J. Am. Chem. Soc. 1993, 115, 9263–9266

Microwave Spectroscopic Characterization of a Strong Hydrogen Bond: Trimethylamine–Water

Michael J. Tubergen and Robert L. Kuczkowski*

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

Received May 10, 1993[⊗]

Abstract: Rotational spectra were observed for 10 isotopomers of the trimethylamine–water complex with use of a Fourier-transform microwave spectrometer. The observed spectra of all 10 isotopomers were characteristic of a symmetric top and are indicative of a free internal rotation of the water about the symmetry axis of trimethylamine. Analysis of the rotational constants reveals a structure with an essentially linear single hydrogen bond (1.82 Å). The dipole moment of the complex was determined to be 2.37 (1) D with use of Stark effect measurements. Ab initio calculations were used to model the structure and intermolecular potential energy surface of the complex.

Introduction

The ubiquity of water and the importance of its hydrogen bonding interactions have made weakly bound complexes of water the focus of a great deal of research. Recently published spectra of benzene–water[1] and ammonia–water[2] have provided new information about both the structure and dynamics of these complexes. A symmetric top spectrum was found for benzene–water and explained by a free internal rotation of the water. The moment-of-inertia data suggested that both water protons were directed toward the aromatic ring, consistent with a double or nearly double hydrogen bond. A very recent analysis of hyperfine splittings and isotopic data indicated that the one water hydrogen is closer to the benzene than the other.[3] The structure of ammonia–water could not be unambiguously determined from its asymmetric top spectrum, although equilibrium structures with a nonlinear hydrogen bond modeled the data best.[2] The spectrum of ammonia–water was complicated by the effects of two tunneling processes: a low barrier internal rotation about the ammonia symmetry axis and a wagging motion about the *c* axis of water which interchanges the hydrogen bonded and free water protons.

It is important to determine if similar structures and dynamics are found over a wide range of interaction strengths; the trimethylamine (TMA)–water system represents a significant extension of the previous ammonia–water studies because of an increase in the proton affinity by 20 kcal/mol.[4] We find evidence for a single, essentially linear hydrogen bond in the TMA–water complex. The free water proton is randomly oriented (by a free internal rotation about the hydrogen bond), leading to a remarkably simple symmetric top spectrum.

Experimental Section

The rotational spectra for 10 isotopomers of the TMA–water complex were observed using a Balle–Flygare type Fourier-transform microwave spectrometer[5] operating in the 4–18-GHz range. In the absence of quadrupole hyperfine splitting, the line widths are found to be 30 kHz, and the accuracy of the center frequency is estimated to be ±4 kHz. The small splittings arising from the ^{14}N nuclear electric quadrupole moment were resolved by using a pulsed valve mounted in one of the cavity mirrors so that the expansion traveled along the axis of the cavity. This nozzle configuration produced Doppler doublets for each quadrupole component split by about 50 kHz, while the line widths decreased to less than 15 kHz. Two 50 cm × 50 cm steel mesh grids 30 cm apart straddle the cavity and are used for Stark effect measurements. Up to 10000 V of opposite polarity can be applied to the grids; the electric field is calibrated by measuring the Stark shift of the $1 \leftarrow 0$ transition of OCS ($\mu = 0.71520$ D).[6]

Each sample contained approximately 1% each of the amine and water species in a 20:80 helium/neon carrier gas mix. TMA-^{14}N (99%) and D_2O (99.9 atom % D) were obtained from Aldrich, TMA-^{15}N·HCl (99 atom % ^{15}N) and $H_2{}^{17}O$ (29.5 atom % ^{17}O) were obtained from Isotech Inc., and $H_2{}^{18}O$ (60–65 atom % ^{18}O) was obtained from Cambridge Isotope Laboratories. The TMA-^{15}N was liberated from the hydrochloride salt by the addition of 2 N NaOH solution and the collection of the evolved gas in a liquid nitrogen trap. Conditioning of the spectrometer gas inlet manifold and sample line with D_2O for several hours was required before the spectra of the deuterium isotopomers could be measured. Proton/deuteron exchange with the residual water was sufficient to produce the partially deuterated isotopomers.

