Conformation and Stability of Adducts of Cyclic Ammines with Water: Free Jet Absorption Millimeter-Wave Spectrum of Pyrrolidine−Water

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Abstract: The free jet millimeter wave absorption spectra of the 1:1 complexes between two isotopomers of pyrrolidine (normal and N-D) and four isotopomers of water (H_2O, HOD, D_2O, and $H_2{}^{18}O$) have been assigned. Although only the rotational spectrum of axial-pyrrolidine has been previously reported, the adduct is formed with equatorial-pyrrolidine. The water molecule lies in the plane of symmetry of pyrrolidine; the water hydrogen involved in the hydrogen bond is axial with respect to the ring, while the "free" hydrogen is entgegen to the ring. The three atoms involved in the hydrogen bond adopt a bent arrangement with a $N_{ring}\cdots H$ distance of about 1.89 Å and $\angle(N_{ring}\cdots H-O) \cong 163°$.

Introduction

Hydrogen bonding is important in biology, in processes in aqueous surroundings and in atmospheric processes. For these reasons, this topic has already deserved the publication of several reviews.[1] The spectroscopy of solvation in hydrogen-bonded aromatic clusters and its usefulness for a molecular-scale understanding of molecular forces and solvation effects has been recently delightfully reviewed by Zwier.[2] The various spectroscopic techniques have been combined with the supersonic expansion,[3] which enables the controlled formation of "a-few-molecules" clusters. Reviews are available describing the studies of molecular complexes by microwave,[4−6] Raman,[7] infrared,[8−10] electronic,[11,12] rotational coherence,[13] and zero electron kinetic energy[14] spectroscopies. The role of the van der Waals systems in physical chemistry and in the biodisciplines has been summarized by Hobza and Zahradnik.[15]

Recently several adducts of water with organic ring molecules have been studied in detail by rotationally resolved spectroscopy. Precise information has been obtained on the multidimensional motion of water with respect to the partner molecule and on its most stable position. Often the pure rotational spectra have been detected with pulsed Fourier transform microwave spectroscopy (FTMW).[16−20] Alternatively rotationally resolved electronic spectra[21,22] in a molecular beam supply this kind of information.

Hydrogen bonds of the kind O−H···N, with a nitrogen atom included in a ring, are of importance since they occur in biological systems. So far only a few adducts of this kind have been investigated by rotationally resolved spectroscopy:[16,23] the water moiety acts as proton donor when an sp^2 or an sp^3 lone electronic pair is available at the nitrogen. This behavior has been observed also in the strongly hydrogen bonded adducts ammonia−water,[24] dimethylamine−water,[25] and trimethylamine−water.[26] The adduct pyrrole−water represents an exception:

