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Research paper

Rotational study of the bimolecule acetic acid-fluoroacetic acid

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ABSTRACT

The rotational spectrum of the acetic acid-fluoroacetic acid bimolecule was measured by using a pulsed jet Fourier transform microwave spectrometer. One conformer, in which fluoroacetic acid is in *trans* form, has been observed. The rotational transitions are split into two component lines, due to the internal rotation of the methyl group of acetic acid. From these splittings, the corresponding V_3 barrier has been determined. The dissociation energy of this complex has been estimated to 66 kJ/mol. An increase of the distance between the two monomers upon the OH → OD substitution (Ubbelohde effect) has been observed.

1. Introduction

Carboxylic acids exist, even in the gas phase, mainly as dimers, with the two subunits linked through two relatively strong $OH\cdots O$ hydrogen bonds (HBs), forming an eight-membered ring structure. Several interesting features of this kind of adduct have been described recently by rotational studies. Precise information has been obtained on: (i) tunnelling splittings due to the concerted transfer of the two hydroxyl protons from one unit to the other [1–5]; (ii) conformational equilibria when the tails of the carboxylic acids can have more than one orientation [6–11]; (iii) internal rotation of parts in the side chains of one or both acids [4,9–11]; and (iv) the Ubbelohde effect, which is due to structural change of the dimer upon OH → OD isotopic substitution in HBs [12].

Some carboxylic acids have, in the side chain, a symmetric group which can undergo a hindered rotation, such as CH_3 in acetic acid (CH_3COOH, AA). It has been shown that the corresponding V_3 barriers to the internal rotation of the CH_3 top decrease considerably upon complexation of acetic acid with one or more water molecules [13], or with another carboxylic acid [4,7,14].

We considered interesting the study of the adduct between acetic acid and fluoroacetic acid (AA-FAA), in order to size the effect of complexation on the V_3 barrier and to study the conformational equilibrium of the complex. FAA can adopt two canonical configurations, with the F atom *trans* or *cis* with respect to the hydroxyl group, to form complexes with other molecules. FAA has been rotationally characterized, but, surprisingly, the *cis* conformer has not been detected, in spite of the fact that the microwave spectrum of a quite less stable species (*cis-anti* form) has been assigned [15]. However, recently rotational studies on its adducts with water [16] and acrylic acid [8] evidenced the existence of *cis*-FAA in the supersonic jet, less stable than the *trans* form by about $\sim 100\ cm^{-1}$. The *cis* form was not detected in the case in FAA-formic acid [17]. Below we report the obtained results from the rotational study of AA-FAA.

2. Experimental section

Molecular clusters were generated in a supersonic expansion, under conditions optimized for the formation of the AA-FAA bimolecule. Details of the FTMW spectrometer [18] (COBRA-type [19]), which covers the range 6.5–18 GHz, have been described previously [20].

Helium at a stagnation pressure of ~0.25 MPa was passed over a 1:1 mixture of AA and FAA (commercial samples) and expanded through a solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity. The line positions were determined after Fourier transformation of the time-domain signal with 8 k data points, recorded with 100 ns sample intervals. Each rotational transition appears as a doublet due to the Doppler effect. The line position is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of the frequency measurements is better than 3 kHz. Lines separated by more than 7 kHz are resolvable.

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The O-D deuterated species have been derived by directly mixing the acids with deuterated water.

3. Results and Disscussions

3.1. Theoretical calculations

Before starting the spectral search, we ran some theoretical calculations, in order to find the relative energies of the possible conformations and to evaluate the spectroscopic parameters of interest for the rotational spectra. Geometry optimizations at MP2/6-311++G(d,p) level of theory have been performed with the Gaussian09 program package [21]. In addition, counterpoise corrections were calculated in order to minimize the well-known basis-set superposition error (BSSE) [22]. As expected when considering the relative energies of the FAA monomer, the *trans* conformer resulted to be the global minimum, followed by the *cis* one.

The shapes (with the principal axes), calculated rotational constants and electric dipole moment components of both conformers are collected in Table 1. Vibrational frequency calculations provide additionally centrifugal distortion constants and allow estimation of the BSSE corrected zero-point dissociation energy, E_{D0}.

3.2. Rotational spectra

According to the calculated rotational constants, the μ_a-type R branch transitions were expected to appear in narrow frequency regions, separated by a $B + C$ spacing. The two conformers have high values of μ_a components of dipole moments and similar sets of $B + C$; so we started the spectral search in the frequency range where their $J = 7 \leftarrow 6$ μ_a-R-type transitions were supposed to fall. Only one set of transitions could be found, which (see ahead) has been assigned to the *trans* conformer. Then the measurements have been extended to the $J = 8 \leftarrow 7$ and $J = 9 \leftarrow 8$ μ_a-R-type transitions, and to several μ_b-type lines. All transitions were split into two (A and E) component lines, due to the internal rotation of the methyl group of AA.

Two different global fits of all A/E transitions have been adopted, both referred to Watson's semi-rigid Hamiltonian in the S reduction and I^r representation [23].