Results

Microwave Spectra. The spectra of all 10 isotopomers (Tables I and II) could be fit to symmetric top expressions[7] of the form $\nu = 2B_0(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)K^2$; the resulting values for the spectroscopic constants are listed in Table III. The ^{14}N nuclear electric quadrupole splittings were fit to a single coupling constant (see Table III) consistent with the symmetric top assignment. Additionally, a symmetric top ^{17}O quadrupole coupling constant $\chi = -5.30(1)$ MHz was obtained for TMA-^{15}N–$H_2{}^{17}O$ by fitting 15 quadrupole hyperfine components of the 2_0–1_0 and 2_1–1_1 rotational transitions (Table IV). The rotational spectra of many weakly bound water complexes (including benzene–water) contain splittings arising from tunneling motions which exchange equivalent protons. Despite a spectral search over a 2-GHz range, no transitions were found which could be assigned to an excited tunneling state.

By using the rotational Stark effect it is possible to determine the dipole moment of the complex. The $K > 0$ transitions had first-order Stark effects while the $K = 0$ transitions were second order; these observations are consistent with an assignment to the

---

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

[1] (a) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3388–3401. (b) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942–945.

[2] Stockman, P. A.; Bumgarner, R. E.; Suzuki, S.; Blake, G. A. *J. Chem. Phys.* **1992**, *96*, 2496–2510.

[3] Gutowsky, H.; Emilsson, T.; Arunan, E. *J. Chem. Phys.*, in press.

[4] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311–317.

[5] (a) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33–45. (b) Hillig, K. W., II; Matos, J.; Scioly, A.; Kuczkowski, R. L. *Chem. Phys. Lett.* **1987**, *133*, 359–362.

[6] Tanaka, K.; Ito, H.; Harada, K.; Tanaka, T. *J. Chem. Phys.* **1984**, *80*, 5893–5905.

[7] Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984; pp 175–182.

