detected as a function of excitation wavelength over a narrow range of frequencies, 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 spectra and are accurate to ±30 MHz.

Results and Interpretation

The low-resolution, supersonic jet, fluorescence excitation spectrum of the ammonia complexes of 2PY is shown in Figure 1A and B. The two lowest frequency bands, displayed in Figure

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⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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

(2) Held, A.; Pratt, D. W. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) Majewski, W. A.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1989**, *90*, 1362.

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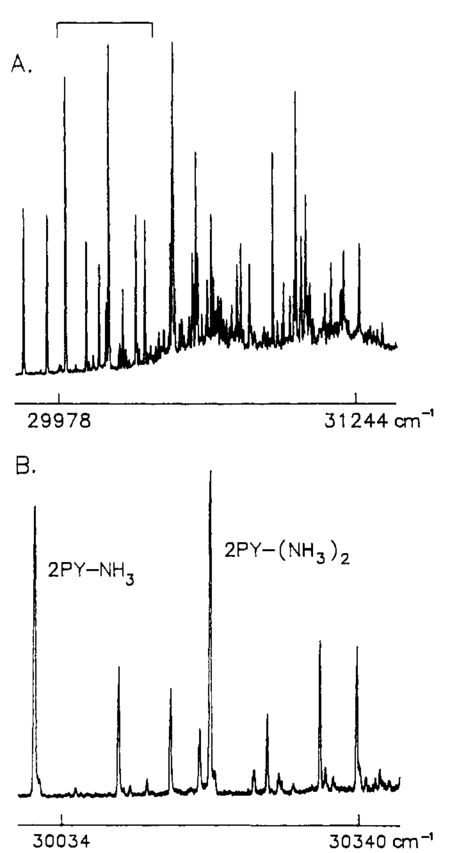


Figure 1. Low-resolution $S_1 \leftarrow S_0$ fluorescence excitation spectrum of 2-pyridone–ammonia in a supersonic jet. The two bands at 29 832 and 29 927 cm^{-1} are the electronic origins of the 2-pyridone (2PY) monomer. The lower panel (B) shows a portion of the observed spectrum in the vicinity of the electronic origin bands of 2PY–NH$_3$ and 2PY–(NH$_3$)$_2$.

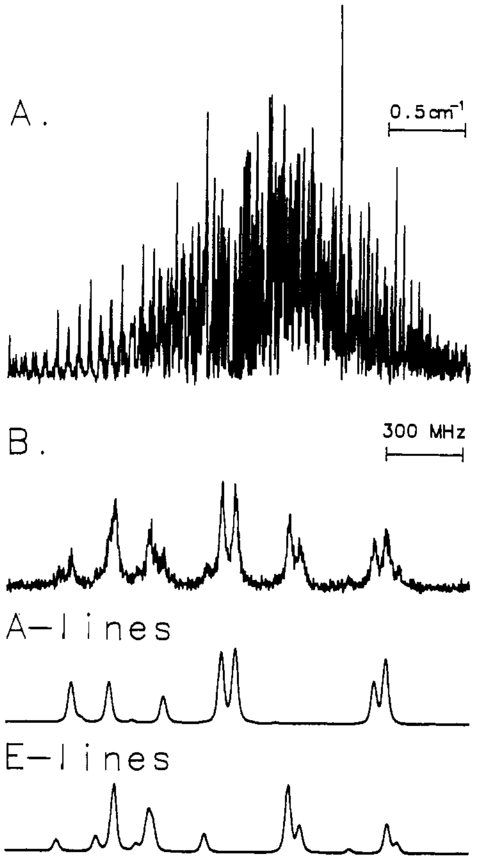
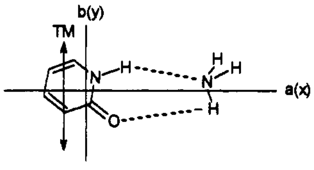


Figure 2. Rotationally resolved fluorescence excitation spectrum of the 2PY–NH$_3$ origin band. Panel B compares a portion of the observed spectrum (taken from the P-branch) at full experimental resolution with the corresponding simulated A- and E-line spectra.

1A at 29 832 and 29 927 cm^{-1}, are the electronic origins of two conformers of the 2PY monomer, differing in the degree of nonplanarity at the ring nitrogen atom in the S_1 state.[4] The electronic origin bands of the monosolvate and disolvate ammonia–2PY complexes are displaced 176 and 356 cm^{-1} to the blue compared to the first 2PY monomer band, respectively. These are clearly shown in Figure 1B, which is an expanded-scale view of a portion of the spectrum in Figure 1A. The frequencies of all of these monomer and ammonia complex bands are in reasonable agreement with those measured in the previous MPI experiments of Nimlos *et al.*[5] The increased vibronic activity found for 2PY–NH$_3$ and 2PY–(NH$_3$)$_2$ relative to bare 2PY (*cf.* Figure 1B) and the blue shifts exhibited by these complex origins indicate that changes in both the shapes and relative displacements of the intermolecular potentials occur on electronic excitation. The other strong transitions, shown in Figure 1A to the blue of the disolvated complex origin, could result from higher order 2PY–(NH$_3$)$_n$, $n \geq 3$, complexes.

