High Resolution Electronic Spectra of Anisole and Anisole−Water in the Gas Phase: Hydrogen Bond Switching in the S_1 State[†]

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Rotationally resolved $S_1 \leftarrow S_0$ electronic spectra of anisole and its hydrogen bonded complex containing one water molecule have been obtained. The results provide evidence for an "in-plane" complex in which the water molecule is attached via two hydrogen bonds to the anisole molecule, a donor O−H- - -O(CH_3) bond and an acceptor H−O- - -H(ring) bond. Analysis of the subbands that appear in the spectrum of the complex suggests that hydrogen bond "switching" occurs when the complex absorbs light. The former O−H- - -O(CH_3) bond is stronger in the ground (S_0) state, whereas the latter H−O- - -H(ring) bond is stronger in the excited (S_1) state. Dynamical consequences of this phenomenon are discussed.

Introduction

Three recent reports have described rotationally resolved spectra of anisole and its hydrogen bonded water complex, anisole−H_2O.[1−3] This complex is interesting because it appears to exhibit a structure in which the water molecule acts as an acid, donating one of its protons to the oxygen atom of the methoxy group. Previously, we have given preliminary descriptions of our own spectra of these two systems.[4,5] In this paper, we present a more thorough account of these findings with special emphasis on the hydrogen bond dynamics in anisole−H_2O that are revealed by a careful study of its high resolution electronic spectrum. The results suggest that the attached water molecule is "amphoteric", behaving as an acid when anisole is in its ground electronic (S_0) state but as a base when anisole is in its excited electronic (S_1) state.

Experimental Section

Anisole was supplied by Aldrich (99% purity) and used as received. High resolution spectra were obtained using the CW molecular beam laser spectrometer described elsewhere.[6] Typically, the sample was heated to 370 K, seeded into ∼300 Torr of Ar and expanded through a 240 μm nozzle. The sample was then skimmed once at 2 cm downstream and probed by the laser 12 cm downstream of the nozzle. Some experiments were performed in a high resolution port, 100 cm downstream. Complexes were formed by adding water to the expansion. More complete details are given elsewhere.[7,8]

Results

Figure 1 shows the rotationally resolved fluorescence excitation spectrum of the origin band of the $S_1 \leftarrow S_0$ transition of anisole at 36384.07 cm^{-1}. In agreement with previous work,[1] this spectrum was found to be a mainly *b*-type band which is consistent with assignment of the S_1 state of anisole as a ^1L_b state, as in the case of most singly substituted benzenes. A small amount of *a*-type character was detected in the spectrum owing to the inertial contribution of the "off-axis" methoxy group. The final fit shown in Figure 2 utilized 2.7% *a*-type character, corresponding to a tilt of the transition moment vector of ±9° with respect to the *b* axis. This is equal in magnitude to the contribution predicted by ab initio calculations.[7] No *c*-type transitions were found in the spectrum.

Four hundred lines were ultimately employed in the least-squares fit of the 0_0^0 band of anisole, resulting in an OMC standard deviation of 2.0 MHz for the spectrum recorded in the high resolution port. The calculated Gaussian and Lorentzian contributions to the observed Voigt line shape profiles of single rovibronic lines are 3 ± 1 and 12 ± 2 MHz, respectively. The two reported lifetimes of S_1 anisole are 30 ns[9] and 22 ns,[10] which would give Lorentzian contributions of 5 and 7 MHz, respectively. Apparently, the true lifetime of S_1 anisole at the band origin is less than 20 ns.

Table 1 lists the rigid rotor constants that were derived from fits of the data in Figures 1 and 2 together with other relevant data for comparison. Our values of the ground state rotational constants are somewhat more precise than those of Eisenhardt et al.[1] but significantly less precise than the microwave values.[3,11] Nonetheless, all three sets of values agree within the stated errors. Theory (MP2/6-31G**)[12] also reproduces the experimental results very well. Structurally, the most significant conclusion about anisole in its S_0 state is that all heavy atoms lie in the aromatic plane. Only the methyl group hydrogen atoms lie out of this plane. The inertial defect of anisole in its S_0 state (−3.4 amu Å^2) is virtually identical to that of 1-methylnaphthalene (−3.3 amu Å^2).[13]

The inertial defect of anisole in its S_1 state (−3.6 amu Å^2) is slightly larger in magnitude than that of the ground state. This provides evidence for increased vibrational amplitude along out-of-plane coordinates. And, as in the case of most other singly substituted benzenes, the S_1 state of anisole has a significantly larger aromatic ring as compared to the ground state. The ΔA, ΔB, and ΔC values of anisole ($\Delta A = A' - A''$, etc.) are very similar to those of phenol.[14] No evidence was found for any methyl or methoxy group torsional activity in the high resolution

