

Indole–H₂O in the Gas Phase. Structures, Barriers to Internal Motion, and S₁ ← S₀ Transition Moment Orientation. Solvent Reorganization in the Electronically Excited State

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Received: June 2, 1998; In Final Form: July 29, 1998

Rotationally resolved S₁ ← S₀ fluorescence excitation experiments have been performed on a solute–solvent complex of indole and water in a molecular beam. The results show that the complex whose S₁ ← S₀ origin is shifted by 132 cm⁻¹ below the bare molecule origin is a 1:1 complex, with the water molecule linked to the indole frame via a quasi-linear N–H···OH₂ σ hydrogen bond. The results also show that both the position and the orientation of the attached water molecule change when the photon is absorbed. The properties of the intermolecular potential-energy surfaces that govern these motions in both electronic states are derived from an analysis of the high-resolution spectrum.

Introduction

Solvent reorganization, or relaxation, is a time-honored concept in the electronic spectroscopy of the condensed phase.¹ Thus, to explain the shift in the frequency of an absorption or emission band that often occurs on going from the gas phase to the condensed phase, a difference in the solvation energies of the ground and excited states is often invoked and attributed to changes in the local solvent structure and/or a variety of less specific, longer range effects. The large red shift of the fluorescence of tryptophan in water, the subject of many experimental and theoretical studies,² is a typical example. That such shifts might occur is certainly reasonable since the absorption of light by a chromophore changes its charge distribution and the ways in which it interacts with its environment. The literature is replete with successful empirical treatments of this phenomenon.³

Our interest is in solvent reorganization at the molecular level, in the changes in the positions and/or orientations of a neighboring solvent molecule that might occur when a chromophore absorbs light. We report here the observation of such changes in the solute–solvent complex of indole and water, studied in the gas phase using the technique of high-resolution electronic spectroscopy in molecular beams.⁴ Indole itself, the chromophore in tryptophan, has been previously studied in the gas phase using both microwave^{5,6} and optical^{7,8} techniques, providing valuable information about the structure and dynamical behavior of the isolated molecule in its S₀ and S₁ states. Concurrently, Wallace and co-workers⁹ discovered two band systems in the vibrationally resolved R2PI spectrum of a jet-expanded mixture of indole and water, one with an S₁ ← S₀ origin located 132 cm⁻¹ to the red of the bare molecule origin and a second weaker system with an origin located ~452 cm⁻¹ to the red. The latter system exhibits long Franck–Condon progressions in at least two low-frequency modes. Subsequent work by this group and others^{10,11} suggested that both band systems should be assigned to single-water complexes of indole;

the –132 cm⁻¹ origin is assigned to the σ -hydrogen-bonded structure N–H···OH₂, and the –452 cm⁻¹ origin is assigned to a π -hydrogen-bonded structure in which the water molecule interacts with the indole π cloud. However, Zwier and co-workers¹² have recently described gas-phase RIDIR experiments and density-functional calculations which, while supporting the first assignment, strongly suggest that the weaker band system should be assigned to a two-water cluster of indole in which the water dimer forms a hydrogen-bonded bridge between the N–H group and the aromatic π cloud.

Experiments on the latter band system are in progress. Here, we focus on the rotationally resolved fluorescence excitation spectrum of the strong band origin at –132 cm⁻¹. We find from our analysis of this spectrum that the carrier of this band is, in fact, the quasi-linear σ -hydrogen-bonded structure N–H···OH₂.¹³ We also find from the analysis that both the position and the orientation of the water molecule in the complex change when the photon is absorbed. We derive the properties of the intermolecular potential-energy surfaces that govern these motions from the high-resolution spectrum. The characterization of these surfaces in this and other surfaces will greatly enhance our understanding of light-induced solvent reorganization at the molecular level.