A. 2-Pyridone–NH$_3$. The rotationally resolved spectrum of the electronic origin band of the 2PY–NH$_3$ complex is shown in Figure 2. This band is a *b*-type band; *i.e.*, the $S_1 \leftarrow S_0$ transition moment (TM) lies parallel to the *b* inertial axis. The corresponding band in the $S_1 \leftarrow S_0$ spectrum of 2PY–H$_2$O also is *b*-axis polarized (≥95%).[2] An approximate geometry of the single ammonia complex may be derived 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. The similarly oriented TMs of 2PY–H$_2$O and 2PY–NH$_3$, together with the relatively small difference in the masses of water and ammonia, suggest that the 2PY–NH$_3$ complex (**I**) has a geometry similar to that of 2PY–H$_2$O (**II**).



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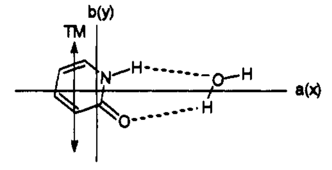

II

From this result, we conclude that in 2PY–NH$_3$ the ammonia molecule forms a hydrogen bond with the amine hydrogen of 2PY. However, in order to conserve the inertial axis orientation of the two complexes with respect to the 2PY subunit, the hydrogen bond in 2PY–NH$_3$ must be far from linear. The nonlinear nature of this hydrogen bond raises the possibility that there is a second hydrogen bond between an ammonia hydrogen and the carbonyl oxygen of 2PY. In other words, NH$_3$ may play a role as *both* a hydrogen bond donor and a hydrogen bond acceptor in 2PY–NH$_3$.

The structural similarities between the water and ammonia complexes of 2PY might lead one to expect very similar $S_1 \leftarrow S_0$ spectra. However, the 2PY–NH$_3$ spectrum is further complicated by coupling to the hindered internal rotation of the ammonia subunit, which splits each rovibronic transition into A and E torsional lines. A splitting of the A and E subbands results, owing to a difference in the threefold NH$_3$ torsional barrier heights in the two electronic states. Additional splittings occur for the high K-lines of the E subband. These torsion-induced splittings make it possible to distinguish the E-lines from the A-lines and to separately fit the two subspectra.

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[4] Held, A.; Champagne, B. B; Pratt, D. W. *J. Chem. Phys.* **1991**, *95*, 8732.

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

Table I. Inertial Parameters of the Zero-Point Vibrational Levels of the S_0 and S_1 Electronic States of 2-Pyridone–NH_3

	A ↔ A transitions		E ↔ E transitions	
	S_0	S_1	S_0	S_1
A (MHz)[a]	3724.5	3670.3	3723.8	3666.3
B (MHz)[a]	1381.3	1350.3	1381.3	1350.3
C (MHz)[a]	1013.1	993.1	1013.0	993.1
D_a (MHz)[a]			27.5	140.2
ΔI (amu Å^2)[b]	−2.74	−3.10	−2.72	−3.23
κ	−0.728	−0.733	−0.728	−0.733
origin (cm^{-1})[c]	30 006.6335		30 006.8142	

[a] ±0.1 MHz. [b] Inertial defects, ±0.03 amu Å^2. [c] Absolute frequency ±0.002 cm^{-1}, relative frequency ±0.0001 cm^{-1}.

A full discussion of the torsion-rotation Hamiltonian and its application to such problems has been given elsewhere.[6,7] The A and E subbands in the $S_1 \leftarrow S_0$ spectrum of 2PY–NH_3 were analyzed using the appropriate torsion-rotation Hamiltonians in the high-barrier approximation. The standard deviations of the fits were both less than 4 MHz, significantly less than the experimental line width. 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 the fluorescence lifetime of about 9 ns. This frequency-determined lifetime is the same, within experimental error, as the observed lifetimes of 2PY, $(2PY)_2$, and 2PY–H_2O.[2,4,8]

A portion of Figure 2A, shown in Figure 2B at full experimental resolution along with the corresponding calculated A- and E-line spectra, demonstrates the quality of the fit. From the fact that the A and E subbands are split by 1858.47 MHz, with the E subband lying at higher frequency, we conclude that the S_1 NH_3 torsional barrier is smaller than the S_0 NH_3 torsional barrier. Because the combined intensity of the E-lines is about the same as the intensity of the corresponding A-lines, we also conclude that there is little or no shift of the S_1 surface relative to the S_0 surface along the torsional coordinate.