0002-7863/93/1515-9263$04.00/0

Table I. Transition Frequencies (MHz) of Trimethylamine-^{14}N–Water Complexes

transition J'_K–J''_K F'–F''	TMA-^{14}N–H_2O	obs – calc, kHz	TMA-^{14}N–DOH[a]	obs – calc, kHz	TMA-^{14}N–HOD[a]	obs – calc, kHz	TMA-^{14}N–D_2O[a]	obs – calc, kHz	TMA-^{14}N–$H_2{}^{18}O$	obs – calc, kHz
1_0–0_0[b]	5017.270	0.4	4965.385	3.6	4812.126	1.4	4766.451	5.1	4733.416	1.9
0–1	5019.776	–1.3	4967.888	–4.4	4814.630	1.3	4768.951	–6.9	4735.917	0.4
2–1	5017.522	1.4	4965.645	9.1	4812.376	0.0	4766.709	7.7	4733.665	–0.9
1–1	5016.016	–0.2	4964.127	–4.6	4810.873	–1.2	4765.196	–0.9	4732.166	0.5
2_0–1_0[b]	10034.479	1.2	9930.697	–3.5	9624.195	0.6	9532.831	–3.2	9466.774	1.6
1–1	10036.985	–1.6	9933.195	–9.3	9626.698	0.4	9535.329	–9.2	9469.277	2.0
1–2	10035.480	–2.2	9931.712	12.1			9533.843	9.2	9467.774	–0.5
3–2	10034.589	2.3	9930.807	2.5	9624.303	1.1	9532.938	–0.3	9466.882	0.6
2–1	10034.479	–0.2	9930.697	0.0	9624.193	–1.6	9532.816	–14.9	9466.773	–1.2
1–0	10033.227	1.5	9929.441	–2.5	9622.946	2.9	9531.594	16.8		
2–2	10032.975	0.2	9929.190	–2.7	9622.690	–2.8	9531.325	–1.5	9465.273	–0.8
2_1–1_1[b]	10031.293	–1.5	9927.641	0.6	9620.426	–1.7	9529.201	–0.9	9463.663	–3.1
1–0	10033.174	–1.0	9929.520	–3.8	9622.303	–1.1	9531.090	4.0	9465.537	–1.1
1–2	10032.050	5.4					9529.937	–12.6	9464.407	–1.9
3–2	10031.605	7.3	9927.960	15.2	9620.731	1.4	9529.520	14.9	9463.963	–0.9
1–1	10031.289	–2.1	9927.637	2.0	9620.424	0.4	9529.196	4.0	9463.659	2.8
2–2	10030.784	–9.1	9927.135	–7.5	9619.925	–1.4	9528.695	–10.0	9463.162	–0.8
2–1	10030.039	–0.6	9926.381	–6.0	9619.175	0.8	9527.947	–0.3	9462.412	1.9
3_0–2_0[b]	15051.561	–2.2	14895.898	3.0	14436.153	–1.8	14299.107	–0.1	14200.018	–1.0
2–2	15053.820	2.8	14898.153	–1.3	14438.406	0.0	14301.361	–2.7	14202.271	2.6
4–3	15051.618	–2.2	14895.960	2.5	14436.216	3.1	14299.179	12.2	14200.076	–1.2
3–2	15051.561	0.6					14299.097	–10.0	14200.020	2.3
2–1	15051.308	–1.7	14895.646	–1.1	14435.901	–2.0	14298.852	–4.3	14199.765	–2.6
3–3	15049.949	0.5	14894.286	0.0	14434.543	–1.1	14297.500	4.8	14198.409	–1.1
3_1–2_1[b]	15046.791	2.7	14891.302	–2.9	14430.507	2.4	14293.660	1.3	14195.356	1.1
2–2	15048.162	–6.2	14892.669	–6.9	14431.879	–2.3	14295.032	1.1	14196.724	–3.6
4–3	15046.925	–0.4	14891.442	5.8	14430.639	–1.6	14293.788	–6.0	14195.488	–1.9
2–1	15046.925	8.3			14430.639	7.1	14293.788	1.8	14195.488	6.5
3–2	15046.476	–1.6	14890.985	–3.6	14430.192	–1.7	14293.343	–3.5	14195.044	0.5
3–3	15045.673	–0.1	14890.191	4.7	14429.389	–1.5	14292.553	6.6	14194.241	–1.4
3_2–2_2[b]	15032.463	–0.4	14877.535	0.6	14413.554	–0.3	14277.313	–0.2	14181.363	0.2
2–1	15033.717	1.7	14878.784	–3.2	14414.805	0.0	14278.580	14.1	14182.608	–4.3
3–3	15032.817	2.5					14277.675	9.6	14181.719	4.6
4–3	15032.817	–3.9	14877.906	13.1	14413.908	–4.2	14277.675	3.5	14181.719	–1.3
3–2	15031.213	4.2	14876.271	–9.9	14412.307	4.1	14276.050	–9.4	14180.117	4.5
2–2	15031.213	–4.5					14276.050	–17.8	14180.117	–3.5

[a] The deuterium nuclear quadrupole hyperfine splittings were not resolved. [b] The first entry is the unsplit center frequency calculated from fitting the ^{14}N quadrupole hyperfine transitions.

Table II. Transition Frequencies (MHz) of Trimethylamine-^{15}N–Water Complexes

transition J'_K–J''_K	TMA-^{15}N–H_2O	obs – calc, kHz	TMA-^{15}N–DOH[a]	obs – calc, kHz	TMA-^{15}N–HOD[a]	obs – calc, kHz	TMA-^{15}N–D_2O[a]	obs – calc, kHz	TMA-^{15}N–$H_2{}^{18}O$	obs – calc, kHz
1_0–0_0	5014.055	2.9	4961.880	–6.5	4808.514	1.4	4762.557	–2.1		
2_0–1_0	10028.044	–0.2	9923.725	9.2	9616.969	–0.4	9525.083	12.7	9458.800	0.3
2_1–1_1	10024.850	–2.1	9920.647	–4.0	9613.193	–0.7	9521.423	–11.0	9455.683	–0.3
3_0–2_0	15041.916	0.1	14885.434	3.5	14425.313	–1.4	14287.485	–0.6	14188.055	–1.2
3_1–2_1	15037.128	0.2	14880.826	–7.3	14419.653	2.1	14282.029	–2.1	14183.383	1.5
3_2–2_2	15022.764	0.3	14867.044	2.5	14402.660	–0.4	14265.670	2.4	14169.357	–0.3

