Shape and non-bonding interactions in the formic acid-difluoromethane complex by rotational spectroscopy

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ABSTRACT

The rotational spectrum of the formic acid-difluoromethane complex was measured by using supersonic-jet Fourier transform microwave spectrometer. Experimental results and *ab initio* calculations support a conformation formed through a relative strong O—H⋯F and a bifurcated weak CH_2⋯O hydrogen bonds. The distances of the non-bonding interactions were determined to be 1.960(2) Å and 2.797(3) Å for O—H⋯F and CH_2⋯O, respectively. The dissociation energy of the complex is estimated to be about 1346 cm^{-1}. The bonding nature of the intermolecular interactions was revealed by non-covalent interaction analysis and electron density difference analysis.

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1. Introduction

Formic acid (FA), a simplest carboxylic acid, can act as the proton donor or acceptor for forming intermolecular adducts with other molecules through hydrogen bond (HB). These adducts serve as a prototype for investigating the nature of HBs. FA forms homodimer through two cooperatively O—H⋯O HBs closing an eight membered ring with interaction energy of about 60 kJ·mol^{-1} which ranks as one of the strongest HB assemblies within neutral species [1,2]. Similarly, these double HBs lead the high stability of the heterodimers of FA with other carboxylic acids [3,4]. The HBs formed between FA and molecules containing other functional groups of aldehyde [5], ethers [6], ketones [7], pyridines [8] and amides [9] are weaker than those of carboxylic acid dimer. O—H⋯O or O—H⋯N HB combined with the C—H⋯O weak HB characterize the stabilization of these complexes.

Contrary to FA, alkyl halide forms homo- or heterodimers through rather weak C—H⋯X—C (X = F, Cl) non-bonding interactions. The bonding energies were estimated to be a few kJ·mol^{-1} with bonding distances ranged between 2.5 and 2.9 Å [10–14]. The bonding energies of FA dimers and those dimers of alkyl halide represent two opposite energetically limits of HBs in the neutral species. Difluoromethane (DFM) is a simple member of alkyl halide, in which the two hydrogens can act as proton donors and two fluorine atoms can act as proton

acceptors. DFM forms complexes with water [15] and formaldehyde [16] through a C—F⋯H and a bifurcated CH_2⋯O weak HBs.

Gas phase spectroscopic information on the complex of FA and alkyl halide is missing. It is interesting to investigate the intermolecular non-bonding interactions within the complex constituted by FA and alkyl halide to see what kind of interaction topology would be adopted between the two subunits. Herein, the 1:1 complex of FA and DFM (FA-DFM) was investigated by pulsed-jet Fourier transform microwave spectroscopy and supplemented with quantum chemical calculations.

2. Methods

2.1. Experimental

The rotational spectrum was measured by using a supersonic-jet Fourier transform microwave (FTMW) spectrometer [17] of coaxially oriented beam-resonator arrangement (COBRA) type [18] at Chongqing University. The spectrometer works in the frequency range of 2–20 GHz and is operated with FTMW++ program [19].

Commercial samples of FA (≥97%) and DFM were used without further treatment. A gaseous mixture containing about 1% DFM and 99% helium, at a stagnation pressure of ~0.4 MPa, was allowed to pass over the FA and expanded through a solenoid valve (Parker-General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity to generate the expansion. The molecules in the jet expansion are excited by a short pulse of microwave radiation and the resulted FID is recorded. The spectral line positions were determined after Fourier transformation of the time-domain signal with 8 k data points, recorded with

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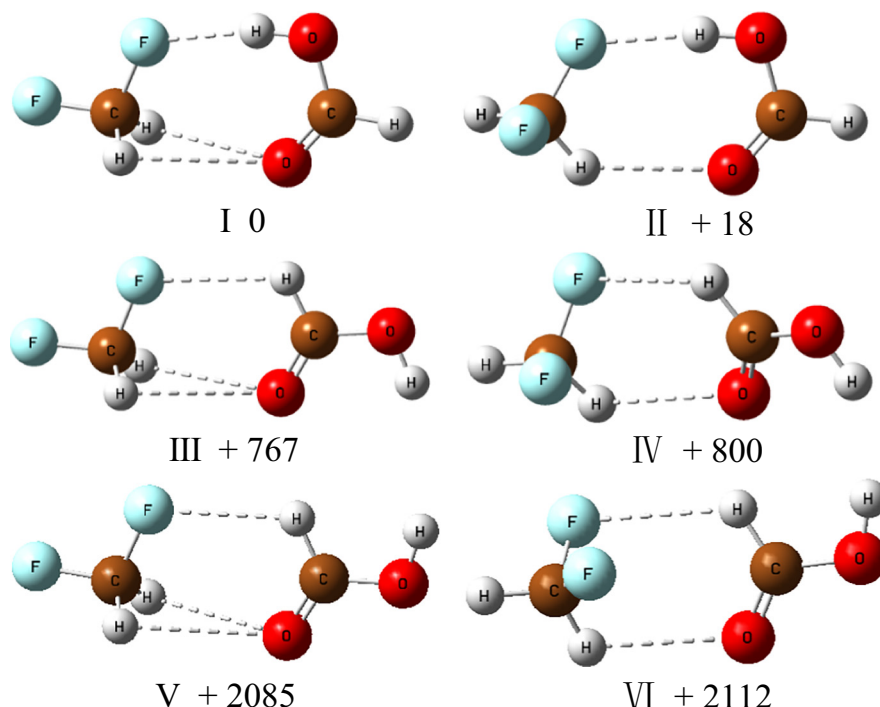
I 0   II + 18