Table I lists the derived inertial parameters, including the first-order torsion-rotation perturbation constants of the zero-point vibrational levels of the S_0 and S_1 electronic states of 2PY–NH_3. The first-order coefficients listed in Table I are defined as $D_a = \rho_a F W_E^{(1)}$, where $\rho_a = \lambda_a A/rF$. λ_a is the direction cosine that describes the orientation of the C_3 axis of the NH_3 rotor in the principal axis frame of the complex. Only the D_a coefficients (one for each electronic state) were required to fit the E subband. This suggests that the C_3 axis of the NH_3 rotor lies essentially parallel to the *a* principal axis of the complex in both states; *i.e.*, $\lambda_a \sim 1$. This finding is consistent with the assignment of a nonlinear hydrogen bond to the amine hydrogen of 2PY (*cf.* structure I).

Having determined the approximate orientation of the NH_3 molecule in 2PY–NH_3, we next used the experimental rotational constants (corrected for the second-order perturbations)[6,7] to calculate the S_0 and S_1 effective structures of 2PY–NH_3. In this calculation, the bond angles and distances in the pyridone ring were fixed at the values determined for α-pyridone by Penfold[9] using X-ray crystallography. We then defined two hydrogen-bonding parameters, the heavy-atom separation R(N–H···NH_3) and the heavy-atom C_2–N···NH_3 in-plane angle θ, as shown in Figure 3. These parameters were adjusted until the calculated and experimental constants converged to within 0.1% of each other. In these calculations, all atoms were restricted to in-plane positions except for two ammonia hydrogens. This restriction is consistent with the small negative inertial defect determined for 2PY–NH_3 (Table I). The orientation of the NH_3 C_3 rotor axis was fixed parallel to the *a* inertial axis of 2PY–NH_3, as determined experimentally (*i.e.*, $\lambda_a = 1$). The NH_3 N–H bond lengths were fixed at the experimentally determined values for free ammonia (1.014 Å),[10] and the angles between each N–H bond and the C_3 rotor axis were fixed at the values required (61.4° in both states) to fit the experimentally determined value of the internal rotor constant *F*. With these assumptions, we find that $R = 2.94 \pm 0.02$ Å and $\theta = 96.9 \pm 0.3°$ in the ground state of 2PY–NH_3. On electronic excitation to the S_1 state of 2PY–NH_3, *R* increases to 3.02 ± 0.3 Å and θ increases to 98.6 ± 0.3°. The increase in the heavy-atom separation on electronic excitation suggests that the 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.

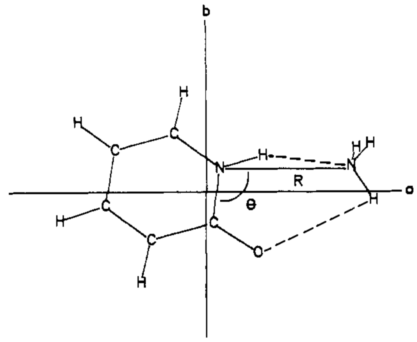

Figure 3. Effective structure of the 2PY–NH_3 complex. *R* is the interatomic distance between the 2PY nitrogen and the ammonia nitrogen. θ is the angle made between these two nitrogens and C_2 of 2PY.

Table II. NH_3 Torsional Parameters in the S_0 and S_1 Electronic States of 2-Pyridone–NH_3

	S_0		S_1	
	A	*E*	*A*	*E*
$W^{(1)}$		7.258 × 10^{-3}		3.756 × 10^{-2}
S		25.937		16.774
$W^{(2)}$	8.756 × 10^{-3}	−4.378 × 10^{-3}	4.479 × 10^{-2}	−2.239 × 10^{-2}
$W_A^{(0)} - W_E^{(0)}$	5.996 × 10^{-3}		3.085 × 10^{-2}	
$\Delta\nu_{A-E}$ (cm^{-1})	−0.1807 (2)			
F (cm^{-1})	7.27 (5)			
V_3 (cm^{-1})	424.3 (2)		274.4 (2)	