[a] The deuterium nuclear quadrupole hyperfine splittings were not resolved.

ground internal rotation state of a symmetric top. Frequency shifts of the M_J components of the TMA-^{15}N–H_2O 3_0–2_0 transition were measured at seven field strengths and gave $\mu = 2.37(1)$ D.

Structure. Because of the C_2 symmetry of water, any rigid complex of TMA and water should have an asymmetric top spectrum. To produce the observed symmetric top spectra, the water must undergo a free internal rotation about the C_3 axis of TMA, so that the vibrationally averaged structure appears to be a symmetric top. Also, the unusual observation of two HDO spectra for the complex indicates that the water hydrogen positions are inequivalent, eliminating the possibility of a bifurcated hydrogen bonded structure.

The detailed structure of the ground internal rotation state of the TMA–H_2O complex was considered with use of Kraitchman's equation for single isotopic substitution on the axis of a symmetric top[8] and least-squares fitting of the structural parameters to the moments of inertia for the 10 isotopomers (the TMA parameters were held fixed to the literature values[9] in the least-squares fitting). Both methods only determine the projections of the N, O, and water hydrogens on the C_3 axis, since the symmetric top rotational constants only provide information about the atomic positions averaged over the range of the internal rotation. The Kraitchman calculations were carried out in both the TMA-^{14}N–H_2O and TMA-^{15}N–H_2O principal axis systems (PAS). The results of the Kraitchman calculations and least-squares fitting are listed in Table V and are in excellent agreement.

The relative atomic positions are strongly suggestive of a linear (or very nearly linear) hydrogen bond (see Figure 1). The difference between the average positions of the oxygen and the hydrogen bonded water hydrogen (H_1) is 1.03 Å—6% longer than the O–H bond distance in the water monomer (0.9724 Å).[10]

---

(8) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984; pp 658–659.

(9) Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1969**, *51*, 1580–1583.

Table III. Spectroscopic Constants for the Isotopic Species of Trimethylamine–Water

isotopic species	B_0, MHz	D_J, kHz	D_{JK}, kHz	$\Delta\nu_{rms}$,[a] kHz	χ, MHz
TMA-^{14}N–H_2O	2508.640(1)	2.56(4)	795.8(1)	1.7	–5.015(3)
TMA-^{14}N–DOH	2482.696(1)	2.60(7)	765.0(2)	2.7	–5.014(7)
TMA-^{14}N–HOD	2406.067(1)	2.28(4)	941.7(1)	1.5	–5.006(2)
TMA-^{14}N–D_2O	2383.228(1)	2.40(7)	908.1(2)	2.5	–5.015(8)
TMA-^{14}N–$H_2{}^{18}O$	2366.712(1)	2.33(5)	777.3(1)	1.7	–5.001(3)
TMA-^{15}N–H_2O	2507.031(1)	2.51(4)	798.0(1)	1.5	
TMA-^{15}N–DOH	2480.948(2)	2.4(2)	766.2(5)	6.0	
TMA-^{15}N–HOD	2404.261(1)	2.33(3)	943.9(1)	1.2	
TMA-^{15}N–D_2O	2381.284(3)	2.0(2)	909.1(6)	7.0	
TMA-^{15}N–$H_2{}^{18}O$	2364.719(1)	2.39(3)	779.1(1)	0.9	