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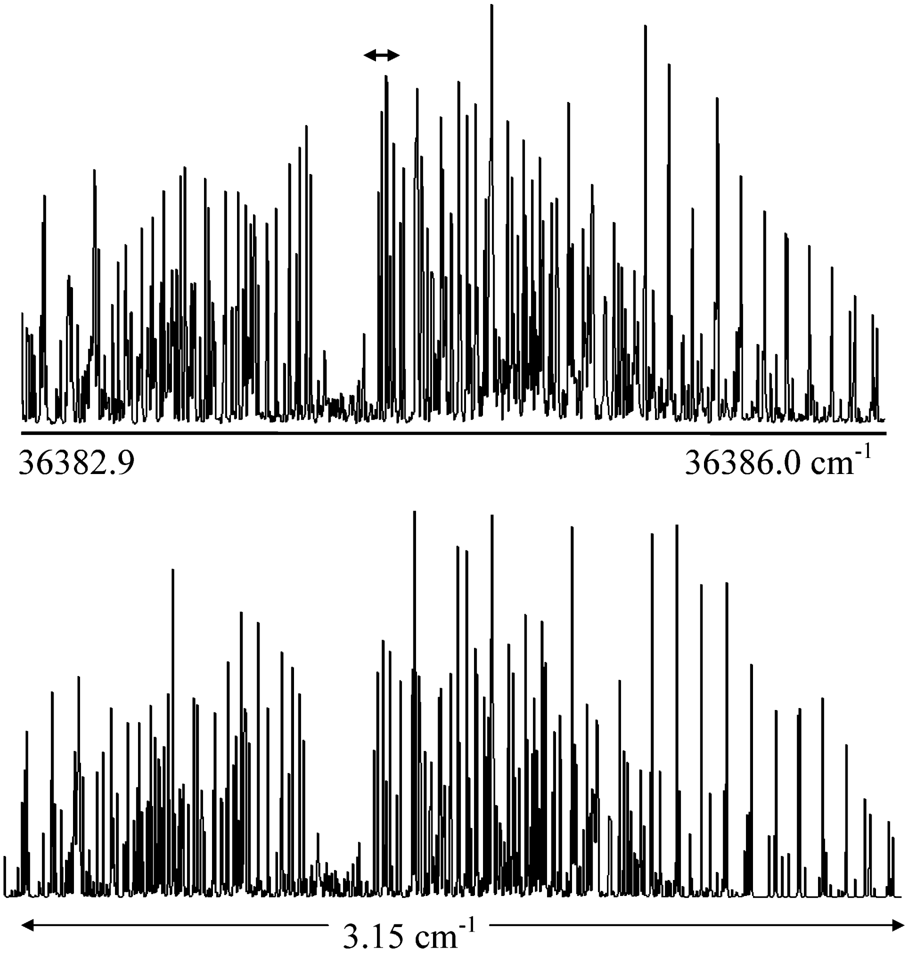


Figure 1. Central portion of the rotationally resolved fluorescence excitation spectrum of the 0_0^0 origin band in the S_1–S_0 electronic transition of anisole. Upper trace, experimental; lower trace, computed.

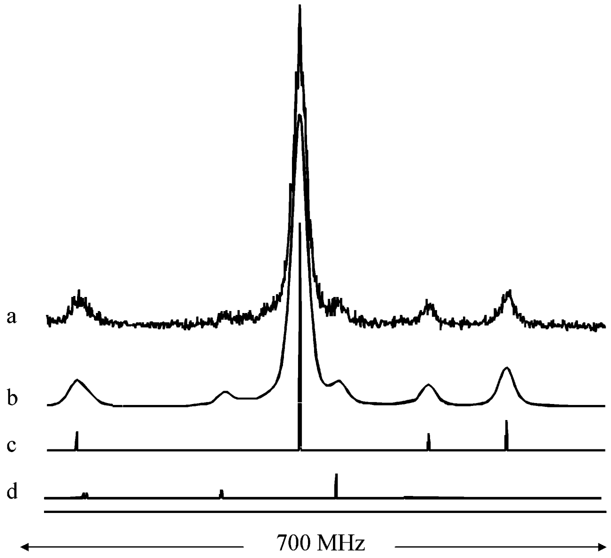


Figure 2. Expanded section (see Figure 1) of the Q-branch in the rotationally resolved S_1–S_0 fluorescence excitation spectrum of anisole is displayed in panel a. The corresponding simulated spectrum, using a Voigt line shape with 18 MHz Gaussian and 12 MHz Lorentzian components, is shown in panel b. Panels c and d show the contributions of *a*- and *b*-type components to this portion of the spectrum.

spectrum of the bare molecule. This is consistent with the results of state-of-the art density functional theory calculations,[15] which clearly show that anisole is "planar" with a ~12 kJ/mol barrier to internal rotation of the methoxy group in the S_0 state.

