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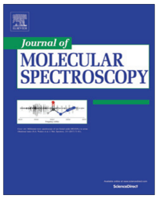

Rotational spectrum and structural analysis of CH···F interactions in the vinyl fluoride···1,1-difluoroethylene dimer

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The structure of the weakly bound dimer of 1,1-difluoroethylene with vinyl fluoride was studied using Fourier-transform microwave spectroscopy in the 6–19 GHz range. In the observed dimer structure each monomer acts as both a weak bond donor and acceptor, giving a cyclic arrangement of C—H···F contacts. The difluoroethylene C═C bond is roughly perpendicular to the vinyl fluoride C═C bond, forming the cross of a T-shaped carbon atom framework, resembling the lowest energy structure predicted by MP2/6-311++G(2d,2p) calculations. Observed C—H···F distances are similar to those of vinyl fluoride and 1,1-difluoroethylene complexes with difluoromethane and HCCH. The dipole moment of the dimer was measured using the Stark effect, giving values of μ_a = 0.9003(19) D, μ_b = 0.030(8) D and μ_{total} = 0.9008 (22) D. A second ab initio structure, with the C═C bonds in a slipped parallel arrangement, was predicted to be about 38 cm^{-1} higher in energy than the T-shaped conformation. This higher energy arrangement has not been observed experimentally..

1. Introduction

Recently, we investigated dimers of vinyl fluoride (VF) with difluoromethane (DFM) and chlorofluoromethane (CFM) [1,2], and studies of the trifluoromethane (TFM)···VF complex are ongoing [3], although spectra are complicated by internal rotation in the latter case. Results from those studies could be combined with previous structural data on DFM complexed with 1,1-difluoroethylene (DFE) and trifluoroethylene (TFE) [4] in order to gain insight into the nature of weak CH···F interactions in these species and the variation of these interactions as the degree of fluorine substitution on the ethylene subunit was varied. It was found that in VF and TFE complexes DFM interacts with the H-C-F edge of VF (referred to as "side-bonded"), rather than along the H-C-C-F edge (referred to as "top-bonded"). In order to maintain a cyclic type interaction with both C—H···F and C—F···H contacts from the fluorinated ethylene to DFM, the arrangement of DFE···DFM is different, and DFM does lie along the top H-C-C-F edge of 1,1-DFE [4]. A summary of observed structures is given in Figs. 2 and 3 of Ref. [1].

A logical extension to these studies is to interactions of various fluoroethylenes with each other. VF dimer would likely be nonpolar, so our first step is investigation of the VF···1,1-DFE complex. We aim to answer three main questions via structural analysis of this dimer. First, is the minimum energy geometry planar, or will these two molecules adopt a nonplanar arrangement, perhaps with a weak C—H···π contact, as has been observed in acetylene complexes with fluorinated methanes [5–8]? Second, if the structure is planar, will DFE interact with the H-C-F side of VF, as has been observed in complexes of DFM and CFM with VF? Finally, how do the strength and orientations of observed C—H···F contacts compare to those in related species?

2. Experimental methods

The sample mixture was prepared in a steel tank and consisted of about 1% VF (98% Synquest Laboratories) and 1% DFE (Synquest Laboratories) diluted in first-run helium-neon (BOC Gases; 82.5% Ne, 17.5% He) and delivered to a General Valve Series 9 pulsed nozzle with 0.8 mm orifice at 2–2.5 atm backing pressure. The spectrum was scanned using the reduced (480 MHz) bandwidth chirped-pulse (CP) Fourier-transform microwave (FTMW) spectrometer at Eastern Illinois University (EIU) [9]. Individual 480 MHz spectra recorded with each center frequency separated by 240 MHz from the previous step across the 7.5–19 GHz range, were compiled into a single broadband spectrum using a LabVIEW routine. At each center frequency, 2000 Fourier-transformed spectra were averaged, and the LabVIEW routine also compared overlapping spectra to translate offsets from each center frequency into absolute transition frequencies. Following initial assignment

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of the spectrum, additional measurements (for Stark effects, ^{13}C isotopologues, and weaker transitions of the most abundant isotopologue) were performed using the resonant cavity(RC) FTMW spectrometer at EIU [10,11].

Stark effect measurements were performed by applying voltages of up to ±5 kV to a pair of steel mesh plates separated by $\sim$31 cm and straddling the gas expansion and Fabry-Perot cavity of the RC-FTMW spectrometer. The electric field was calibrated using the $J = 1–0$ transition of OCS, assuming a dipole moment of 0.71519(3) D [12].

3. Results

3.1. Ab initio calculations

Two planar structures for VF···DFE, both containing a pair of weak CH···F interactions, were optimized at the MP2/6-311++G (2d,2p) level using Gaussian 03 (Fig. 1) [13]. Tight SCF convergence criteria and MP2 densities for properties were used. In the resulting structures, the slipped parallel orientation (Fig. 1(b), structure II) of double bonds was about 38 cm^{-1} less stable than the perpendicular double bond orientation (Fig. 1(a), structure I) at the zero point energy and basis set superposition error uncorrected level (Table 1). Since optimizations did not strictly enforce symmetry, optimized configurations are not quite planar, giving small values for out of plane dipole moment components ($\mu_c \sim 0.01$ D and 0.02 D) and planar moments ($P_{cc} \sim 0.002$ u Å^2 and 0.007 u Å^2), respectively, for structures I and II. The μ_b dipole components are also predicted to be very small (less than 0.1 D) for both orientations of the dimer as a result of the monomers aligning such that one component of the VF dipole moment (experimental values: $\mu_a = 1.284(4)$ D, $\mu_b = 0.712$ (12) D, $\mu_{\text{total}} = 1.468(7)$ D [14]) opposes the dipole moment of DFE (experimental value: $\mu_a = 1.3893(14)$ D [15]). Principal axis coordinates for both structures I and II are given in Supplementary Materials. Attempts to locate stationary points corresponding to any nonplanar structures were unsuccessful.

