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Internal Dynamics in the Molecular Complex of CF_3CN and H_2O

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The rotational spectrum of trifluoroacetonitrile-water complex has been studied by pulsed-nozzle, Fourier transform microwave spectroscopy. Both *a*-type and *b*-type transitions have been observed. The rotational constants, centrifugal distortion constants, and the ^{14}N nuclear quadrupole coupling constants have been determined. The complex is T-shaped, with the oxygen atom from the water located 3.135 Å from the carbon atom of CF_3 of the trifluoroacetonitrile molecule.

Introduction

Trifluoroacetonitrile, CF_3CN, is a symmetric top molecule. The microwave spectrum, as well as millimeter-wave spectrum of the monomeric form CF_3CN have been extensively studied due to its large dipole moment and large thermal population in the excited vibrational states[1,2,3,4,5,6,7,8,9,10,11,12,13]. We have reported the rotational analysis of the CF_3CN-Argon complex.[14]

The hydrogen bonding in small water containing clusters has received considerable attention. Water can serve as a proton donor, a proton acceptor, or in some cases as both. The types of hydrogen bonds involving water and its internal dynamics were summarized by Caminati *et al*.[15] Microwave spectroscopy is a particularly suitable technique to study the structure and internal dynamics of water containing clusters. Several clusters formed by water and CF_3-X (X = F, Cl, COOH) type molecules have been characterized. In the case of CF_4-H_2O,[16] an anti-hydrogen bond which was first proposed by Novick *et al.*[17] is formed due to the strong dipole-induced dipole interaction. Whereas Evangelisti *et al*[18] observed an O-Cl halogen bond in CF_3Cl-H_2O that binds the water to CF_3Cl, as opposed to the expected $O\text{-}H\cdots Cl$ or $O\text{-}H\cdots F$ hydrogen bond. The symmetric top spectrum for CF_3Cl-H_2O is rather surprising, indicating that the internal motion of water must convert the complex from an asymmetric to a symmetric top, similar to the case of CF_4-H_2O. This has also been recently found by Lovas *et al*[19] for CH_3CN-H_2O. One hydrogen of water bonds to the nitrogen along the C_{3v} axis of the acetonitrile; internal rotation of the other O-H of water about this C_{3v} axis turns this asymmetric top into an effective symmetric top. This does not happen in our analogous molecule CF_3CN-H_2O, whose spectrum is that of a true asymmetric top. Ouyang *et al* studied CF_3COOH- H_2O,[20] in which water molecule forms a ring with the COOH by forming two hydrogen bonds. It will be interesting to see the effect of a cyanide group attaching to the CF_3 group. The simplest cyanide containing molecule, HCN, acts as a H atom donor when forming a complex with H_2O.[21,22,23] Omron *et al*[24] observed similar hydrogen bonded structure in HCCCN-H_2O. Lee *et al*[25] studied the rotational spectra of NCCN-H_2O and NCCN-D_2O in which they derived a planar T-shaped asymmetric top structure arising from dipole-dipole interaction. An early report of the Lovas result[26] on CH_3CN-H_2O inspired this study. We started our project expecting that CF_3CN-H_2O, too, would behave as a symmetric top. The dominating force will still be hydrogen bonding after we replace CH_3 group with CF_3 group.

In this paper we report the rotational analysis of the CF_3CN-H_2O complex with Fourier transform microwave spectroscopy as well as a detailed theoretical analysis of the orientation of the water molecule and the potential energy surface of the complex.

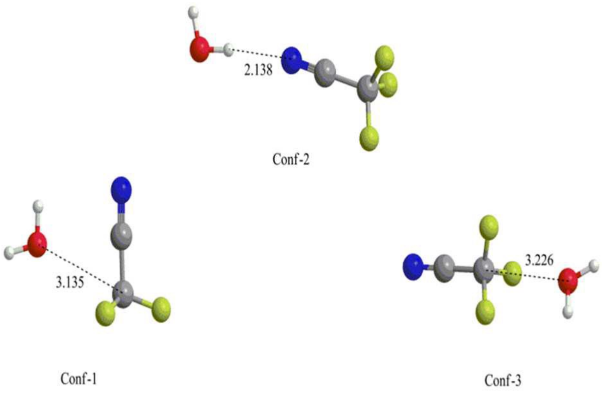
Experimental Section

The spectrum of trifluoroacetonitrile-water was measured using the Wesleyan pulsed-jet Fourier transform microwave spectrometer which has been described elsewhere[27,28]. Trifluoroacetonitrile was prepared as a gas mixture of 1% in argon carrier gas. The sample gas was then bubbled through a reservoir of deionized water then expanded through a general valve nozzle into the vacuum chamber. The backing pressure is approximately 0.5 atm. The CF_3CN-H_2O complexes were generated in the supersonic expansion. The spectrum was measured in the frequency range 16-19 GHz. Each line appears as a doublet due to the Doppler effect. The line position is calculated as the average frequencies of the two Doppler components. The full-width-half-maximum (fwhm) of the observed lines was ~5-7 kHz. With this fwhm, we can estimate peak centers to within 1 kHz.