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

Table IV. Transition Frequencies (MHz) of Trimethylamine-^{15}N–$H_2{}^{17}O$

J'_K–J''_K	F′–F″	TMA-^{15}N–$H_2{}^{17}O$	obs – calc, kHz
2_0–1_0[a]		9730.926	
	1.5–2.5	9732.155	2.7
	2.5–2.5	9731.395	–0.2
	0.5–1.5	9731.245	1.2
	3.5–2.5	9731.121	–9.2
	4.5–3.5	9731.038	–1.4
	1.5–1.5	9730.567	4.6
	3.5–3.5	9730.019	1.7
	2.5–1.5	9729.806	0.7
2_1–1_1[a]		9727.764	
	0.5–1.5	9728.669	3.5
	1.5–1.5	9728.325	0.8
	4.5–3.5	9728.079	–7.1
	2.5–1.5	9727.950	5.0
	3.5–3.5	9727.570	–4.2
	2.5–2.5	9727.157	5.6
	3.5–2.5	9727.015	–3.7

[a] The first entry is the unsplit center frequency calculated from fitting the quadrupole hyperfine transitions.

A similar 4.4% increase in the bond length of HF upon complexation with TMA was found by Legon and Rego by analysis of the H, ^{19}F spin–spin coupling constant.[11] Nonlinear hydrogen bonded structures require an even greater increase in the O–H_1 bond length to match its projection on the C_3 axis and seem unlikely. However, a small deviation from the linear hydrogen bonded structure could still be masked by the effect of zero-point bending motions of the two monomer units (see below). It is interesting to note that the TMA–water hydrogen bond is approximately 1.82 Å long, which is among the shortest gas-phase hydrogen bonds measured.[12]

Discussion

Free internal rotation of the water about the C_3 symmetry axis of TMA has been inferred from the measurement of symmetric top spectra for 10 isotopomers of the TMA–water complex. The internal rotation produces a manifold of torsional energy levels with energies $E = Fm^2$ (m is the torsional quantum number and F is the effective torsional rotational constant). The $m = 0$ torsional level is nondegenerate while the $|m| \geq 1$ levels are doubly degenerate. The second-order Stark effects measured for the $K = 0$ transitions indicate that the transitions arise from the nondegenerate $m = 0$ torsional level. If the off-axis water proton (H_2) of the linearly hydrogen bonded structure is considered to be the internal rotor, then $E(m=\pm1) \approx 22.6$ cm^{-1}. Rotation about the C_3 axis does not exchange equivalent protons, so there are no proton spin restrictions associated with the torsional levels and the excited internal rotation states will be cooled in the supersonic expansion so that only the $m = 0$ state is significantly populated.

Table V. Relative Atomic Positions along the Trimethylamine–Water Complex Symmetry Axis

	Kraitchman analysis		
	^{14}N PAS	^{15}N PAS	least-squares fit[a]
Δ(N–H_1)[b]/Å	1.818	1.818	1.853(7)
Δ(N–O)/Å	2.849	2.849	2.881(4)
Δ(N–H_2)[b]/Å	3.303	3.303	3.333(3)
Δ(O–H_1)[b]/Å	1.031	1.031	1.028(7)
Δ(O–H_2)[b]/Å	0.454	0.454	0.452(3)

[a] Least-squares fit of 10 isotopic moments of inertia; $\Delta I_{rms} = 0.0063$ amu Å^2. The angle between the C_2 axis of H_2O and the C_3 axis of TMA is estimated as 65.5° from the value of Δ(O–H_2) and the bond angle of water.[10] [b] H_1 = water hydrogen participating in the hydrogen bond; H_2 = free water hydrogen.

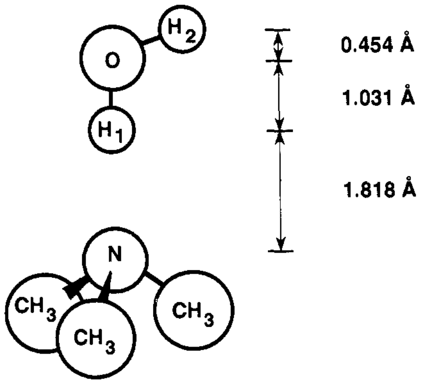

Figure 1. Relative atomic positions along the effective C_3 axis of the TMA–water complex.