Figure 3 shows the rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectrum of anisole–H_2O. Again in agreement with previous work,[2] this spectrum is found to be mainly a *b*-type band, consistent with assignment of the S_1 state of the complex as a ^1L_b state. However, a more careful examination of this spectrum reveals several interesting features not apparent at lower resolution. First, an in-plane binding site of the attached H_2O is suggested by the observed band polarization. A binding site above or below the plane of the ring would result in a mainly

TABLE 1: Inertial Parameters of Anisole in Its Ground (S_0) and Electronically Excited (S_1) States

	this work	Eisenhardt et al.[a]	microwave[b]	MP2/ 6-31G**
A″ (MHz)	5028.8 (1)	5028.9	5028.867	5021.3
B″ (MHz)	1569.3 (1)	1569.4	1569.375	1570.4
C″ (MHz)	1205.8 (1)	1205.8	1205.836	1205.4
κ	−0.810	−0.81	−0.810	−0.8087
ΔI (amu Å^2)	−3.415	−3.41	−3.410	−3.200
$\Delta A'$ (MHz)	−233.2 (4)	−233.9		
$\Delta B'$ (MHz)	−13.5 (1)	−13.6		
$\Delta C'$ (MHz)	−21.3 (1)	−21.2		
κ	−0.794	−0.79		
ΔI (amu Å^2)	−3.584	−3.60		
OMC (MHz)	2	10		
assigned lines	400	440		
band origin (cm^{-1})	36384.07	36384		
% *b*-type	97	96		
temp (K)	3.6	1.9		

[a] Ref 1. [b] Ref 11.