Theoretical Calculations

Several factors play roles in the CF_3CN-H_2O complex. It is hard to state either the hydrogen bonding or the dipole-dipole interaction is the predominant interaction. And, if the hydrogen bonding plays the leading role, both nitrogen and fluorine may be involved in the H bond. There is also the possibility that the halogen bond is preferred as in the cases of the Freons. To answer these questions, we performed *ab initio* calculations at MP2/6-311++G(3df,3pd) level of theory using the Gaussian09 program package.[29] Out of the three plausible conformers located from the calculation, the one dominated by dipole-dipole interactions, namely conf-1, as presented in Figure 1, is predicted to be the most stable conformation.

Figure 1. Three stable conformers of the CF_3CN-H_2O complex



Results and discussion

We scanned the region between 16 and 19 GHz following the prediction from the theoretical calculations. The ^{14}N atom has a nuclear spin of 1, and the nuclear electric quadrupole coupling splits each rotational transition into a characteristic hyperfine pattern. The scan yielded almost two hundred transitions as expected from the hyperfine splitting. We first identified the transitions of the CF_3CN monomer, then identified the transitions of the CF_3CN-Argon complex based on the prediction from previous work. These CF_3CN-Argon transitions were outside of the previously scanned region. We combined these transitions with those from the previous work; the analysis is included in the following section. After removing these transitions, the remaining transitions were analysed using the predicted rotational constants and hyperfine coupling constants.

Rotational spectrum of the CF_3CN-Argon complex

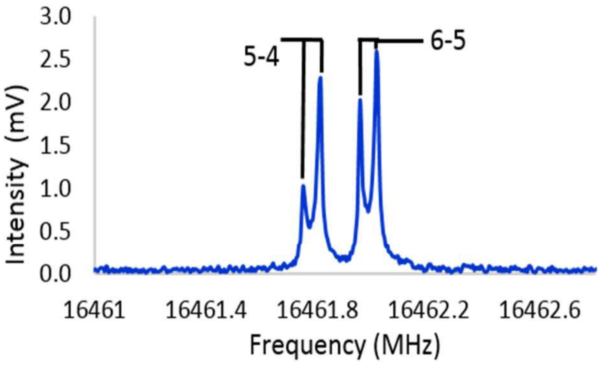
A total of 18 transitions with 68 resolved hyperfine components have been identified as the transitions from the CF_3CN-Argon complex using the spectroscopic constants previously determined. Table S1 lists the newly measured frequencies of CF_3CN-Ar with their assignments.

These transitions were then combined with the previously measured transitions for the CF_3CN-Ar complex to obtain improved spectroscopic constants. The resulting spectroscopic constants are listed in Table S2 with the comparison to the literature. The rms error of the new fit is 2 kHz, which is consistent with the estimated experimental uncertainty.

Rotational spectrum of the CF_3CN-H_2O complex

The candidate transitions for the CF_3CN-H_2O complex were analysed with Pickett's least-squares fitting program, SPFIT,[30] using Watson's standard asymmetric rotor Hamiltonian[31] (*A*-reduction, I^R representation) with an exact treatment of the nuclear quadrupole interaction. Both *a*-type and *b*-type transitions have been observed, allowing the determination of a complete set of rotational constants and centrifugal distortion constants. The nuclear quadrupole coupling constants of ^{14}N are determined together with the rotational and centrifugal distortion constants. The coupling scheme used is $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where **J** is the molecular end-over-end angular momentum, **I** is ^{14}N nuclear spin angular momentum where $I = 1$ is the nuclear spin of ^{14}N, and **F** is the total angular momentum. Each transition appeared as a doublet due to the tunnelling of the two equivalent forms of the water subunit within the dimer. Each of the hydrogen atom has a nuclear spin number of $I = ½$. The coupling of the two hydrogen nuclear spins results in two possible symmetry states. We will label the two symmetry states as A state (*para*-) for $I = 0$ and B state (*ortho*-) for $I = 1$ following reference 19. The intensity ratio of the two observed split transitions is approximately 1:3, which is in agreement with the $(2I + 1)$ spin statistical weight. We assigned the weaker line of the two components to the A state. The splitting varies from transition to transition but is normally within a dozen MHz. Table S3 lists the measured frequencies and their assignment. Two hyperfine components of the 5_{05}-4_{04} transition of the B state are shown in Figure 2. This spectrum was obtained with 64 averaging cycles. The doublets shown in Figure 2 for both hyperfine components are due to Doppler splitting which is because of the parallel setting of the molecular beam and the radiation direction.