Tunneling motions which exchange the water hydrogen positions are not completely cooled to the lowest tunneling state because of proton spin restrictions associated with the tunneling states. However, the ability to resolve tunneling splittings requires observable differences in the rotational constants of the ground and excited tunneling states or rotational transitions crossing between tunneling states. An internal rotation Hamiltonian was used to estimate the tunneling splitting as a function of the barrier to internal rotation of water about its C_2 axis.[13] The Hamiltonian predicts observable splittings (within the resolution of the spectrometer and the spectral range searched) for barriers ranging from 25 to 1000 cm^{-1}.[14] The barrier to a wagging motion about the water c axis exchanging the bound and unbound water protons cannot be described by a simple 2-fold potential, so an estimate of the Coriolis terms leading to different rotational constants and a barrier for this motion is less tractable. A 113-MHz splitting of b-dipole transitions in the far-infrared spectrum of NH_3–H_2O (which cross tunneling states) was assigned to tunneling along this coordinate and used to estimate a 700-cm^{-1} barrier.[2] The a-type rotational transitions in the microwave region were not found to be split because the top-to-top and bottom-to-bottom selection rules minimize the effect of the small difference in rotational constants of the two lowest tunneling states. The a-type

---

(10) Cook, R. L.; De Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1974**, *53*, 62–76.

(11) Legon, A. C.; Rego, C. A. *Chem. Phys. Lett.* **1989**, *154*, 468–472.

(12) (a) $(H_2O)_2$; R(O···O) = 2.976 Å: Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062–5070. (b) H_2O···$HCONH_2$; $R_{H\text{-bond}}$ = 1.99 and 2.03 Å: Lovas, F. J.; Suenram, R. D.; Fraser, G. T.; Gillies, C. W.; Zozom, J. *J. Chem. Phys.* **1987**, *88*, 722–729. (c) $(CH_3)_3N$···HCN; R(N···C) = 3.1035 Å: Rego, C. A.; Batten, R. C.; Legon, A. C. *J. Chem. Phys.* **1988**, *89*, 696–702. (d) H_3N···H_2O; R(N···O) ≈ 2.98 Å: ref 2.

(13) Andrews, A. M.; Taleb-Bendiab, A.; LaBarge, M. S.; Hillig, K. W., II; Kuczkowski, R. L. *J. Chem. Phys.* **1990**, *93*, 7030–7040. This calculation neglected the dependence of the moments of inertia on torsional angle, but this approximation does not severely affect the barrier estimate.

(14) A barrier of less than 25 cm^{-1} may produce splittings outside the spectral range covered. However, large irregular isotope effects upon deuteration would be expected and were not observed.

rotational transitions of CO–H_2O were split by an interchange motion about the water *c* axis due to a lower barrier[15] (210 cm^{-1}) and a concomitant increase in vibration–rotation effects on the rotational constants of the two lowest tunneling states. By analogy with these systems, 700 cm^{-1} probably represents the lower bound for the barrier to interchange of the water hydrogens. TMA–water is expected to form a stronger hydrogen bond than ammonia–water, suggesting an even greater barrier to tunneling processes which exchange water hydrogen positions.

Legon et al.[16] studied hydrogen halide (HX) complexes with both TMA and ammonia and found evidence for a stronger interaction in the TMA complexes. Analysis of the nitrogen and halogen quadrupole coupling constants indicated that there is significant electronic distortion of the quadrupole coupling constants caused by partial proton transfer in the TMA complexes, but not in the ammonia–HCl complex. The TMA–water complex does not display evidence for substantial charge (proton) transfer. First, $\chi(N) = -5.015$ MHz for TMA–water, which is much more similar to the TMA monomer value ($\chi = -5.5024$ MHz)[12c] than that for the TMA–HX complexes ($\chi(N) = -3.504$ MHz for TMA–HCl).[16b] For comparison, the TMA nitrogen quadrupole coupling constant was measured to be −5.061 MHz for the hydrogen bonded complex TMA–HCN.[12c] Secondly, the dipole moment of the complex (2.37 D) is reasonably predicted by vector addition of the two monomer dipole moments ($\mu = 0.612$ D for TMA,[17] $\mu = 1.8546$ D for H_2O,[18] and $\mu = 1.747$ D predicted for a linear hydrogen bonded structure); the 0.62 D difference can be attributed to polarization of the TMA lone pair electrons by the nearby water. The measured dipole moment of the strong charge transfer complex TMA–SO_2 is almost 3 D greater than the vector sum of the monomer dipole moments.[19]