Computer program XIAM (based on the combined axis method, CAM), provides a set of rotational and first order centrifugal distortion constants - common to the A and E sublevels - together with the parameters describing the internal rotation of the methyl group [24]. These include the V_3 barrier, the moment of inertia of the top (I_α), and the angles between the symmetry axis of the CH_3 top and the principal axes of the entire molecule, $\angle(i,g)$, where $g = a$, b and c. Due to the C_s symmetry of AA-FAA, the angle $\angle(i,b)$ is the complement of $\angle(i,a)$ to 90°, while $\angle(i,c)$ is 90°.

Briefly, the Hamiltonian for XIAM can be expressed as [24,25]:

$$H = H_{rot} + H_{tor} + H_{CD} \quad (1)$$

where H_{rot} (the rotational part) includes a single set of rotational constants, corresponding to the hypothetical infinite barrier limit, H_{CD} includes a set of centrifugal distortion parameters common to both states, and H_{tor} is the torsional part:

$$H_{tor} = F(p - \rho P_a)^2 + V_3/2(1 - \cos 3\alpha) \quad (2)$$

In this relation, F ($=\hbar/[2\cdot(1 - \Sigma_g \lambda_g I/I_g)I]$) is the reduced rotational constant for internal rotation. p represents the total angular momentum of the internal rotor, whereas P_a is the component of the total angular momentum of the molecule along a axis. The obtained spectroscopic parameters with XIAM have been collected in Table 2.

With Pickett's SPFIT program [26], which is based on the principal axis method (PAM), the rotational constants have been fitted separately for the A and E states. In addition, some first order correction parameters (D_g, $g = a$ and b) related to the internal rotation of $-CH_3$ group (non-zero only for the E state) have been determined. The Hamiltonian can be summarized as:

$$H = H_{rot,A} + H_{rot,E} + H_{CD} + H_{cor,E} \quad (3)$$

in which H_{rot} is the rotational part, including a set of rotational constants for each state. H_{CD} includes a set of centrifugal distortion parameters common to both states, and $H_{cor,E}$ represents the first order corrections to state E, according to [26,27]:

$$H_{cor,E} = -D_a P_a - D_b P_b + CD\ terms \quad (4)$$

The spectroscopic parameters determined with SPFIT are reported in Table 3. From them it is possible to estimate the V_3 barrier [28]. First, the coefficients $W_E^{(1)}$ can be derived through the relation:

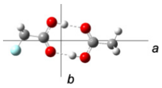
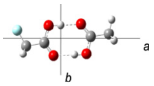
$$W_E^{(1)} = D_g/(F\rho_g) \quad (5)$$

where $\rho_g = \lambda_g I_\alpha / I_g$. I_α and I_g are the moments of inertia along the symmetry axis of the internal rotor and along the principal axis g, and $\lambda_g = \cos\angle(i,g)$. Then, the reduced barrier s can be obtained from the perturbation coefficients $W_E^{(1)}$ [28]. Finally, the V_3 barrier is calculated from s according to:

$$V_3 = 9/4F \cdot s \quad (6)$$

D_a and D_b lead to a common value of $W_E^{(1)}$ ($= -0.23 \pm 0.01$), which corresponds to $s = 7.6$ and to $V_3 = 93\ cm^{-1}$. In addition, the angle $\angle(i,a)$ can be calculated (=3.8°) from the relation [29–31]:

Table 1
MP2/6-311++G(d,p) calculated spectroscopic parameters of the two conformers of AA-FAA.

	trans	*cis*
		
A/MHz	4612	4884
B/MHz	607	601
C/MHz	540	538
μ_a, μ_b, μ_c/D	1.6, 1.5, 0.0	1.6, 1.3, 0.0
D_J, D_{JK}, D_K/kHz	0.03, 0.12, 1.62	0.02, 2.88, 37.28
d_1, d_2/Hz	3.4, −1.2	−3.7, −0.2
ΔE, ΔE_{BSSE}/cm^{-1}	0, 0[a]	278, 280
E_{D0}/kJ/mol	62	61

[a] Absolute values are −556.227479 and −556.222342 E_h, respectively. E and E_{BSSE} are the calculated energies without and with counterpoise correction, respectively.

Table 2
Spectroscopic and internal rotation constants of the parent species of *trans*-AA-FAA obtained with XIAM (S-reduction, I^r representation).

Overall rotation		Internal rotation	
A/MHz	4669.291(3)[a]	V_3/cm^{-1}	100.558(3)
B/MHz	616.0464(2)	s[b]	8.28
C/MHz	548.4128(2)	I_α/uÅ^2	3.218(1)
D_J/kHz	0.034(1)	F_0/GHz	157.051(3)
D_K/kHz	2.5(6)	$\angle(i, a)$/°[c]	3.6(1)
d_1/Hz	−5.0(8)	$\Delta_{\pi 2J}$/kHz^{-1}	−13.60(8)
N[d]	74	σ[e]/kHz	4.2

[a] Error in parentheses in units of the last digit.

[b] Reduced barrier.

[c] The values of the $\angle(i,b)$ is the complement of $\angle(i,a)$ to 90° while the $\angle(i,c)$ is 90° (from the planarity of the main frame).

[d] Number of lines in the fit.

[e] RMS error of the fit.