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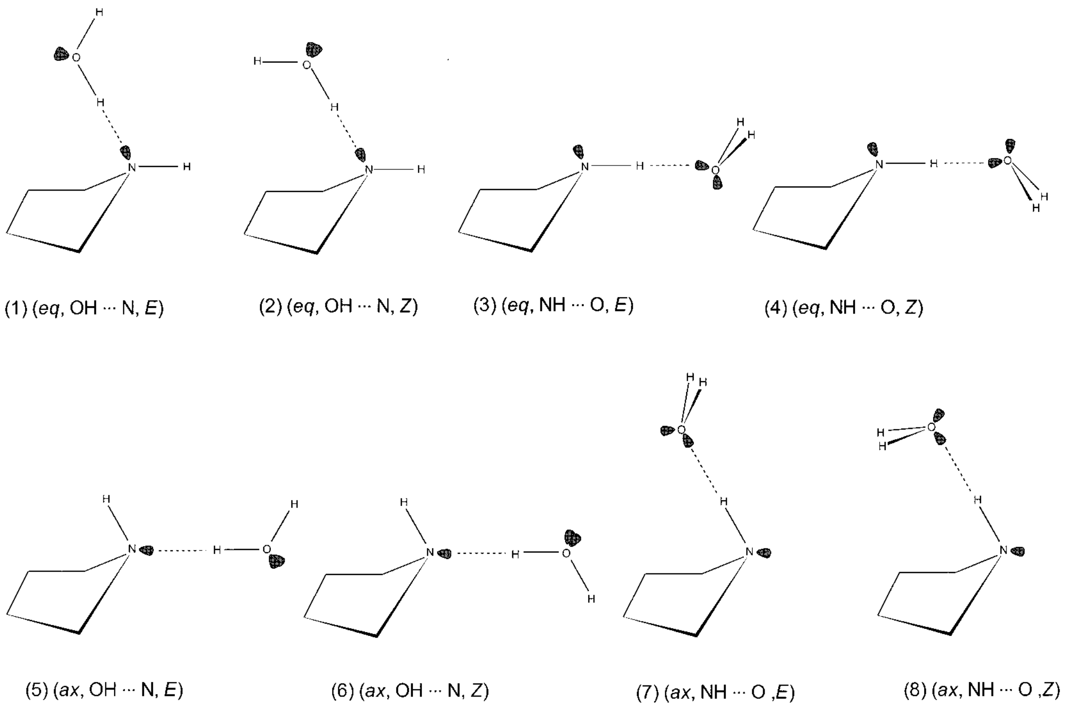
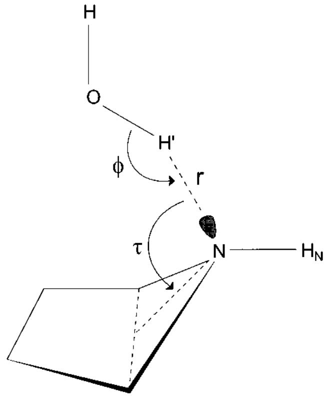


(1) (*eq*, OH ··· N, *E*) (2) (*eq*, OH ··· N, *Z*) (3) (*eq*, NH ··· O, *E*) (4) (*eq*, NH ··· O, *Z*)

(5) (*ax*, OH ··· N, *E*) (6) (*ax*, OH ··· N, *Z*) (7) (*ax*, NH ··· O ,*E*) (8) (*ax*, NH ··· O ,*Z*)

Figure 1. Plausible conformers of the PRL−water adduct.



(*eq*, OH ··· N, *E*)

Figure 2. Geometry and principal axes system of the observed conformer (*eq*, OH···N, *E*) of PRL−water.

with only π-electrons available at the nitrogen, the complex with an N−H···O hydrogen bond is favored.[16]

We have recently been successful in investigating molecular complexes of ring molecules with argon[27−30] and water[23,31] with supersonic jet millimeter-wave absorption spectroscopy (a more direct technique than pulsed FTMW). Here we apply this technique to the study of the complex of water with pyrrolidine (PRL, see Figure 1), a ring amine. Only the axial conformer has been observed in the rotational spectrum of isolated PRL, but it has been pointed out that a small μ_a dipole moment component could have prevented the observation of the rotational spectrum of the equatorial conformer.[32] Ab initio calculations and electron diffraction experiments suggested the axial form to be the most stable.[33] Following the hypothesis that a plane of symmetry was preserved in the adduct, we could expect eight different conformers for the water−PRL adduct. All of them are shown in Figure 1. The notation (vv, XH···W, Y), where vv = *eq* or *ax*, X and W = O or N (X ≠ W), and Y = E or Z, has been used. *Eq* and *ax* mean the equatorial or axial position of the amino hydrogen in PRL, XH···W indicates which of the OH···N or NH···O intermolecular hydrogen bond is formed, and E or Z are for the entgegen of zuzammen position of the water hydrogen(s) not involved in the hydrogen bond.