Figure 2. The 5_{05}-4_{04} transition of the B state of the CF_3CN-H_2O complex. Lines are Doppler doubled, and the *F′*-*F″* quantum numbers are labelled for each transitions.



The resulting spectroscopic constants are listed in Table 1. The rms error of the fit is 2 kHz, which is consistent with the estimated experimental uncertainty.

Table 1. Spectroscopic constants of CF_3CN-H_2O.

	A state	B state
A /MHz	3187.81379(48)	3190.33856(43)
B /MHz	1981.2828(15)	1981.7161(14)
C /MHz	1554.8307(18)	1554.8797(17)
Δ_J /kHz	2.743(32)	2.709(29)
Δ_{JK} /kHz	-3.004(21)	-2.831(19)
Δ_K /kHz	4.979(61)	4.680(55)
δ_J /kHz	0.7668(34)	0.7732(32)
δ_K /kHz	0.316(47)	0.407(44)
χ_{aa} /MHz	0.263(3)	0.2737(25)
χ_{bb} - χ_{cc} /MHz	-5.0392(44)	-5.0528(40)
N	49	45
σ/kHz	2.3	1.9

Structure Confirmation of the CF_3CN-H_2O complex

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From the *ab initio* calculations at MP2/6-311++G(3df,3pd) level of theory three plausible conformers were located. Their energy, rotational constants and structures are given in Table 2 and Figure 1. We found that the conformer dominated by dipole-dipole interactions, namely conf-1, is predicted to be the most stable conformation. The calculated rotational constants from the equilibrium structure also agree well with experiment. The conformer with O-H···N H bond (conf-2) is about 0.32 kcal/mol less stable than conf-1. The conformer with halogen bond, conf-3, is significantly less stable by 2.13 kcal/mol. The dipole moments of CF_3CN and CH_3CN were determined to be 1.262 ± 0.010 D[32] and 3.913 ± 0.002 D[33], respectively. The perfluorination of the acetonitrile significantly reduces the overall dipole moment of that moiety. Dipole-dipole interaction is expected to play an important role in their complexes with water. In the case of water-acetonitrile, the spectrum of a symmetric top molecule was observed[19]. This suggests that the oxygen atom of the water molecule is effectively on the axis of C-C≡N. The fitted structure of CH_3CN-H_2O complex suggests a hydrogen bonding distance of 2.075 Å between the nitrogen and hydrogen atoms. This conformation also favours the local dipole-dipole interaction of the C≡N group and O-H group. The nitrile group has much stronger polar effect than the carbon-fluorine bond, as is evidenced in the comparison of the dipole moments of acetonitrile (3.913 ± 0.002 D) and monofluoromethane (1.8572 ± 0.0010 D)[33]. However, in the case of CF_3CN-H_2O complex, the local dipole moments of C-F bonds do play a more significant role than the C-H bonds in CH_3CN-H_2O complex. We speculate that molecular alignment in conf-1 may maximize the overall dipole-dipole interactions between local bonds, and by doing so stabilize conf-1 with respect to conf-2. This calls for further systematic investigation on the partially fluorinated acetonitriles. We also note that the ab initio rotational constants of conf-1 fit very well with the experimental values, with a maximum difference of about 1%, while those of conf. 2 and conf. 3 exhibit significant deviations. This indicates that the actual geometry of CF_3CN-H_2O is very close to that of the calculated conf. 1.

Table 2. *ab initio* (MP2/6-311++G(3df,3pd)) calculated results of energy, spectroscopic constants of the three stable conformers of the CF_3CN-H_2O complex.