Experimental Section

High-resolution data were obtained using a molecular beam laser spectrometer described in detail elsewhere.⁴ Indole (>99%) was purchased from Aldrich and used without further purification. The molecular beam was formed by flowing Ar carrier gas (500 Torr) over room-temperature water and then over indole (heated to ~375 K) and, finally, expanding the resulting mixture through a heated 240 μ m quartz nozzle into a differentially pumped vacuum system. The expansion was skimmed 2 cm downstream with a 1 mm skimmer and crossed 13 cm further downstream by a continuous-wave ring dye laser operating with R590 and intracavity frequency doubled in BBO,

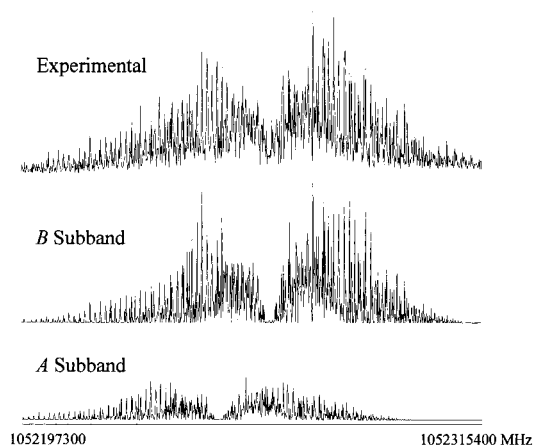


Figure 1. Rotationally resolved fluorescence excitation spectrum of the origin band of the $S_1 \leftarrow S_0$ transition of indole- H_2O , shifted 132 cm^{-1} to the red of the $S_1 \leftarrow S_0$ origin band of indole. The origin band of the complex is a superposition of two subbands which are separated by 0.4441 cm^{-1} . The top trace is the experimental spectrum. The second and third traces are the calculated B and A subbands, respectively.

yielding $350\text{ }\mu\text{W}$ of ultraviolet radiation. Under these conditions, the Doppler-limited spectral resolution is 18 MHz in the UV.

Fluorescence was collected using spatially selective optics, detected by a photomultiplier tube and photon counting system, and processed by a data acquisition system. Relative frequency calibration of the excitation spectrum was performed using a near-confocal interferometer having a mode-matched FSR of $299.7520 \pm 0.0005\text{ MHz}$ at the fundamental frequency of the dye laser. Absolute transition frequencies in the spectrum were determined by comparison to the iodine absorption spectrum and are accurate to $\pm 30\text{ MHz}$.

Results

Figure 1 shows the high-resolution spectrum of the -132 cm^{-1} origin band of indole-water. Given the extreme congestion in the spectrum, it was first subjected to an autocorrelation analysis¹⁴ to assess whether multiple bands might be present. This analysis revealed that there are two overlapping bands in the spectrum, separated by $\sim 13\text{ GHz}$, with significantly different relative intensities. We initially worked to fit the stronger of these two subbands. Rotational analyses were performed with ASYROT,¹⁵ which utilizes Watson's Hamiltonian¹⁶ for the distortable asymmetric rotor. All calculations were done using the A-reduction in the prolate I' representation ($x \rightarrow b$, $y \rightarrow c$, $z \rightarrow a$). The fitting procedure began with the simulation of a spectrum using assumed geometries of the complex, with a single undistorted water molecule attached via a linear σ -hydrogen bond to the indole NH group, with a heavy-atom separation of 3.0 \AA . The rotational constants of the bare molecule in its ground and excited electronic states were taken to be identical to those previously measured.⁵⁻⁸ b -Type selection rules were assumed, initially, in view of the absence in the subband spectrum of a strong Q branch.

Quantum number assignments of single transitions in the simulated spectrum to corresponding transitions in the experimental spectrum were made using a mouse-driven graphical interface.⁴ With an initial guess at the rotational temperature to estimate the J values associated with particular transitions, $K = 0$ progressions were first assigned using a rigid rotor Hamiltonian, followed by $K = 1, 2,$ and 3 progressions because the intensities were expected to decrease with increasing K . These preliminary assignments were then iteratively optimized