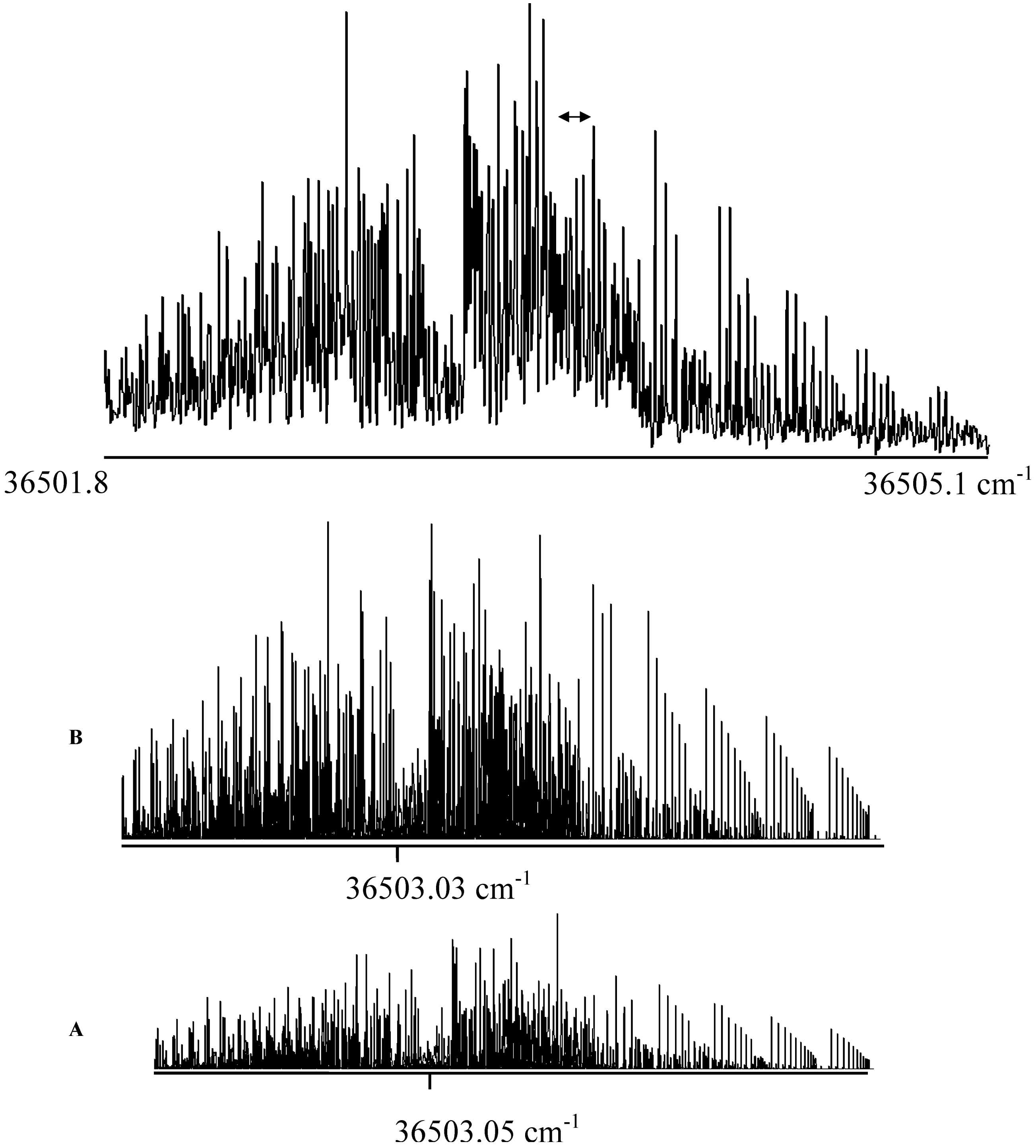


Figure 3. Rotationally resolved fluorescence excitation spectrum of the origin band in the S_1-S_0 transition of anisole$-H_2O$, shifted 119 cm^{-1} to the blue of the S_1-S_0 origin band of anisole. The origin band of the complex is a superposition of two subbands that are separated by 0.024 cm^{-1}. The top trace is the experimental spectrum. The second and third traces are the calculated B and A subbands, respectively.

c-type band as in the case of aniline$-H_2O$.[16] Second, the spectrum consists of two overlapping subbands separated by ~0.024 cm^{-1}. These two subbands were detected by Becucci et al.[2] and called "vibrational satellites". We have found that the two subbands have different relative intensities that are independent of temperature. The observed intensity ratio is ~3:1. This provides evidence that two protons are being exchanged by some large amplitude motion. (An exchange of three or more protons would result in two or more subbands with different relative intensities.) A likely explanation for this behavior is that the attached water molecule is undergoing a hindered internal motion that exchanges its two protons. The two subbands are then "torsional" subbands that connect the nuclear-spin distinguishable A and B sub-torsional levels in the two electronic states. These result from tunneling along a 2-fold symmetric torsional coordinate in the two states. Similar behavior has been observed in several other systems such as indole$-H_2O$,[17] benzonitrile$-H_2O$,[18] and *p*-difluorobenzene$-H_2O$.[19] And third, a satisfactory fit of the two subbands could only be obtained by incorporating Watson distortion terms into the rotational Hamiltonians of the two electronic states.[20]

Figure 4 shows an example of this fit. Individual rovibronic lines have widths of ~20 MHz. A Voigt line shape analysis suggests comparable Lorentzian and Gaussian contributions of

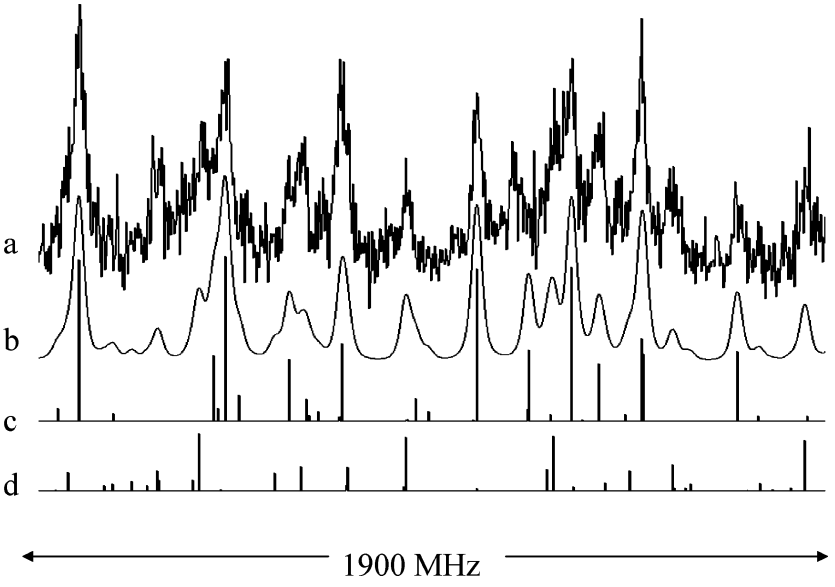


Figure 4. Portion (see Figure 3) of the high resolution spectrum of anisole−H_2O at full experimental resolution, extracted from the R branch of the stronger subband. The top trace (a) is the experimental spectrum. The corresponding simulated spectrum with a Voigt line shape is shown in panel b. The third (c) and fourth (d) traces show the separate calculated contributions of the two subbands in this region of the spectrum.