Experimental Section

The Stark and pulse-modulated free jet absorption millimeter-wave spectrometer used in this study has already been described elsewhere.[27,34] The adducts were formed flowing argon, at room temperature and at a pressure of ca. 70 kPa, over a solution of PRL and water in a molecular ratio of 1/1. The mixture was then expanded to ca. 50 mPa through a pulsed nozzle (repetition rate of 5 Hz) with a diameter of 0.35 mm, reaching an estimated “rotational” temperature of about 10 K. All samples were commercial and were used without further purification. The accuracy of the frequency measurements is about 0.05 MHz.

Rotational Spectrum. From model calculations, using the ab initio geometries of axial and equatorial PRL,[33] and assuming a hydrogen bond distance of about 1.9 Å, we found that, with respect to the values of the rotational constants, conformers of Figure 1 could have been divided into two groups: **1**, **2**, **7**, and **8**, with $A \cong 4.0$ GHz and $(B + C) \cong 4.5$ GHz, and **3**, **4**, **5**, and **6**, with $A \cong 6.0$ GHz and $(B + C) \cong 3.4$ GHz. We assigned one rotational spectrum consistent with the first group. This was rather surprising, because, supposing PRL to adopt the axial configuration, a hydrogen bond of the kind NH···O

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Table 1. Experimental Transition Frequencies of Normal and Five Isotopomers of Pyrrolidine−Water[a]

$J'(K'_aK'_c)$-$J''(K''_aK''_c)$[b]	PRL(H)−H_2O	PRL(D)−D_2O	PRL(H)−$H_2{}^{18}O$	PRL(H)−DOH	PRL(H)−HOD	PRL(D)−H_2O
8(8)−7(7)	61667.80		61469.60	61599.56	61465.93	59663.91
9(6)−8(5)	59671.37					
9(7)−8(6)	62969.25	60411.96	62293.17	62788.65	62382.93	61137.62
9(8)−8(7)	66271.72	63726.98	65829.67	66144.94	65871.22	64222.26
9(9)−8(8)	69579.79	67046.22	69371.42	69506.29	69364.59	67311.94
10(5)−9(4)	60985.87			60637.67		
10(6)−9(5)	64278.00	61414.45	63123.87	63984.32	63306.50	62617.41
10(7)−9(6)	67573.48	64724.46	66653.67	67334.20	66788.70	65696.18
10(8)−9(7)	70873.54	68037.76	70187.79	70688.23	70274.76	68778.94
10(9)−9(8)	74179.16	71355.13	73727.04	74047.53	73765.94	71866.29
10(10)−9(9)	77491.02	74677.22	77272.70	77412.62		74959.35
11(4,8)−10(3,7)						61021.20
11(4,7)−10(3,8)						61029.00
11(4,8)−10(3,8)	62304.78			61843.11	60760.41	
11(4,7)−10(3,7)	62303.91			61842.40	60760.00	
11(5)−10(4)	65592.61	62420.41	63960.63	65185.50		
11(6)−10(5)	68882.58	65727.03	67484.84	68530.12	67712.65	67176.12
11(7)−10(6)	72175.72	69035.31	71012.17	71877.76	71192.50	70252.79
11(8)−10(7)		72346.73	74543.85	75229.47	74676.41	73333.56
11(9)−10(8)		75662.09	78080.69			76418.55
12(2,11)−11(1,11)	60882.03					
12(2,10)−11(1,10)	59936.05					
12(3,10)−11(2,9)		59956.94				
12(3,9)−11(2,10)		60231.72				
12(3,10)−11(2,10)	63658.33		61302.16	63078.59	61717.29	
12(3,9)−11(2,9)	63576.07		61252.72	63008.01	61660.38	
12(4,9)−11(3,8)		63419.43				65575.43
12(4,8)−11(3,9)		63429.34				65589.12
12(4,9)−11(3,9)	66911.49		64801.81	66390.63	65168.56	
12(4,8)−11(3,8)	66909.87		64801.10	66389.65	65167.73	
12(5)−11(4)	70197.34	66732.45	68321.85	69731.64		
12(6)−11(5)	73485.08	70037.72	71843.70	73074.03		
12(7)−11(6)	76775.81		75368.73			74807.50
12(8)−11(7)		76653.89				77885.70
13(0,13)−12(0,12)	59993.51					
13(1,13)−12(1,12)	59918.62					
13(1,12)−12(1,11)	60130.05					
13(1,12)−12(0,12)	62490.87					
13(2,12)−12(2,11)	60025.10					
13(2,11)−12(2,10)	60068.34					
13(2,12)−12(1,12)	65590.87		62638.36			
13(2,11)−12(1,11)	64493.05		61730.96			
13(3,11)−12(3,10)	60032.51					
13(3,10)−12(3,9)	60034.24					
13(3,11)−12(2,11)			65672.81			
13(3,10)−12(2,10)	68162.31		65603.65			
13(4)−12(4)	60023.87					
13(4,10)−12(3,9)		67725.23				
13(4,9)−12(3,10)		67741.25				
13(4,10)−12(3,10)	71516.41		69163.08			
13(4,9)−12(3,9)	71513.61		69161.98			
13(5)−12(5)	60014.19					
13(5)−12(4)	74800.13		72681.11			
13(6)−12(6)	60002.98					
13(6)−12(5)	78085.58		76200.67			
13(7)−12(7)	59990.07					
14(0,14)−13(0,13)	64594.90		61196.71			
14(1,14)−13(1,13)	64519.21		61128.48			
14(1,13)−13(1,12)	64747.10		61310.95			
14(2,13)−13(2,12)	64634.60		61219.32			
14(2,12)−13(2,11)	64688.13		61251.84			
14(2,13)−13(1,13)			67088.74			
14(2,12)−13(1,12)			66044.70			
14(3,12)−13(3,11)	64644.60	60526.18	61223.47			
14(3,11)−13(3,10)	64646.99	60539.39	61224.59			
14(3,12)−13(2,12)			70043.46			
14(3,11)−13(2,11)			69949.45			
14(4)−13(4)	64635.28	60517.26	61214.98			
14(4,11)−13(3,11)			73522.62			
14(4,10)−13(3,10)			73520.62			
14(5)−13(5)	64624.48	60505.98	61205.04			
14(5)−13(4)			77038.38			
14(6)−13(6)	64612.34	60495.15	61193.56			