III + 767   IV + 800

V + 2085   VI + 2112

Fig. 1. Shapes of the six stable conformers of the FA-DFM complex optimized at MP2/6-311++G(d,p) level of theory. Relative energies (in cm^{-1}) were obtained at the CCSD(T)/aug-cc-pVTZ level of theory.

100 ns sample intervals. Each rotational transition appears as a doublet due to the Doppler effect arising from the COBRA arrangement. 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. The instrumental resolution is better than 6 kHz.

2.2. Theoretical

Before searching for the rotational spectrum, geometry optimizations on several possible configurations of the titled complex were carried out at the second order Møller–Plesset (MP2) level of theory employing the 6-311++G(d,p) basis set. Harmonic frequency calculations at the same level of theory were also performed to verify that the resulted structures are real local minima, providing the zero-point energies. The basis-set superposition error (BSSE) [20] was counterpoise created (CP). The single point (SP) energy of each conformer was calculated at CCSD(T)/aug-cc-pVTZ level of theory to provide more robust estimates for the relative energies. All the calculations were carried out by using the Gaussian09 suite of program package [21].

Johnson's non-covalent interaction (NCI) analysis [22] and the electron density difference analysis were performed to understand the intermolecular interactions by using the Multiwfn program [23,24].

Table 1
Theoretical spectroscopic parameters of the six stable conformers of FA-DFM.

	I	II	III	IV	V	VI
A/MHz	8205	6006	12,804	6494	12,724	6330
B/MHz	1363	1526	1039	1411	1042	1422
C/MHz	1178	1364	967	1349	970	1361
P_{cc}/uÅ^2	1.68	22.41	1.63	30.68	1.86	31.95
$|\mu_a|$/D	1.1	0.2	2.5	0.02	2.2	0.8
$|\mu_b|$/D	0.6	0.1	1.0	0.1	2.1	0.0
$|\mu_c|$/D	0.0	1.2	0.0	1.0	0.0	2.0
D/cm^{-1}	2220	2201	1452	1419	1611	1584

3. Results and Discussion

3.1. Theoretical Results

Ab initio calculations provided six energy minima, whose shapes are shown in Fig. 1. One can note that, when the carboxyl —OH group plays as the proton donor, linking with one of the fluorine atoms of CH$_2$F$_2$, the resulted minima (isomer I and II) lie in the lowest energies. The global minimum (Conformer I) is characterized by a O—H···F and a bifurcated weak CH$_2$···O HBs. The two subunits in conformer II are held together with a O—H···F and a weak C—H···O HBs, which lies only 18 cm^{-1} higher in energy than the global minimum. When the —CH hydrogen in FA plays as a weak proton donor and involved in the HB, the resulted conformers (III–VI) are all much higher in energy, which are not expected to be observed in the pulsed jet. The theoretical rotational constants, planar moment of inertia (P_{cc}) and dipole moment components
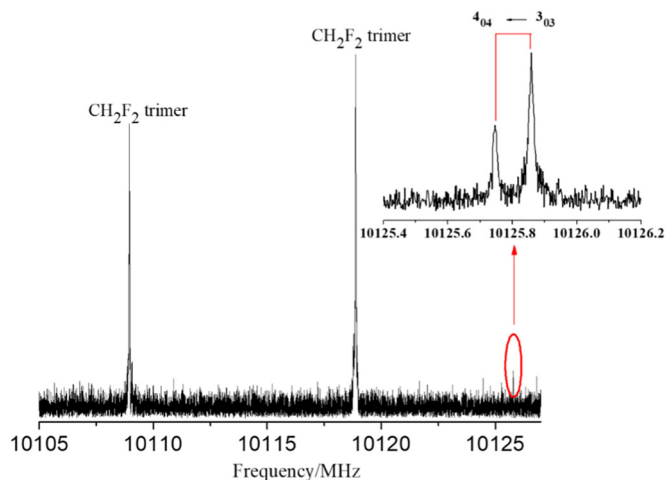

Fig. 2. Recorded $4_{04} \leftarrow 3_{03}$ transition of FA-DFM. Each of the transitions is doubled by the Doppler effect.