TABLE 2: Inertial Parameters of Anisole−H_2O in Its Ground (S_0) and Electronically Excited (S_1) States[a,b]

		strong (B)			weak (A)		
state	parameter	this work	ref 2	ref 3	this work	ref 2	ref 3
S_0	A''	2944.5 (2)	2941.4	2943.578	2945.4 (3)	2941.3	2943.058
	B''	900.3 (1)	899.7	900.0276	900.7 (2)	899.7	900.1885
	C''	694.4 (1)	693.9	694.1155	694.4 (2)	694.1	694.1488
	D_J''	0.004 (4)		0.00422	0.008 (2)		0.00425
	D_{JK}''	−0.052 (2)		−0.0538	−0.028 (5)		−0.0540
	D_K''	0.218 (3)		0.2183	0.208 (5)		0.2190
	d_j''	−0.0015 (2)		−0.001751	−0.0032 (8)		−0.001760
	d_k''	−0.0001 (8)		−0.000106	0.0024 (3)		−0.000108
	κ''	−0.817	−0.817	−0.817	−0.817	−0.817	−0.817
	$\Delta I''$	−5.198	−5.284	5.0870	−4.909	−5.426	−5.0519
S_1	A'	3090.2 (1)	3089.3		3091.4 (2)	3089.5	
	B'	848.0 (1)	847.5		848.4 (2)	847.6	
	C'	671.4 (1)	671.2		671.0 (2)	671.3	
	D_J'	0.0003 (4)			0.001 (1)		
	D_{JK}'	−0.003 (2)			0.018 (4)		
	D_K'	0.016 (2)			0.006 (4)		
	d_j'	−0.0001(2)			−0.0026 (6)		
	d_k'	−0.0001(1)			−0.0026 (3)		
	κ'	−0.854	−0.854		−0.853	−0.854	
	$\Delta I'$	−6.830	−6.970		−6.044	−7.003	
	band origin	36503.03	36503		36503.05	36503	
	assignments	176	328	42	83	219	42
	OMC	3.56	10	0.005	3.72	10	0.005

[a] Band origins in cm^{-1}, inertial defects in amu Å^2, all other parameters in MHz. [b] See ref 3 for sextic distortion constants.

~18 MHz. The Gaussian contribution is larger in this spectrum because it was recorded in the low resolution port.

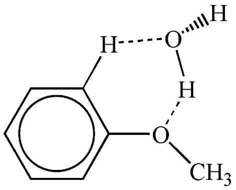
Table 2 lists the rotational constants that were derived from fits of the two subbands in the spectrum of anisole−H_2O. The two subband origins are at 36503.03 and 36503.05 cm^{-1} and are separated by 732.65 MHz. The rotational constants of the two subbands are very different from those of the bare molecule (Table 1), reflecting the additional mass and displacement of the attached water molecule. Despite this fact, the inertial defect of the complex is found to be very similar to that of the bare molecule, increasing in magnitude by only 1.8 amu Å^2. For comparison, aniline−H_2O has a greatly enhanced inertial defect ($\Delta I = 141.4$ amu Å^2)[16] compared to the bare molecule ($\Delta I =$ 0.406 amu Å^2).[21]

Finally, we note that the rotational constants of the two subbands are not the same. In the ground state, the A'' values differ by 1.0 MHz, outside of experimental error (±0.5 MHz). The two B'' values are equal, within error. But there also is a small difference in the two C'' values of 0.5 MHz (compared to the estimated error of ± 0.3 MHz). The two ground-state levels have inertial defects that differ by 0.4 amu Å^2. These differences have been confirmed in a recent study of the ground state of anisole−H_2O using microwave techniques (cf. Table 2).[3] In the excited state, the two A' values differ by 1.2 MHz, the two B' values differ by 0.8 MHz, and the two C' values differ by 0.9 MHz, with all differences being greater than the errors. There also are differences in their inertial defects, ~0.3 amu Å^2 in the S_0 state and ~0.8 amu Å^2 in the S_1 state. The fact that the rotational constants of the two subbands are not the same is intimately related to the internal rotation dynamics of the attached water molecule in both electronic states, as the following discussion will show.