The quadrupole coupling constants of van der Waals complexes are often used to estimate the zero-point bending amplitudes of the constituent monomers. The expression

$$\chi = \chi_0\langle 3\cos^2\theta_t - 1\rangle/2$$

was used with χ and χ_0, the quadrupole coupling constants from the spectra of TMA-^{14}N–H_2O and the TMA-^{14}N monomer, to evaluate θ_t, the vibrationally averaged angle between the *a* axis of the complex and the symmetry axis of TMA. An estimate of θ_w (a similar angle for the water subunit) was made by rotating the quadrupole coupling tensor[20] of $H_2{}^{17}O$ about the water *c* axis until the resulting value for χ_{aa} matched the measured value of χ_{aa}(TMA-^{15}N–$H_2{}^{17}O$). This analysis yielded $\theta_t \approx 14°$ and $\theta_w \approx 43°$, which is consistent with vibrational averaging about a nearly linear hydrogen bond (in a rigid, linear hydrogen bonded complex $\theta_w = 52.25°$, half the bond angle of water[10]). These vibrational averaging angles are in good agreement with those obtained for TMA–HCN,[12c] although they represent upper bounds because electronic distortion of the quadrupole coupling constants has been neglected.

Optimized values for θ_w and R_{com} were determined with use of Gaussian90[21] at the Hartree–Fock level with the 6-31G** basis set. θ_w optimized to 52.1° and R_{com} to 3.36 Å, which is equivalent to a single, linear hydrogen bond.[22] The binding energy, ϵ, of the optimized structure was calculated to be 2075 cm^{-1}; the estimation of ϵ from D_J with use of the diatomic approximation[23] was 1600 cm^{-1}. Calculations of the intermolecular potential energy surface for several possible tunneling pathways were also made. The barrier to internal rotation of water about the hydrogen bond (TMA C_3 axis) was less than 1 cm^{-1}, which agrees well with our inference of a free internal rotation in this coordinate. The barrier to tunneling along the θ_w coordinate, which exchanges the free and bound water hydrogens, was found to be much higher, 1200 cm^{-1}. A 2200-cm^{-1} barrier was found along the internal rotation pathway about the local C_2 axis of water (which also exchanges bound and free water hydrogens). Although these calculations neglect correlation and BSSE effects, the high calculated barriers are likely reliable enough to confirm that tunneling processes other than rotation about the hydrogen bond are suppressed because of the very strong hydrogen bonding interaction. The greater basicity of TMA (compared with ammonia) has led to a dramatic change in both the rotational spectrum and the dynamics of the internal motions for the hydrogen bonded TMA–water complex.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Professor Gutowsky for a preprint of the benzene–water complex results.

---

(15) Yaron, D.; Peterson, K. I.; Zolandz, D.; Klemperer, W.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1990**, *92*, 7095–7109.

(16) (a) Legon, A. C.; Rego, C. A. *Chem. Phys. Lett.* **1989**, *162*, 369–375. (b) Legon, A. C.; Rego, C. A. *J. Chem. Phys.* **1989**, *90*, 6867–6876. (c) Legon, A. C.; Wallwork, A. L.; Rego, C. A. *J. Chem. Phys.* **1990**, *92*, 6397–6407.

(17) Lide, D. R., Jr.; Mann, D. E. *J. Chem. Phys.* **1958**, *28*, 572–576.

(18) Dyke, T. R.; Muenter, J. S. *J. Chem. Phys.* **1973**, *59*, 3125–3127.

(19) Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, K. W., II; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 4732–4738.

(20) De Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1975**, *56*, 138–145.

(21) Gaussian90, Revision I; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1990.

(22) The experimental value of R_{com}, the distance between the centers of mass of TMA and water, is 3.21 Å.

(23) Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477–1479.