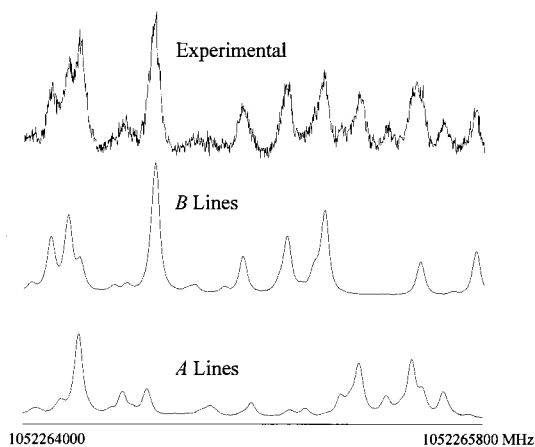


Figure 2. Portion of the high-resolution spectrum of indole- H_2O at full experimental resolution, extracted from the R branch of the stronger subband. The top trace is the experimental spectrum. The second and third traces show the separate calculated contributions of the two subbands in this region.

by a least-squares analysis. This analysis showed that transitions involving high J ($J \geq 10$) are shifted from their predicted rigid rotor positions, by as much as 100 MHz . Quartic distortion terms were then incorporated in the fit. A total of 484 line assignments were made, yielding a standard deviation of 3.5 MHz . Higher order distortion terms were found to be ill-determined.

To fit the weaker subband, a second spectrum was generated using the rotational constants of the stronger subband. Placement of the former subband origin at -13 GHz with respect to the latter resulted in a better match to the experimental spectrum. Quantum number assignments were then made in the manner described above. Again, a least-squares analysis revealed significant distortion effects; the final fit of 200 lines in the weaker subband utilized quartic distortion terms only, yielding a standard deviation of 3.7 MHz .

A single, unique temperature of 4.0 K was found to reproduce the relative intensities of all lines in each subband, resulting in significant population of ground-state levels up to $J \approx 30$. The hybrid band characters of both subbands were determined by choosing a set of single transitions and varying the ratio of a -, b -, and c -type transition moments until a best fit was obtained. No evidence for a - or c -type transitions was found in either subband; at least 98% of the experimentally observed intensity can be accounted for by b -type selection rules. Further, intensity anomalies arising from axis tilting, observed in the electronic spectrum of the bare molecule,⁸ were not detected in our fit of the spectrum of the complex nor are they expected given its pure b -type character.¹⁷ Finally, careful measurements of the relative intensities of comparable transitions in the two subbands gave an intensity ratio of 3:1, within $\pm 5\%$.

A portion of the experimental spectrum, expanded to full experimental resolution from the R branch of the stronger subband, is shown in Figure 2 together with the separate calculated contributions of the two subbands in this region. The quality of the fit is evident; omitting the distortion terms increases the standard deviations of the fits by factors of greater than 2. Owing to the spectral congestion, individual transitions could not be used to reliably determine the experimental line shape. A Voigt convolution ($\sim 18\text{ MHz}$ Gaussian and $\sim 30\text{ MHz}$ Lorentzian fwhm's) adequately models this line shape, yielding a line width of $44 \pm 5\text{ MHz}$. The observed Lorentzian component suggests a fluorescence lifetime significantly shorter

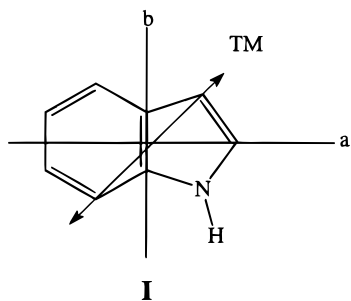
than that previously measured for indole–water, ~ 5 ns vs 21.0 ns.¹⁸ The lifetime of the bare molecule is 17.6 ns.¹⁸

Table 1 lists the inertial parameters of the complex in its two electronic states that were derived from this analysis.

Discussion

The data in Table 1 bear all of the expected signatures of a 1:1 complex in which the N–H group of indole acts as a hydrogen-bond (HB) donor to the water molecule, as recently concluded by Helm, et al.¹³ However, our spectrum of the -132 cm^{-1} band was recorded at substantially higher resolution, revealing some extremely interesting properties of the complex that were not previously known. For example, the fact that this spectrum is split into two subbands with relative intensities of 3:1 shows immediately that the water molecule undergoes a motion that renders its two hydrogen atoms equivalent, at least in the ground state. A similar splitting, attributed to a simple torsional motion of the water molecule about the HB axis, was found in the S_1 – S_0 spectrum of the phenol– H_2O complex.¹⁹ We also find from the analysis of our spectrum that there are small but significant differences in the inertial parameters of the two subbands (cf. Table 1). These are intimately linked to this motion. In what follows, we provide a preliminary interpretation of these data, focusing on the S_0 and S_1 structures of the complex, the barriers to internal motion, and the $S_1 \leftarrow S_0$ transition moment orientation. A more refined description of these and other properties of the complex will require isotopic labeling experiments, currently underway.