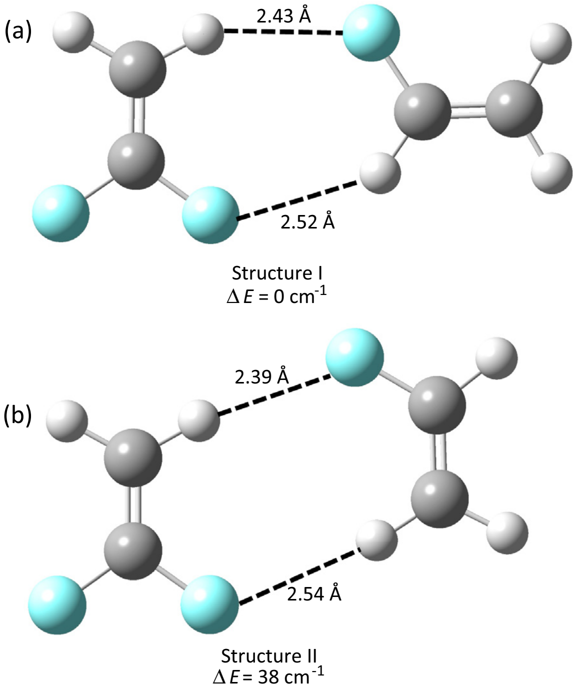

Fig. 1. MP2/6-311++G(2d,2p) structures for the vinyl fluoride···1,1-difluoroethylene dimer, (a) Structure I, (b) Structure II. ΔE is the relative energy (zero point energy and basis set superposition error uncorrected).

Table 1
Ab initio (MP2/6-311++G(2d,2p)) parameters for structures I and II, shown in Fig. 1.

	Structure I	Structure II
A/MHz	6627.9	5284.6
B/MHz	837.9	884.8
C/MHz	743.8	757.9
P_{aa}/u Å^2 [a]	603.2	571.2
P_{bb}/u Å^2 [a]	76.2	95.6
P_{cc}/u Å^2 [a]	0.002	0.007
μ_a/D	0.84	1.60
μ_b/D	0.10	0.04
μ_c/D	0.01	0.02
μ_{total}/D	0.85	1.60
E/E_h	−454.046056	−454.045885
E_B/kJ mol^{-1} [b]	9.6	9.1
ΔE/cm^{-1} [c]	0.0	38.0

[a] Planar moments, $P_{aa} = ½(I_b + I_c - I_a) = \Sigma m_i a_i^2$, with permutations for P_{bb} and P_{cc}.

[b] Binding energy of dimer without basis set superposition error correction, $E_B = |E_{\text{dimer}} - E_{\text{VF}} - E_{\text{DFE}}|$, where monomers were optimized independently of the dimer.

[c] Relative energies calculated at the zero point energy and basis set superposition error uncorrected level.

For the purposes of prediction and assignment of observed spectra, B and C for both structures I and II are very similar and are not sufficiently different to distinguish between the two possible configurations based only on these values; however, A is significantly different for the two structures, even accounting for expected higher uncertainty in experimental values of A for a-type spectra. In addition, predicted P_{bb} planar moments are quite different for structures I and II, as are μ_a dipole components, and these should help confirm which ab initio structure corresponds most closely to the experimental result.

For later comparison with our approximate experimental values (Section 4, below), the binding energies for both dimer structures were estimated using MP2/6-311++G(2d,2p) calculations by taking the difference between each dimer's absolute energy and the sum of the energies of the separate monomers. If separately optimized monomer structures are used for this, the binding energies of $\sim$9 kJ mol^{-1} reported in Table 1 are obtained, with Structure I more strongly bound by 0.5 kJ mol^{-1}. More sophisticated calculations incorporating monomer relaxation and basis set superposition error corrections might give more accurate binding energies, but these are beyond the scope of the present work, and the difference between the two structures is not expected to change significantly.

3.2. Spectra

The spectrum of VF···DFE was scanned using the EIU CP-FTMW spectrometer in the 7.5–19 GHz range, although loss of sensitivity above about 16 GHz prevented assignment of transitions at the high end of the frequency range. A series of $K_a = 0$ and $K_a = 1$ transitions with J' ranging from 5 to 7 was identified very close to the ab initio prediction for structure I. Initial assignments and pattern matching utilized Kisiel's AABS suite of programs [16], interfaced with Pickett's SPFIT/SPCAT package [17]. These were fitted to a Watson A-reduction Hamiltonian in the I^r representation [18]. After additional transitions were measured using the more sensitive RC-FTMW spectrometer, a final fit of 37 a-type transitions with an RMS deviation of 0.97 kHz was obtained. Fitted transition frequencies are listed in Table 2, and resulting constants are given in Table 3. Although the dimer is very near prolate ($\kappa \sim -0.97$), an S reduction fit gave identical results. The predicted very small μ_b dipole component meant that b-type transitions could not be observed, and this led to a higher than usual uncertainty in the A rotational constant, since a-type transition frequencies for near-

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