The torsional barrier heights in each electronic state of 2PY–NH_3 were determined as follows. First, $W_E^{(1)}$ values were calculated from the relation $W_E^{(1)} = rD_a/\lambda_a A$, and the reduced barrier heights *s* were determined from the $W_E^{(1)}$ values using Herschbach's tables.[11] Then, the average *F* values of the NH_3 rotor in both states were determined from the relation $\Delta\nu_{AE}/\Delta\Delta W_{AE}^{(0)}$. Here, $\Delta\nu_{AE}$ is the difference between the ground- and excited-state tunneling splittings and $\Delta\Delta W_{AE}^{(0)} = \Delta W_{AE}^{\prime(0)} - \Delta W_{AE}^{\prime\prime(0)}$, where the $\Delta W_{AE}^{(0)}$ values are the differences in the zero-order perturbation coefficients calculated from *s*. Finally, the V_3 barrier heights were determined from the relation $V_3 = 9sF/4$. The calculations were iterated several times until self-consistent values of V_3 were obtained. We find that $V_3(S_0) = 424.3$ cm^{-1} and $V_3(S_1) = 274.4$ cm^{-1}. Less accurate values of $V_3(S_0) = 400$ cm^{-1} and $V_3(S_1) = 280$ cm^{-1} were obtained from the second-order contributions to the effective A- and E-line rotational constants.[6,7] Table II summarizes the NH_3 torsional parameters derived for the S_0 and S_1 states of 2PY–NH_3.

B. 2-Pyridone–$(NH_3)_2$. The strong band at 30 187 cm^{-1} in Figure 1B is the 0_0^0 transition of 2PY–$(NH_3)_2$. The rotationally

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(6) Tan, X.-Q.; Majewski, W. A.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1991**, *94*, 7721.

(7) Plusquellic, D. F.; Tan, X.-Q.; Pratt, D. W. *J. Chem. Phys.* **1992**, *96*, 8026.

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(10) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules;* van Nostrand Co.: Princeton, NJ, 1945; p 439.

(11) See: Hayashi, M.; Pierce, L. *J. Chem. Phys.* **1961**, *35*, 1148.

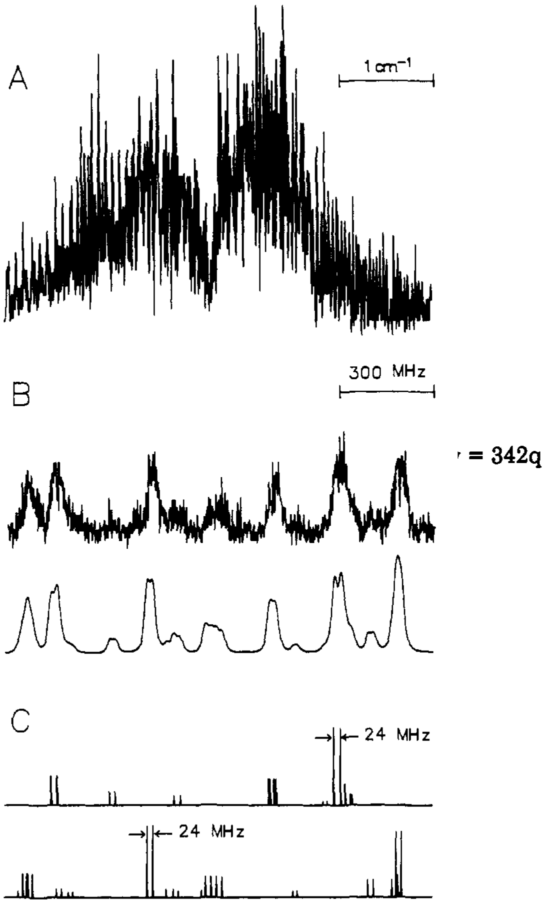

Figure 4. Rotationally resolved fluorescence excitation spectrum of the 2PY-$(NH_3)_2$ origin band. Panel B shows a portion of the observed spectrum (taken from a region in the spectrum where all four bands overlap) at full experimental resolution, compared to the corresponding simulated spectrum. The band is a superposition of four closely overlapping bands, as shown from the simulated stick spectra in panel C.

resolved spectrum of this band is shown in Figure 4A. The band spans ~5 cm^{-1} and contains over 4000 lines. While not apparent from Figure 4A, the spectrum actually consists of four overlapping bands. These overlapping bands are divided into two sets, of two bands each. The strategy used to fit each of these bands began with an estimate of the rotational constants in both states determined from an approximate 2PY-$(NH_3)_2$ geometry. We started with constants calculated from a geometry constructed by replacing the two hydrogen-bonded water molecules in the derived effective structure of 2PY-$(H_2O)_2$[2] with two ammonia molecules. Employing a rigid-rotor Hamiltonian, we then obtained fits of all four observed spectra[12] with standard deviations less than 4 MHz, significantly less than the experimental line width. The two sets of bands are separated by 0.0616 cm^{-1} while the smaller splitting between the bands within each set is 0.0008 ± 0.0001 cm^{-1}.