Structures of Indole– H_2O . We begin with a discussion of the structure of indole– H_2O in its two electronic states. Shown below is a sketch of the bare molecule (I), its principal in-plane inertial axes a and b , and the orientation of the $S_1 \leftarrow S_0$ transition moment (TM) in the inertial frame.⁸ Now the inertial defects



(Table 1, $\Delta I = I_c - I_a - I_b$) of indole– H_2O , though larger in magnitude than those of the bare molecule,^{5–8} are still relatively small and negative, indicating that the water molecule lies approximately in the indole plane in both electronic states. Attachment of the H_2O to the NH group of the bare molecule will rotate its a and b axes in a clockwise fashion, toward the NH group, resulting in a TM orientation in the complex that is close to its b axis, as observed. These two experimental observations thus establish the geometry of indole– H_2O in both states as the σ -hydrogen-bonded structure $\text{N}-\text{H}\cdots\text{OH}_2$.

More information about the structure of the complex and the possible motions of the water molecule with respect to the indole frame can be deduced from a comparison of the rotational constants of the complex with those of the bare molecule using Kraitchman's equations.²⁰ (Here, we used the rotational constants of a hypothetical rigid rotor complex, corrected for the higher order effects of torsional motion, inversion, and centrifugal distortion (see below).) Treating the water molecule as a single particle with mass 18 yields the coordinates of its

TABLE 1: Inertial Parameters of Indole– H_2O in Its Ground (S_0) and First Electronically Excited (S_1) States (-132 cm^{-1} Band)^a

state	parameter	strong subband	weak subband
S_0	A''	2062.5 ± 0.1	2064.2 ± 0.2
	B''	945.1 ± 0.1	945.0 ± 0.3
	C''	649.3 ± 0.1	649.2 ± 0.2
	Δ_J''	0.0011 ± 0.003	0.0001 ± 0.0010
	Δ_{JK}''	-0.006 ± 0.001	-0.006 ± 0.004
	Δ_K''	0.014 ± 0.001	0.014 ± 0.004
	δ_J''	0.0005 ± 0.0002	0.00006 ± 0.00050
	δ_K''	0.001 ± 0.002	-0.002 ± 0.007
	κ''	-0.581	-0.582
	$\Delta I''$	-1.412	-1.142
	S_1	A'	1987.6 ± 0.1
B'		963.5 ± 0.1	964.1 ± 0.3
C'		650.4 ± 0.1	650.4 ± 0.2
Δ_J'		0.0010 ± 0.0003	0.0001 ± 0.0011
Δ_{JK}'		-0.005 ± 0.001	-0.006 ± 0.005
Δ_K'		0.011 ± 0.001	0.011 ± 0.004
δ_J'		0.0004 ± 0.0001	0.00005 ± 0.00053
δ_K'		0.0007 ± 0.0014	-0.001 ± 0.008
κ'		-0.532	-0.531
$\Delta I'$		-1.745	-1.249
ν_0		35099.7 ± 0.1	35099.2 ± 0.1
assign	484	200	
OMC	3.51	3.70	

^a A , B , and C are the rotational constants (MHz), Δ and δ are the quartic distortion constants (MHz), κ is Ray's asymmetry parameter, ΔI is the inertial defect ($\text{amu } \text{Å}^2$), ν_0 is the band origin (cm^{-1}), and OMC is the standard deviation of the fit (MHz), based upon the number of assignments shown. Double primes refer to the S_0 state, single primes refer to the S_1 state.