Table 1. (continued)

$J'(K'_aK'_c)$-$J''(K''_aK''_c)$[b]	PRL(H)−H_2O	PRL(D)−D_2O	PRL(H)−$H_2{}^{18}O$	PRL(H)−DOH	PRL(H)−HOD	PRL(D)−H_2O
14(7)−13(7)	64598.48	60483.72	61180.27			
14(8)−13(8)	64582.77		61165.07			
14(9)−13(9)			61148.10			
15(0,15)−14(0,14)	69193.44		65555.98			
15(1,15)−14(1,14)	69117.98		65486.39			
15(1,14)−14(1,13)	69362.12		65682.26			
15(2,14)−14(2,13)	69242.36		65584.21			
15(2,13)−14(2,12)	69307.73		65624.11			
15(3,13)−14(3,12)	69255.37	64844.37	65590.13			
15(3,12)−14(3,11)	69259.05	64862.94	65591.73			
15(4)−14(4)	69245.28		65580.91			
15(5)−14(5)	69233.43	64822.61	65570.13			
15(6)−14(6)	69220.37	64810.81	65557.53			
15(7)−14(7)	69205.37		65543.35			
15(8)−14(8)	69188.46		65527.13			

[a] An inversion of the *b* and *c* axes takes place upon deuteration of the amino hydrogen. As a consequence normal, PRL(H)−$H_2{}^{18}O$, PRL(H)−DOH, and PRL(H)−HOD species have a μ_a- and μ_c-type spectra, while PRL(D)−D_2O and PRL(D)−H_2O species have a μ_a and μ_b-type spectra. [b] When transitions are doubly overlapped due to the near prolate degeneracy of the involved levels only K_a is given.