Figure 4C shows calculated stick spectra of the two separate sets of lines while Figure 4B demonstrates the quality of the fit with all four bands included. (Only a small portion of Figure 4A is shown here; the fit is equally good over the entire spectrum.) The line shape was fit with the same Voigt profile used for 2PY-NH_3, with Lorentzian and Gaussian contributions of 18 and 20 ± 2 MHz, respectively. The intensities of all four bands were fit to a rotational temperature of 6 K. All four bands in the 2PY-$(NH_3)_2$ spectrum are *b*-type transitions. The lack of any J or K dependence in the splittings observed within each set of bands eliminates Coriolis-type interactions or internal rotations as possible sources of the splittings. The derived rotational constants of the four bands of 2PY-$(NH_3)_2$ in its S_0 and S_1 electronic states are listed in Table III. The derived rotational constants are the same, within error, for all four bands in the ground and excited states, respectively.

Table III. Inertial Parameters of the Four Rotationally Resolved Bands in the $S_1 \leftarrow S_0$ Fluorescence Excitation Spectrum of 2-Pyridone-$(NH_3)_2$

band energy[a]	S_0		$S_1 - S_0$	
band 1	A''^b	2436.3	ΔA^b	40.9
30 187.5750 cm^{-1}	B''^b	840.1	ΔB^b	−32.3
	C''^b	630.0	ΔC^b	−15.3
	κ''	−0.767	$\Delta\kappa$	−0.026
	$\Delta I''^c$	−6.85	$\Delta\Delta I$	−0.59
band 2	A''	2436.1	ΔA	40.9
30 187.5758 cm^{-1}	B''	840.3	ΔB	−32.3
	C''	630.0	ΔC	−15.3
	κ''	−0.767	$\Delta\kappa$	−0.025
	$\Delta I''$	−6.60	$\Delta\Delta I$	−0.65
band 3	A''	2436.3	ΔA	41.0
30 187.6370 cm^{-1}	B''	840.3	ΔB	−32.4
	C''	629.9	ΔC	−15.3
	κ''	−0.767	$\Delta\kappa$	−0.025
	$\Delta I''$	−6.49	$\Delta\Delta I$	−0.67
band 4	A''	2436.3	ΔA	41.0
30 187.6378 cm^{-1}	B''	840.3	ΔB	−32.4
	C''	629.9	ΔC	−15.3
	κ''	−0.767	$\Delta\kappa$	−0.025
	$\Delta I''$	−6.53	$\Delta\Delta I$	−0.68

[a] Absolute frequencies accurate to ±0.002 cm^{-1}; relative frequencies accurate to ±0.0001 cm^{-1}. [b] ±0.1 MHz. [c] Inertial defects, ±0.03 amu Å².

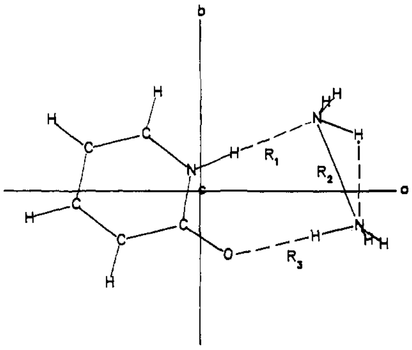

Figure 5. Effective structure of the 2PY-$(NH_3)_2$ complex. R_1, R_2, and R_3 are the intermolecular heavy-atom separations varied in the structural fit.

An effective structure of 2PY-$(NH_3)_2$ was calculated from its experimentally derived rotational constants using a procedure similar to that used for 2PY-NH_3. The fixed structural parameters for the pyridone ring and the ammonia molecules were the same as those described earlier. The parameters used to construct the effective geometry of 2PY-$(NH_3)_2$ are the three intermolecular heavy-atom separations R_1(N—H···NH_3), R_2[N(H_3)···H—NH_2], and R_3[(C=)O···H—NH_2] shown in Figure 5. These parameters were adjusted until the experimental and calculated constants converged to within 0.1% of each other. The resulting ground- and excited-state values are $R_1'' = 3.09$, $R_2'' = 2.87$, $R_3'' = 3.03 \pm 0.03$ Å and $R_1' = 3.24$, $R_2' = 2.72$, $R_3' = 3.18 \pm 0.03$ Å, respectively. The orientations of the two NH_3 molecules were fixed so that the two hydrogen bonds made with 2PY were linear and planar. The hydrogen atom bridging the two ammonia subunits also was restricted to lie in the 2PY plane. The four remaining ammonia hydrogens, two on each NH_3, were fixed out-of-plane by angles of ±60°. In this conformation, 2PY-$(NH_3)_2$ has a calculated inertial defect of −5.59 amu Å². Comparing this value to the average experimental ground-state value of −6.62 amu Å² suggests that all heavy atoms of 2PY-$(NH_3)_2$ lie in the plane.

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[12] 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.