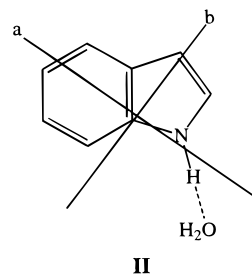
TABLE 2: Center of Mass (COM) Coordinates of the Water Molecule in the Principal Axis Frames of the Bare Indole Molecule and of the Indole– H_2O Complex^a

state	coordinate	bare molecule frame (Å)	complex frame (Å)
S_0	$ a $	2.282 ± 0.001	3.889 ± 0.001
	$ b $	4.056 ± 0.002	1.107 ± 0.001
	$ c $	0.35 ± 0.03	0.093 ± 0.007
	$ r $	4.666 ± 0.001	4.044 ± 0.001
S_1	$ a $	2.117 ± 0.001	3.828 ± 0.001
	$ b $	4.070 ± 0.003	1.116 ± 0.001
	$ c $	0.37 ± 0.03	0.100 ± 0.007
	$ r $	4.602 ± 0.001	3.988 ± 0.001

^a The distance between the water's COM and the indole's COM is given by r . Errors in the COM displacements were determined by propagating the errors in the measured rotational constants through the Kraitchman analysis.

center of mass in the principal axis frame of bare indole. These are listed in Table 2 for both electronic states. This analysis assumes that the structures of the two component parts are unchanged on complex formation.

The data in Table 2 show that the water molecule is attached to the indole frame via a quasi-linear $\text{N}-\text{H}\cdots\text{OH}_2$ hydrogen bond, as illustrated below (II). The vibrationally averaged



structure of the complex is one in which the oxygen atom lies

in the indole plane with the water plane perpendicular to the indole plane. However, the out-of-plane displacement coordinates $|c|$ are both nonzero, 0.35 Å in the S_0 state and 0.37 (± 0.03) Å in the S_1 state; the in-plane displacement coordinates are also different from simple expectations based on this model. We know from the observed tunneling splitting that the water molecule is undergoing some large amplitude motion. But this motion cannot be a simple torsional motion about the HB axis because such a motion would not displace the oxygen atom from the indole plane. Thus, we conclude that there are additional large amplitude motions of the water molecule in and out of the plane, and probably in the plane perhaps as large as 30° away from the HB axis.

The data in Table 2 also show that the equilibrium position of the water molecule in the complex changes on excitation of indole-H₂O to its S_1 state. This is apparent from the relatively large positive value of $\Delta B = B' - B''$ (Table 1; indole itself has negative ΔA and ΔB values^{7,8}) and from the differences in the S_0 and S_1 coordinates listed in Table 2. To estimate the light-induced changes in the position of the solvent molecule in the complex, we first performed a geometry optimization of the ground state of the bare molecule using MP2 with a 6-31G** basis set.²¹ The resulting structure yields rotational constants that are in excellent agreement with experiment (5–8, differences $\leq 0.08\%$). Then we placed the water molecule in the inertial frame of the bare molecule, using the coordinates in Table 2, and rediagonalized the inertia tensor, obtaining the COM coordinates of the water molecule in the inertial frame of the complex in both electronic states. These are also listed in Table 2. Examination of these results shows that the principal light-induced motion of the position of the solvent molecule is toward the solute; i.e., the donor-acceptor distance $R(\text{N}-(\text{H})\cdot\cdot\text{O}(\text{H}_2))$ decreases on electronic excitation. The calculated heavy-atom separation in the ground state of the complex is 3.07 Å; this appears to decrease by nearly 0.1 Å when the photon is absorbed. Our analysis neglects the known light-induced changes in the structure of the bare molecule.^{7,8} However, given the aforementioned changes in A and B , such effects are believed to be relatively small. A decrease in R would be consistent with an increased acidic character of the N-H hydrogen in the S_1 state,²² which strengthens the HB and produces the -132 cm^{-1} red shift of the S_1-S_0 origin band of the complex with respect to that of the bare molecule.