Discussion

As noted, the observed rotational constants, inertial defects, and transition moment orientations of anisole$-$$H_2O$ in its electronic ground state place the water molecule approximately in the aromatic plane, closest to the oxygen atom of the methoxy group. The likely structure is thus the σ-hydrogen bonded structure shown in Scheme 1:

SCHEME 1



Here, the oxygen atom lone pair electrons on the OCH_3 group accept at least one proton from the attached water molecule. Water thus behaves primarily as an acid in anisole$-$$H_2O$ rather than as a base. Additionally, there is a "basic" interaction involving the water molecule; its oxygen atom donates a lone pair of electrons to an ortho hydrogen atom, forming a weaker H$-$O- - -H hydrogen bond with the aromatic ring. Strong support for such a structure is found in the results of the molecular mechanics calculations described by Becucci et al.[2]

Refinements in our understanding of the structure and dynamics of the complex may be made in the following way. First, we compare the rotational constants of anisole-H_2O in its ground state with those of the bare molecule using Kraitchman's equations.[22] (Here, we used the average constants of a hypothetical rigid rotor complex of anisole$-$$H_2O$, corrected for the higher order effects of centrifugal distortion.) Treating the water molecule as a single particle with mass 18 yields the COM coordinates listed in Table 3. These data confirm the proposed structure shown in Scheme 1. They also show that the COM of the water molecule is displaced vertically from the plane defined by the aromatic ring, either because the equilibrium structure is distorted along that coordinate or because of a large amplitude vibrational motion in this direction (see Scheme 1). The displacement ($|c| = 0.43$ Å) is not large but it is significant. Finally, the data show that this displacement increases by at least 0.04 Å on excitation of anisole$-$$H_2O$ to its S_1 state. At the same time, the distance of the hypothetical particle of mass 18 from the COM increases by ~0.13 Å in the excited state as compared to the ground state. Whatever the nature of the intermolecular hydrogen bonds, they get weaker when the photon is absorbed.

TABLE 3: Center of Mass (COM) Coordinates (in Å) of the Water Molecule in the Principal Axis Frames of the Bare Anisole Molecule and the Anisole$-$$H_2O$ Complex

state	coordinate	bare molecule frame (Å)	complex frame (Å)
S_0	$\lvert a\rvert$	3.243 (1)	3.661 (1)
	$\lvert b\rvert$	3.055 (4)	1.142 (1)
	$\lvert c\rvert$	0.43 (2)	0.124 (8)
	$\lvert r\rvert$	4.477 (1)	3.837 (1)
S_1	$\lvert a\rvert$	3.5897 (6)	3.814 (1)
	$\lvert b\rvert$	2.849 (4)	1.013 (1)
	$\lvert c\rvert$	0.47 (2)	0.141 (8)
	$\lvert r\rvert$	4.607 (1)	3.949 (1)

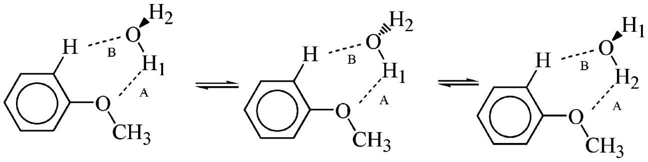


Figure 5. Combined inversion and restricted internal rotation pathway for the water molecule in anisole$-$$H_2O$.

That the intermolecular hydrogen bonds in the S_1 state of anisole$-$$H_2O$ are weaker than those in the S_0 state also is clear from the observation that the origin band of the complex is blue shifted (by ~119 cm^{-1}) relative to that of the bare molecule. This is typical of water donor hydrogen bonds.[23,24] The oxygen lone pair electrons of the methoxy group are less available for hydrogen bonding in the S_1 state owing to their increased conjugation with the aromatic ring. In contrast, hydrogen bonds in which the water molecule accepts a proton from an attached group are typically stronger in the S_1 state, leading to red shifts of their spectra relative to the bare molecule. Indole$-$$H_2O$, with an NH···$OH_2$ hydrogen bond in which water acts as a base, is a prototypical example of this behavior.[17]

More surprising is the observation, concerning the two subbands that lie within the S_1-S_0 origin band of the complex, that the weaker A subband is blue shifted with respect to the stronger B subband, by ~0.024 cm^{-1}. This shows that the barrier controlling the motion of the attached water molecule is *higher* in the S_1 state than in the S_0 state. A higher barrier implies that the motion of the water molecule cannot be a simple torsional motion about one of the two hydrogen bond axes. As we have seen, both subbands are blue shifted relative to the origin band of the bare molecule, showing that, on balance, the hydrogen bonding in the S_1 state is weaker than that in the ground S_0 state. A weakening of these bonds should lead to a decrease in the magnitude of the barrier, if the motion were a simple torsional motion about one of the hydrogen bond axes. Thus, the "torsional" dynamics of the attached water molecule in anisole$-$$H_2O$ must be more complicated than first imagined.