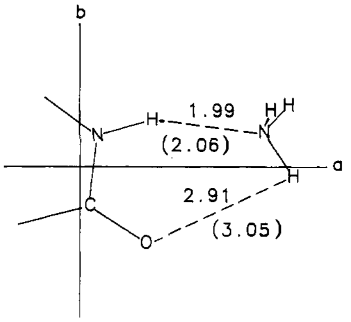

Figure 6. Hydrogen bond geometries of $2PY–NH_3$ in its S_0 and S_1 states. The hydrogen bond lengths shown were derived from the effective structures of $2PY–NH_3$; values in parentheses are for the S_1 state.

Discussion

The most interesting conclusion that can be drawn from these results is that *two* hydrogen bonds exist in $2PY–NH_3$, one hydrogen bond in which ammonia acts as proton acceptor (N–H···*N*) and a *second* hydrogen bond in which the *same* ammonia molecule acts as a proton donor (O···H–*N*). The principal evidence for the existence of this second hydrogen bond is the large barrier to hindered internal rotation of the NH_3 group in $2PY–NH_3$, V_3 = 424 cm^{-1} in the ground state. Now, in $2PY–H_2O$, we have shown that the single water molecule forms two planar, nonlinear hydrogen bonds with the amine hydrogen and the carbonyl oxygen of 2PY, in both electronic states.[2] In $(H_2O)_2$[13] and $(NH_3)_2$,[14] one could argue that one of the two units in each dimer is the hydrogen donor and the other is the acceptor. But in spite of the importance of ammonia and amines in serving as both hydrogen bond donors and acceptors in the condensed phase, there is no known example of a single ammonia molecule acting simultaneously as a hydrogen bond donor and acceptor in the gas phase.[15] $2PY–NH_3$ apparently is the first exception to this rule.

"All of us know that hydrogen bonds are important, for example in making the structure of water peculiar, in holding the strands of DNA together, or in accounting for the way in which protein molecules cohere with themselves, but few of us know what hydrogen bonds are like."[16] Pauling[17] described the hydrogen bond as "largely ionic in character and only formed between electronegative atoms". According to Pimentel and McClellan,[18] "A hydrogen bond exists when there is evidence of bonding and there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom". And, more recently Jeffrey and Saenger[1] have stated, "A hydrogen bond is the attractive force that arises between a donor bond and another acceptor atom." These broad definitions certainly suggest that the intermolecular interactions between NH_3 and 2PY in $2PY–NH_3$ and $2PY–(NH_3)_2$, between H_2O and 2PY in $2PY–H_2O$ and $2PY–(H_2O)_2$,[2] and between the two 2PY molecules in $(2PY)_2$[8] are those of hydrogen bonding. But what are the specific pieces of evidence for the existence of hydrogen bonds in the ammonia complexes of 2PY?

Geometric parameters such as hydrogen bond distances and angles often are used to determine the extent to which a hydrogen bond exists. There is a significant tendency for stronger hydrogen bonds to be shorter and more linear than weaker hydrogen bonds.[1] The S_0 hydrogen bond lengths and angles in our effective structure of $2PY–NH_3$ are r_1[(N—)H···N(H_3)] = 1.99 ± 0.03 Å and r_2[(C=)O···H(—NH_2)] = 2.91 ± 0.1 Å, and $\angle_1$[N—H···N(H_3)] = 154.2 ± 3° and $\angle_2$[(C=)O···H—N(H_2)] = 87.2 ± 10°, as shown in Figure 6. r_2 is nearly 1 Å longer than r_1. By this criterion, then, the interaction between the carbonyl oxygen and a hydrogen atom of the ammonia molecule in $2PY–NH_3$ must be very weak, if it exists at all.

The fully resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of $2PY–NH_3$ provides definite evidence for the existence of this bond. It also gives a quantitative measure of its strength. The spectrum exhibits torsion-rotation perturbations from which the barriers to hindered internal rotation of the attached NH_3 group in both electronic states have been determined. The ground-state value of this barrier is V_3 = 424 cm^{-1}. For comparison, the NH_3 torsional barriers in the ground and excited states of the hydrogen bonded complexes of 2-naphthol (2HN) and ammonia are $V_3(S_0)$ = 41.1 and $V_3(S_1)$ = 53.8 cm^{-1} for the *cis* rotamer and $V_3(S_0)$ = 34.2 and $V_3(S_1)$ = 58.2 cm^{-1} for the *trans* rotamer.[7] The hydrogen bond distances in these complexes are r[(O–)H···N(H_3)] = 1.76, 1.58, 1.79, and 1.52 Å, respectively, significantly smaller than those in 2PY complexes. As a result, model calculations of the barriers in the $2HN–NH_3$ clearly show that they are steric in origin. The barriers are caused by repulsive van der Waals interactions between the NH_3 hydrogens and the neighboring naphthalene ring hydrogen atoms.[7] No such interactions exist in $2PY–NH_3$. Despite this fact, and despite the fact that the (C=)O···H(—NH_2) hydrogen bond length in $2PY–NH_3$ is ~1 Å larger, the NH_3 torsional barrier in ground-state $2PY–NH_3$ is nearly an order of magnitude larger than the corresponding *steric* barriers in $2HN–NH_3$. We therefore conclude that the NH_3 torsional barrier in $2PY–NH_3$ is *electronic* in origin. In other words, what hinders the rotation of NH_3 about its C_3 axis in $2PY–NH_3$ is a weak *donor* hydrogen bond between a hydrogen atom of the attached ammonia and the carbonyl oxygen of 2-pyridone. Further, the torsional barrier height (424 cm^{-1}) must be a measure of the strength of this bond, since the barrier would be near zero if no such bond existed. Comparable torsional barriers that are principally electronic in origin have been observed in other systems.[6]