Barriers to Internal Motion. Equally interesting is the further finding that the equilibrium orientation of the water molecule in the complex also changes on electronic excitation. This conclusion comes from a careful analysis of the observed tunneling splitting of $\sim 13\text{ GHz}$ and the small but significant differences in the rotational constants of the two subbands in both electronic states (Table 1). These signal the contribution of some large amplitude motion to the spectrum. Suppose we assume, at the outset, that this motion is a simple torsional motion of the water molecule about a unique axis. In that event, the appropriate potential is of the form

$$V(\alpha) = \left(\frac{V_2}{2}\right)(1 - \cos 2\alpha) \quad (1)$$

This leads to a splitting of the zero-point vibrational level in each state into two subtorsional levels, $\sigma = 0$ and 1, which have unique symmetries (A and B) in the G_4 molecular symmetry group.¹⁹ The $\sim 13\text{ GHz}$ splitting of the two subbands is equal to the difference in the subtorsional splittings in the two electronic states, since the observed transitions obey the selection rule $\Delta\sigma = 0$. The two subbands will have different intensities

TABLE 3: Internal Rotation Calculations on Indole-H₂O

state	parameter	rotation about water's b axis	rotation about an axis in the bc plane, 55° off the b axis
S_0	rotor constant (GHz)	435.352	339.277
	θ (deg)	0 ± 15	0 ± 15
	V_2 (cm^{-1})	198.2 ± 14.0	168.5 ± 12.0
	subtorsional splitting (GHz)	15.273 ± 3.021	9.276 ± 2.000
S_1	rotor constant (GHz)	435.352	339.277
	θ (deg)	55 ± 15	55 ± 15
	V_2 (cm^{-1})	140.1 ± 25.0	121.7 ± 20.0
	subtorsional splitting (GHz)	36.592 ± 13.550	22.223 ± 8.231

since the $\sigma = 0$ and 1 levels have different nuclear spin-statistical weights (1 and 3, respectively¹⁹) and the four subtorsional levels will have different rotational constants, owing to the coupling between torsional motion and overall rotation.²³ All of these expectations are qualitatively consistent with the experimental results. However, one observation is quantitatively inconsistent; only the A'' values of the two ground-state subtorsional levels are different ($\Delta A'' = 1.69 \pm 0.25\text{ MHz}$), whereas both the A' and the B' values of the two excited-state subtorsional levels are different ($\Delta A' = 1.27 \pm 0.27$, $\Delta B' = 0.59 \pm 0.31\text{ MHz}$). (The quoted values are corrected for the effects of centrifugal distortion.) This shows that the axes about which the motion of the water molecule is occurring in the two states cannot be the same.

Two limiting models have been developed to deal with this problem, summarized in Table 3. In the first, the motion of the water molecule is assumed to be a simple rotation about its b axis, with an internal rotor constant of 435 GHz in both electronic states of the complex.²⁴ Then, using the principal axis method in the high-barrier approximation,²³ we estimate from the observed differences in the rotational constants of the two subtorsional levels a rotor axis angle (with respect to the a axis of the complex) of $\theta = 0^\circ$ and a barrier height of $V_2 = 198\text{ cm}^{-1}$ in the ground state and $\theta = 55^\circ$ and $V_2 = 140\text{ cm}^{-1}$ in the excited state. This leads to a predicted subband splitting of 21.319 GHz, in poor agreement with the experimental value of 13.314 GHz. In the second model, the water molecule is assumed to rotate about an axis in its bc plane, 55° off the b axis, with an internal rotor constant of 339 GHz.²⁴ This model yields rotor angles of $\theta(S_0) = 0^\circ$ and $\theta(S_1) = 55^\circ$ as before but significantly lower values of the barriers, $V_2(S_0) = 169\text{ cm}^{-1}$ and $V_2(S_1) = 122\text{ cm}^{-1}$. This leads to a predicted subband splitting of 12.947 GHz, in good agreement with the experimental value. We cannot explain our data by assuming that the water internal rotation axis itself changes when the photon is absorbed (cf. Table 3). Therefore, we conclude that the axis about which the water molecule is moving lies in its bc plane, 55° off the b axis, in both electronic states of the complex and that the orientation of this axis relative to the a axis of indole-H₂O changes by 55° on S_1 excitation.