Detailed information about these dynamics is contained in the measured rotational constants of the two subbands of anisole$-$$H_2O$, in both electronic states. Recall that, in the ground state, the two A values differ by 1.0 MHz. There is also a small difference in the two C values. These differences have their origins in a vibrational motion of the attached water molecule. In the case of a 2-fold barrier, the contributions to A and C are second-order in nature, and their relative magnitudes depend on the axes about which the motion is occurring, among other factors.[13] So, since the two A values are different in the ground state, with some smaller differences in C, we can conclude that whatever the nature of the motion, it occurs mainly about the *a* principal axis of the complex. In contrast, the A, B, *and* C values in the two subbands are all different in the S_1 excited state, so the motion of the attached water molecule must be very different in this state as compared to the ground state.

The fact that the two subbands have a 3:1 intensity ratio means that the motion that is responsible for them must exchange the two water hydrogens, at least in the ground state. In the language of NMR, they must be "equivalent". As we[19] (and others[25]) have discussed elsewhere, one mechanism that accomplishes this is the "two-step" process shown in Figure 5. Step one in this scheme is an inversion, in which the oxygen lone pairs on water are switched in hydrogen bond B, moving hydrogen H_2 from "above" the plane to "below". Step two in this scheme is an internal rotation, in which the two hydrogen atoms of the water molecule are switched, hydrogen H_2

replacing hydrogen H_1 in hydrogen bond A. The two steps taken in concert exchange the roles of hydrogens H_1 and H_2, accomplishing the desired objective.

The mechanism described above is probably best viewed as a single-step process, along a "diagonal" reaction coordinate, with a single activation energy. But for some purposes, it is more convenient to imagine the process as a two-step process with separate activation energies for each step. Step one, inversion at oxygen, requires breaking hydrogen bond B, whereas step two, internal rotation, requires breaking hydrogen bond A. We suppose that, of the two bonds, hydrogen bond A is the stronger bond in the ground state, in which water acts as an acid and anisole acts as a base. Therefore, step two must be more important in this state. But as we have seen, the energy of the O−H- - -O(CH_3) bond is observed to decrease on excitation of anisole−H_2O to its S_1 state, whereas the barrier impeding the motion of the attached water molecule is observed to increase. Therefore, step one must be more important in the S_1 state, breaking hydrogen bond B. We conclude, then, that hydrogen bond "switching" has occurred; hydrogen bond A is the stronger bond in the S_0 (ground) state, but hydrogen bond B is the stronger bond in the S_1 (excited) state. The water molecule acts as a base in this state, accepting a proton from the attached anisole molecule.

Quantitative estimates of the two barrier heights may be obtained in the following way. We assume that the water molecule undergoes an internal rotation about an axis making an angle of 55° with its *b* axis, with an internal rotor constant of 339 MHz,[17] in the ground state. This axis is approximately parallel to the *a* axis of the complex. Then, from the difference in the two rotational constants ($\Delta A_{\mathrm{eff}}'' = A_a'' - A_b'' = 1.0$ MHz), we calculate a barrier of $V_2'' = 224$ cm^{-1} in the ground state. Next, we assume that the water molecule undergoes an inversion motion about an axis making an angle of −55° with its *b* axis, with a similar internal rotor constant, in the excited state. In this case, all three rotational constants are different since the motion of the water molecule is about an axis that makes nonzero projections along *a*, *b*, and *c*, making it difficult to model the observed behavior. So, we chose to vary the excited state barrier until we fit the observed difference in tunneling splittings in the two states (~733 MHz), obtaining the value $V_2' = 237$ cm^{-1}. The determined values of V_2 are the effective barrier heights for the combined inversion-torsion motion described above. Thus, V_2 increases in the S_1 state because the H−O- - -H(ring) bond is stronger in this state.

More detailed information about the motion of the attached water molecule in the two electronic states of anisole−H_2O will require a careful analysis of the data on different isotopomers. Such data have been recently reported for the ground state by Giuliano and Caminati.[3] Comparable data will be required for the excited state.