Several additional pieces of evidence may be cited to support the view that ammonia acts as both a hydrogen bond donor and acceptor in $2PY–NH_3$. One is the structural similarity between $2PY–NH_3$ and $2PY–H_2O$. Additionally, there are similarities in the isotope shifts of the 0_0^0 bands of several deuterated isotopomers of $2PY–NH_3$[5] and $2PY–H_2O$.[2,5] The single-water complex of 2PY is known to exist in a double-hydrogen-bonded geometry.[2] And, in a theoretical study,[19] it has been shown that the *ab initio* geometry of the hydrogen-bonded formamide–ammonia complex exhibits two hydrogen bonds, one acceptor bond involving the amine hydrogen and a second, weaker *donor* bond to the carbonyl oxygen.

All complex 0_0^0 bands exhibit significant frequency shifts relative to the $S_1 \leftarrow S_0$ electronic origin of the bare molecule. These shifts are measures of the differences in the strengths of the hydrogen bonds in the two electronic states. In order of increasing displacement, the shifts with respect to the lower frequency conformer of bare 2PY are $2PY–NH_3$ (176 cm^{-1}), $2PY–(NH_3)_2$ (356 cm^{-1}), $2PY–H_2O$ (633 cm^{-1}),[2] $2PY–(H_2O)_2$ (888 cm^{-1}),[2] and $(2PY)_2$ (944 cm^{-1}).[8] All shifts are blue shifts; *i.e.*, shifts to higher energy. This shows that, in general, the strengths of the hydrogen bonds decrease on electronic excitation and that these bonds are weaker in $2PY–NH_3$ and $2PY–(NH_3)_2$ than in $2PY–H_2O$, $2PY–(H_2O)_2$, and $(2PY)_2$. All heavy-atom separations increase on electronic excitation, with the exception of the "dimer" bonds in $2PY–(NH_3)_2$ and $2PY–(H_2O)_2$. This shows that the heavy-atom separations are qualitative measures of hydrogen bond strengths in the gas phase, as they are in the condensed phase. The increases in the heavy-atom separations

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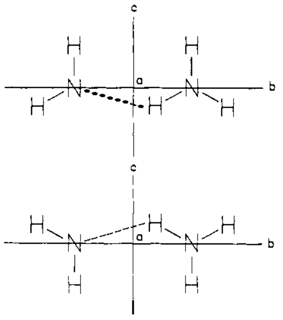
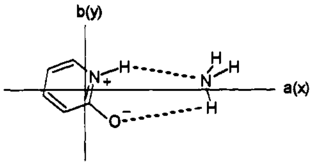


Figure 7. Out-of-plane hydrogen bond connecting the two ammonia molecules in 2PY-$(NH_3)_2$. The view is along the *a* inertial axis, showing a projection of atomic positions in the *bc* plane.

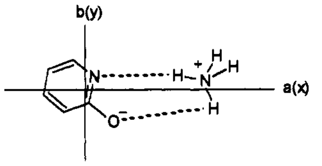
in 2PY-NH_3, which are comparable to those in 2PY-H_2O,[2] lead to a decrease in the barrier to internal rotation of the attached NH_3 group, from 424 cm^{-1} in the S_0 state to 274 cm^{-1} in the S_1 state. Notably, this decrease of 150 cm^{-1} is comparable to the blue shift of its origin band, 176 cm^{-1}.