Table 2. Rotational and Distortion Centrifugal Constants for Normal and Six Isotopic Species of Pyrrolidine−Water

	PRL(H)−H_2O	PRL(D)−D_2O	PRL(H)−$H_2{}^{18}O$	PRL(H)−DOH	PRL(H)−HOD	PRL(D)−H_2O
A/MHz	3957.975(8)[a]	3817.46(2)	3952.897(9)	3955.37(2)	3951.09(2)	3825.86(1)
B/MHz	2318.531(3)	2177.13(2)	2194.673(4)	2288.23(3)	2216.88(21)	2302.30(4)
C/MHz	2302.517(3)	2148.36(2)	2181.922(4)	2273.34(3)	2203.72(21)	2271.46(4)
D_J/kHz	4.257(7)	3.58(3)	3.963(9)	4.24(9)	3.67(9)	4.18(8)
D_{JK}/kHz	37.41(5)	28.06(18)	36.47(5)	34.95(17)	33.50(16)	32.60(14)
D_K/kHz	−38.77(11)	−29.05(23)	−37.34(11)	−36.36(9)	−34.59(13)	−34.15(8)
d_1/kHz	0.284(3)	−0.291(78)	0.232(4)	[0.284][b]	[0.284][b]	[−0.291][c]
d_2/kHz	0.0249(10)	0.0711(95)	0.0177(7)	[0.0249][b]	[0.0249][b]	[0.0711][c]
H_{KJ}/Hz	6.21(79)	4.0(17)	6.42(64)	[6.21][b]	[6.21][b]	[4.0][c]
H_K/Hz	−3.64(59)	−1.8(11)	−4.49(47)	[−3.64][b]	[−3.64][b]	[−1.8][c]
N[d]	69	32	61	22	15	19
J_{max}	15	15	15	12	12	12
σ/MHz	0.059	0.084	0.050	0.115	0.069	0.078
$M^{\perp}$[e]/uÅ^2	64.601	64.638	64.598	64.608	64.635	64.558

[a]Errors in parentheses are expressed in units of the last digit. [b]Fixed to PRL(H)−H_2O value. [c]Fixed to PRL(D)−D_2O value. [d]Number of transitions in the fit. [e]Planar moment of inertia perpendicular to the plane of symmetry of the complex (see text).

should have been formed. To complete the conformational assignment, we investigated the rotational spectra of several D- or ^{18}O-substituted isotopomers. We will see in the next section that the assigned spectrum belongs to the (*eq*, OH···N, *E*) species. Correspondingly, the notation ($H_NH'H$) is used to indicate the three hydrogens which easily exchange with deuterium, where H_N, H′, and H represent the amino hydrogen, the water hydrogen involved in the hydrogen bond, and the "free" water hydrogen, respectively. The measured frequencies are reported in Table 1. All isotopic species showed a μ_a-type spectrum; in addition, those with H_N showed a μ_c-type spectrum, while those with D_N showed a μ_b-type spectrum. This because the amino deuteration causes the interchange of the *b* and *c* axes.

The transition frequencies have been fitted with the Watson Hamiltonian[35] by using the I^r representation and the S reduction. The full set of quartic and two sextic centrifugal distortion parameters have been determined. The results of the fittings are shown in Table 2.