Summary

We have observed and assigned the high resolution electronic spectra of anisole and its single water complex, anisole−H_2O. The data provide evidence for an "in-plane" complex in which the water molecule is attached to the anisole molecule via two hydrogen bonds, an O−H- - -O(CH_3) donor bond and an H−O- - -H(ring) acceptor bond. Excitation of the chromophore with light changes its electron distribution. These changes are reflected in observed differences in the strengths of the two hydrogen bonds and in the nature of the water motion in the two electronic states. This motion involves both internal rotation and inversion coordinates, but the barrier to the former is larger in the ground state, whereas the barrier to the latter is larger in the excited state. As a result, the water molecule in anisole−H_2O behaves like an acid when anisole is in its ground state, but it behaves like a base when anisole is in its excited state.

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References and Notes

(1) Eisenhardt, C. G.; Pietraperzia, G.; Becucci, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1407.

(2) Becucci, M.; Pietraperzia, G.; Pasquini, M.; Piani, G.; Zoppi, A.; Chelli, R.; Castellucci, E.; Demtröder, W. *J. Chem. Phys.* **2004**, *120*, 5601.

(3) Giuliano, B. M.; Caminati, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 603.

(4) Ribblett, J. W.; Pratt, D. W. *The $S_1 \leftarrow S_0$ Fluorescence Excitation Spectra of Anisole and Styrene Using High Resolution Techniques*; 52nd International Symposium on Molecular Spectroscopy, Columbus, OH, June 16−20, 1997.

(5) Ribblett, J. W.; Borst, D. R.; Pratt, D. W. *The High Resolution $S_1 \leftarrow S_0$ Spectrum of the Anisole/Water Complex: Water as an Acid*; 55th International Symposium on Molecular Spectroscopy, Columbus, OH, June 12−16, 2000.

(6) Majewski, W. A.; Pfanstiel, J. F.; Plusquellic, D. F.; Pratt, D. W. *Laser Techniques in Chemistry*; Rizzo, T. R., Myers, A. B., Eds.; John Wiley & Sons: New York, 1995; p 101.

(7) Ribblett, J. W. Ph.D. Thesis, University of Pittsburgh, Pittsburgh, PA, 1999.

(8) Borst, D. R. Ph.D. Thesis, University of Pittsburgh, Pittsburgh, PA, 2001.

(9) Köhler, G.; Getoff, N. *J. Mol. Struct.* **1984**, *115*, 331.

(10) Zehnacker, A.; Lahmani, F.; Breheret, E.; Desvergne, J. P.; Bouas-Laurent, H.; Germain, A.; Brenner, V.; Millie, P. *Chem. Phys.* **1996**, *208*, 243.

(11) (a) Oda, M.; Toda, A.; Mori, S.; Yamaguchi, I. *J. Mol. Struct.* **1986**, *144*, 47. (b) See also Desyatnyk, O.; Pszczolkowski, L.; Thorwirth, S.; Krygowski, T. M.; Kisiel, Z. *Phys. Chem. Chem Phys.* **2005**, *7*, 1.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakreqewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.;. Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*, Revision A9; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

(14) Berden, G.; Meerts, W. L.; Schmitt M.; Kleinermanns, K. *J. Chem. Phys.* **1996**, *104*, 972.

(15) Tsuzuki, S.; Houjou, H.; Nagawa, Y.; Hiratani, K. *J. Phys. Chem. A.* **2000**, *104*, 1332.

(16) Spoerel, U.; Stahl, W. *J. Mol. Spectrosc.* **1998**, *190*, 278.

(17) Korter, T. M.; Pratt, D. W.; Küpper, J. *J. Phys. Chem. A* **1998**, *102*, 7211.

(18) Schäfer, M.; Borst, D. R.; Pratt, D. W.; Brendel, K. *Mol. Phys.* **2002**, *100*, 3553.

(19) Kang, C.-H.; Pratt, D. W.; Schäfer, M. *J. Phys. Chem. A* **2005**, *109*, 767.

(20) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; John Wiley & Sons: New York, 1970.

(21) Sinclair, W. E.; Pratt, D. W. *J. Chem. Phys.* **1996**, *105*, 7942.

(22) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.

(23) Dickinson, J. A.; Hockridge, M. R.; Robertson, E. G.; Simons, J. P. *J. Phys. Chem. A* **1999**, *103*, 6938.

(24) Federov, A. V.; Cable, J. R. *J. Phys. Chem. A* **2003**, *104*, 4943.

(25) Schütz, M.; Bürgi, T.; Leutwyler, S.; Fischer, T. *J. Chem. Phys.* **1993**, *98*, 3763.