2PY-$(NH_3)_2$, whose structure is shown in Figure 5, contains two rings. One is the relatively rigid six-membered 2PY ring, and the second is an eight-membered ring formed *via* hydrogen bonds between the two ammonias and 2PY. As noted earlier, the inertial defect of 2PY-$(NH_3)_2$ in its ground state, -6.62 amu Å^2, suggests that all heavy atoms in the two rings lie in a common plane and that at least four of the ammonia hydrogens lie above or below this plane. However, orienting the ammonia subunits so that all hydrogen bonds are linear will introduce significant ring strain. This ring strain is analogous to that exhibited by the cycloalkanes. It is not unreasonable, then, to suggest that the eight-membered ring distorts into a nonplanar conformation in order to relieve this strain. Our comparison of the experimental and calculated inertial defects suggests that the distortion in the ground state may occur at one or more of the bridging hydrogen atoms, most likely at the hydrogen atom connecting the two ammonia molecules. This leads to two different conformations of 2PY-$(NH_3)_2$, shown in Figure 7. The two different conformations, apparently equivalent in Figure 7, could be inequivalent, owing to the fact that the "left-hand" ammonia also acts as a hydrogen bond donor with the carbonyl oxygen of 2PY, whereas the "right-hand" ammonia also acts as a hydrogen bond acceptor with the amine hydrogen of 2PY. This inequivalence could lead to differences in the linearities of the hydrogen bonds connecting the two ammonia molecules to 2PY. Rotation of one or both ammonia molecules about an axis other than the hydrogen bond axis will introduce differences in the exocyclic hydrogen atoms attached to the same ammonia nitrogen. This inequivalence could be responsible for the existence of two sets of bands in the $S_1 \leftarrow S_0$ spectrum of 2PY-$(NH_3)_2$, without requiring that the two sets of levels have significantly different rotational constants. Further, as can be seen from Figure 7, the bridging hydrogen atom can invert between the two structures, which could lead to a secondary tunneling splitting in each set of bands. This type of motion requires only that the two NH_3 molecules rotate about their hydrogen bonds to 2PY, without significantly distorting the apparent linearity of the bonds, and therefore is clearly "feasible". Isotope substitution experiments will be necessary to determine whether or not this explanation of the four bands in the $S_1 \leftarrow S_0$ spectrum of 2PY-$(NH_3)_2$ is correct.

The current view of the amphoteric properties of ammonia is that it is a strong proton acceptor but has very little proclivity to donate protons. We may ask then, "What changes occur in the ammonia molecule, when it is complexed to 2PY, that activate an N-H group to form donor hydrogen bonds?" To answer this question, we need to examine the changes in the electronic properties of 2PY that take place when it is complexed with polar solvent molecules. Simple valence bond theory describes the structure of a polyatomic molecule as a superposition of all canonical structures of the molecule, including ionic structures. Recent *ab initio* calculations[20] show an increased importance in the weight of the ionic resonance structures in 2PY on going from the gas phase to polar solvents. These results are substantiated by our own experimental results on 2PY-H_2O and 2PY-$(H_2O)_2$, which show that 2PY distorts toward the zwitterionic form when the hydrogen bonds to the solvent are formed.[2] The ionic structures that are likely to be important in 2PY-NH_3 are shown in structures III and IV. The partial negative charge on the carbonyl oxygen in both structures may introduce enough polarity into the N-H bond to persuade the ammonia to form two hydrogen bonds. Structure **IV** corresponds to an ionic, proton-transferred structure of 2PY-NH_3. In this structure, the ammonia molecule is replaced by its conjugate acid, NH_4^+, which is an excellent proton donor. Analogous ionic structures may be drawn for 2PY-$(NH_3)_2$, which should exhibit an even greater propensity for proton donation than 2PY-NH_3. For this reason, higher order 2PY-$(NH_3)_n$, $n \geq 3$, complexes, if they can be produced in the gas phase, will be extremely interesting candidates for future study by fluorescence excitation techniques.



III



IV

Summary

We have obtained and fit the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of the hydrogen-bonded complex of ammonia with 2PY. The resolved spectrum exhibits perturbations that have their origin in an interaction between the hindered torsional motion of the attached NH_3 and the overall rotational motion of the complex. Analyses of these data yield the effective structure of the complex and the barriers to internal rotation of the ammonia in both electronic states. The correlations between the hydrogen bond distances and the barriers to internal rotation in the S_0 and S_1 states strongly suggest the existence of two hydrogen-bonding interactions. One is between the ammonia nitrogen and the 2PY amine hydrogen, and the second, less obvious, is between an ammonia hydrogen and the 2PY carbonyl oxygen. The experimental results reported here provide the first evidence of a single gas-phase ammonia molecule acting as both a hydrogen bond donor and hydrogen bond acceptor.

Spectra of the disolvated ammonia complex also were obtained. 2PY-$(NH_3)_2$ is planar with respect to the heavy atoms, in both states. It exhibits three hydrogen bonds: one between an ammonia and the amine hydrogen, one between a second ammonia molecule and the carbonyl oxygen, and one between the two ammonia molecules themselves. The hydrogen bonds in 2PY-$(NH_3)_2$ are stronger than the corresponding bonds in 2PY-NH_3. We found no evidence for any internal rotation of either ammonia molecule in 2PY-$(NH_3)_2$. The hydrogen bond formed between the two ammonia molecules in 2PY-$(NH_3)_2$ 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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