Conformation and Structure. The planar moments of inertia perpendicular to the plane of symmetry of the adduct, $M^{\perp}$, are reported in Table 2. They have practically the same value for the six isotopomers, showing that the oxygen, the amino hydrogen (H_N), and the two water hydrogens (H′ and H, where the primed one participates in the hydrogen bond) lie in the symmetry plane. We used the unusual notation $M^{\perp}$ for this quantity because the substitution of the amino hydrogen with a deuterium causes the interchange of the *b* and *c* axes, in such a way that $M^{\perp}$ coincides with M_{bb} for four isotopomers [PRL(H)−H_2O, PRL(H)−$H_2{}^{18}O$, PRL(H)−H′OD, and PRL(H)−D′OH] and with M_{cc} for the other two ones [PRL(D)−H_2O and PRL(D)−D_2O]. The planar moments of inertia are defined as $M_{gg} = \sum m_i g_i^2$, where g_i represents one of the principal axis of inertia, and are easily obtained from combinations of the moments of inertia. The value of $M^{\perp} \cong 64.6$ uÅ^2 was consistent with an adduct formed between equatorial-PRL and with an OH···N internal hydrogen bond. The experimental rotational constants and substitution coordinates,[36] compared in Table 3 to the model calculated values of the various configurations, show that the measured spectrum belongs to the (*eq*, OH···N, *E*) species. The small nonzero values of the $|b|$ coordinates are interpretable as due to the large-amplitude motions of the water moiety with respect to PRL (see, for example, ref 28) and, therefore, are compatible with zero equilibrium values. But, even if the r_s coordinates are likely to be affected by the large amplitude motions of water with respect to the ring, and by the shrinkage of the O···N distance upon deuteration (Ubbelhode effect[36]), we believe that they are reliable for conformational assignments. The 18 experimental rotational constants and the r_s coordinates have been used to estimate the hydrogen bond structural parameters, reported at the bottom of Table 4, of the assigned (*eq*, OH···N, *E*) species. The bent arrangement of the hydrogen bond is shown in Figure 2. The geometries of the two subunits have been fixed to the values of isolated water and PRL.[33]

Potential Energy Surface of the Internal Motions of the Water Subunit. Six large-amplitude motions of water with respect to PRL arise upon formation of the adduct: they correspond to the three translational and to the three rotational degrees of freedom of the isolated water molecule. Information on one or more of these motions is available from the rotational spectrum; depending on the symmetry of the complex, they can be more or less directly and more or less

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Table 3. Comparison of the Experimental Rotational Constants (MHz) and Substitution Coordinates (Å) to the Model Calculated Values of the Eight Conformers[a]

	expt	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
A	3957.9	3957.5	3915.7	6678.9	6664.5	6475.9	6435.8	4483.4	4404.4
B	2318.5	2324.7	2381.3	1637.7	1640.0	1758.4	1757.6	1954.3	1976.0
C	2302.5	2302.2	2372.9	1384.9	1387.3	1490.0	1491.5	1818.9	1851.2
$\|a\|$ (O)	2.48	2.47	2.50	3.18	3.18	3.10	3.10	2.78	2.80
$\|b\|$ (O)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\|c\|$ (O)	0.31	0.38	0.27	0.08	0.03	0.17	0.08	0.45	0.32
$\|a\|$ (H′)	1.68	1.76	1.76	3.45	3.41	2.14	2.15	3.21	2.84
$\|b\|$ (H′)	0.0	0.0	0.0	0.73	0.73	0.0	0.0	0.73	0.73
$\|c\|$ (H′)	0.29	0.26	0.34	0.47	0.54	0.13	0.06	0.01	0.94
$\|a\|$ (H)	3.13	3.27	2.08	3.45	3.41	3.38	3.33	3.21	2.84
$\|b\|$ (H)	0.33[b]	0.0	0.0	0.73	0.73	0.0	0.0	0.73	0.73
$\|c\|$ (H)	0.37	0.15	1.14	0.47	0.54	0.74	1.01	0.01	0.94
$\|a\|$ (H_N)	0.25	0.03	0.03	1.30	1.30	0.21	0.17	1.04	1.03
$\|b\|$ (H_N)	0.31[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\|c\|$ (H_N)	2.08	2.09	2.10	0.02	0.08	1.47	1.50	0.35	0.31

[a] The geometries of water and PRL have been fixed (see text). The primed hydrogen participates in the hydrogen bond when water acts as proton donor (conformers **1**, **2**, **5**, and **6**). When PRL is the proton donor H and H′ are equivalent (conformers **3**, **4**, **7**, and **8**). [b] Value different from zero because of vibrational motions of H_2O molecule.