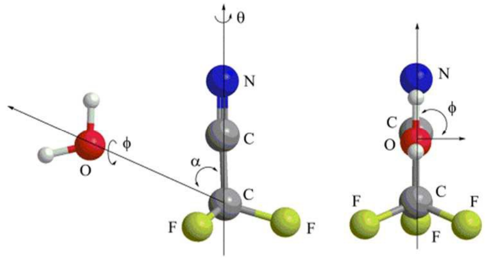
Type	Conf-1	Conf-2	Conf-3	Exp.
***E*(kcal/mol)**	0.00	0.32	2.13	
E_0(kcal/mol)[a]	0.00	0.61	1.68	
***A*/MHz**	3257.68	5628.49	5614.75	3228.85
***B*/MHz**	2007.23	826.68	1365.78	2034.66
***C*/MHz**	1587.25	824.83	1360.71	1598.49
μ_a(Debye)[b]	1.39	2.93	-3.66	
μ_b(Debye)[b]	1.27	-1.66	0.47	
μ_c(Debye)[b]	0.00	0.00	0.00	

[a] E_0 is the ZPE corrected relative energy of each conformer.
[b] μ_x are the dipole moment components.

Internal dynamics of the CF_3CN-H_2O complex

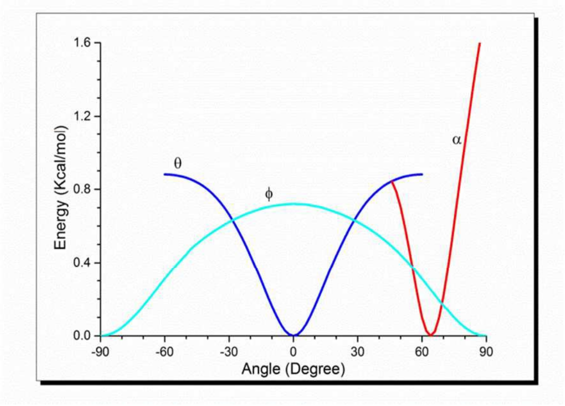
To rationalize the tunnelling motion of the CF_3CN-H_2O complex, we performed potential-energy surface scan using the coordinates defined in Figure 3. The angle α measures the bending amplitudes of the two constituent molecules. The angle θ reflects the rotation of water molecule around CF_3CN, and φ is defined as the angle between the norm of H_2O plane and the axis passing through two C atoms (see Fig. 3), which describe the internal rotation of H_2O with respect to CF_3CN.

Figure 3. Definition of geometrical parameters used to discuss the internal dynamics



To evaluate the potential curve for each geometrical parameter, an *ab initio* grid was calculated in steps of 2°. While the angle/dihedral angles were kept fixed at each step, the rest of geometrical parameters were fully optimized for each point. The results are plotted in Figure 4. As shown in Figure 4, the potential energy as a function of the angles α, θ and φ, which describe the bending motions of CF3CN and water molecules, exhibits a single minimum, at $\alpha = 64^\circ$, $\theta = 0$, and $\varphi = 90^\circ$, i. e., conf-1.

Figure 4. *ab initio* potential surface profile along α, θ, φ which are defined in Figure 3.



For the 3D potential surface scan, steps of 5° were employed. The results are plotted in Figure 5.

Conclusions

High resolution rotational spectrum of the CF_3CN-H_2O complex has been measured for the first time to produce rotational and centrifugal distortion constants, along with nuclear quadrupole coupling constants. We studied the internal dynamics of CF_3CN-H_2O complex using the rotational spectroscopic technique and the *ab initio* calculations. The observed conformation was characterized by a dipole-dipole interaction. The structure of CF_3CN-H_2O is completely different from that of CH_3CN-H_2O.

Figure 5. *ab initio* 3D potential surface with respect to θ, φ, which are defined in Figure 3.

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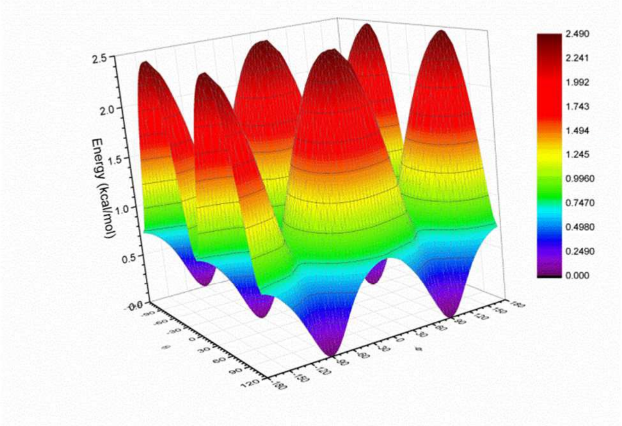

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Notes and references

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