Shown in Figure 3 are sketches of the local solvent structures in indole-H₂O in the two electronic states that are consistent with these results. Both structures have linear (or nearly linear) HB's; however, the orientation of the water plane relative to the HB axis in the two states is different. In the ground state, the N-H hydrogen is linked to one of the two sp^3 lone pairs of the oxygen atom, resulting in an angle between the water plane and the HB axis of $\sim 55^\circ$. In the excited state, the N-H hydrogen is linked to both lone pairs, resulting in a bifurcated structure with an angle between the water plane and the HB axis of $\sim 0^\circ$. Apparently, the observed solvent reorganization

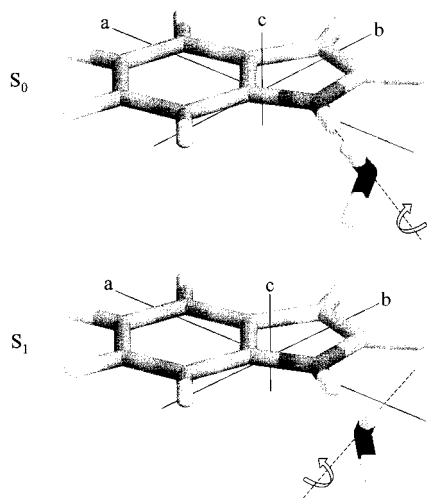
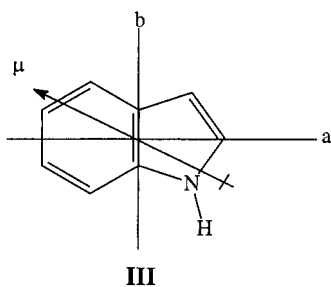


Figure 3. Solvent reorganization in indole-H₂O. The dashed line and arrow denote the axis about which the water molecule internal motion is occurring. The orientation of this axis (and the water plane) changes by $\sim 55^\circ$ on S₁ excitation.

is a consequence of “radial-angular coupling”; i.e., decreasing the heavy-atom separation R by electronic excitation produces in a change in the preferred orientation of the solvent plane with respect to the HB axis.²⁵

In retrospect, it is clear that the axis about which the water molecule is moving in the ground-state cannot be its b axis because such a motion would require a breaking of the HB, a much higher energy process than 100–200 cm⁻¹. It is also clear that the motion of the water molecule cannot be a simple torsional motion about an axis 55° off its b axis, since such a motion would not render the two water hydrogens equivalent. Therefore, the observed tunneling splitting (and differences in rotational constants) must, in fact, be due to the combined effects of internal rotation and inversion, or “wag”, similar to the “1–4” acceptor H₂O rotation in the water dimer and the phenol–H₂O complex, which have similar activation energies.²⁶ Such a motion accounts, at least in a qualitative way, for the observed out-of-plane motion of the water molecule. The derived values of V_2 are thus effective barrier heights for the torsion–inversion motion.

S₁ ← S₀ Transition Moment. Driving the observed solvent reorganization in indole–H₂O are significant changes in the electronic properties of the chromophore when it absorbs light. The S₁ ← S₀ optical TM is a sensitive measure of these changes. Currently, both experiment⁸ and theory^{27,28} agree that the S₁ state of the isolated molecule is the ¹L_b state, with a relatively small in-plane TM rotated away from the nitrogen and making an angle of $\sim 40^\circ$ with respect to a (see I). Our results on the complex are consistent with this view. Now indole itself has a permanent dipole moment of 2.09 D in the S₀ state,⁶ oriented in the manner shown below (III, $\mu_a = 1.59$, $\mu_b = 1.36$ D).



Unfortunately, we do not know the corresponding values in the

S₁ state. Chang et al.²⁹ found $|gD\mu_a| = 0.14$ D from an optical Stark measurement in the gas phase; theory^{27,28} suggests a small change in the magnitude of μ but is ambiguous concerning its orientation. Nonetheless, examination of the MO's that principally contribute to the S₁ ← S₀ excitation (and correctly reproduce the orientation of the TM) clearly shows that the direction of charge migration makes a large angle with the orientation of μ in III. This suggests, in turn, that a light-induced change in the orientation of μ in the solute is responsible for the observed reorientation of the solvent molecule on electronic excitation. Further experiments will be necessary to confirm this suggestion.

Acknowledgment. We thank Jason Ribblett and Prof. Leo Meerts for helpful discussions. This work has been supported by the NSF (CHE-9617208) and a grant from the Pittsburgh Supercomputing Center.

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