Table 4. Experimental Substitution Coordinates of the Water Atoms of PRL−water Compared to the Model Calculated Values after the Structural Refinement, That Is with the Hydrogen Bond Parameters Reported at the Bottom of the Table (Å and deg)[a]

(1) r_s Coordinates

		$\|a\|$		$\|b\|$		$\|c\|$	
parent molecule	atom	exptl	calcd[b]	exptl	calcd[b]	exptl	calcd[b]
PRL−H_2O	O	2.4857(1)[c]	2.470	0.00	0.0	0.3110(4)	0.378
	H′	1.679(1)	1.760	0.00	0.0	0.294(7)	0.263
	H	3.1354(6)	3.269	0.334(6)	0.0	0.3175(5)	0.149
	H_N	0.246(7)	0.028	0.31(1)	0.0	2.120(2)	2.086

(2) r_0 Hydrogen Bond Parameters (see Figure 2)

$r = 1.89(1)$ $\tau = 118.8(8)$ $\phi = 163.5(25)$ $R^d = 3.128$

[a] The quoted errors of these parameters are just fitting errors: supplementary uncertainties come, for example, from the assumption that the geometries of water and PRL have been fixed to those of the isolated molecules (see text). The primed hydrogen participates in the hydrogen bond. [b] Calculated with the r_0 structure (see bottom of the table and text). [c] Error (in parentheses) is expressed in units of the last digit.. [d] Distance between the center of mass of the monomers.

easily achieved. For example, in the case of pyrazine−water,[23] the tunneling splitting was measured and the barrier to internal rotation of the water group was determined. Information on the potential energy surface is often obtained from the "pseudo centrifugal distortion constants", whose abnormally high values are due to these motions. It is generally possible to obtain the force constants for the stretching and for the two bendings when the complex involves a rare gas atom.[30] Millen developed some equations to obtain the stretching force constant for high-symmetry complexes,[38] considering them as "pseudodiatomic" complexes. It has been shown by Lovas et al.[39] that Millen equations can be used also in a general case when the stretching takes place along (or nearly along) the a axis. This is the case for PRL-W, and the following equation can be used

$$k_s = 16\pi^4 \mu_D R_{CM}{}^2[4B_D{}^4 + 4B_D{}^4 - (B_D - C_D)^2(B_D + C_D)^2]/hD_J \tag{1}$$

to derive the stretching force constant (k_s): μ_D, R_{CM}, and D_J are the reduced mass, the distance between the centers of mass, and the first-order centrifugal distortion constant, respectively. The value $k_s = 7.0$ N/m, corresponding to a stretching frequency of 91 cm^{-1}, has been calculated. Our OH···N internal hydrogen bond appears to be weaker, for instance, than the OH···O internal hydrogen bond of the water dimer[39] ($k_s = 10.8$ N/m), as expected.

Conclusions

The rotational spectra of several isotopomers of the 1/1 complex of water/PRL in the jet-cooled mixtures have been assigned and measured with the relatively simple and new technique of millimeter-wave free jet absorption spectroscopy, confirming its efficacy for the study of molecular complexes.

Rather surprisingly, although only the rotational spectrum of axial-PRL has been reported,[32] the complex is formed between water and equatorial-PRL. Rotational transitions of both axial- and equatorial-PRL have been observed in the jet-cooled mixture, but the axial form disappears by enhancing the cooling conditions (that is, increasing the pressure of the carrier gas). The observed conformational relaxation indicates that (1) the equatorial species is more stable and (2) the barrier to conformational interconversion is low. This last aspect is very precisely described in the case of the free jet study of the conformational equilibrium of glycolic acid.[40] The missed observation of the equatorial species in the room-temperature spectrum is to be imputed to the accidentally zero or almost zero value of its μ_a dipole moment component. This was also the case for N-methylethylenediamine, for which the intermediate-energy conformer (over the three detected) was assigned in

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the jet-cooled condition[41] but not in the room-temperature spectrum.[42]

Experimental information on the strengths of solvation of cyclic amines, important in biological systems, are given here for the first time, although within some approximations, through eq 1.

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