Rotational study on the van der Waals complex 1-chloro-1,1-difluoroethane-argon

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ABSTRACT

The rotational spectrum of the van der Waals complex formed between 1-chloro-1,1-difluoroethane and argon has been investigated by using a pulsed jet Fourier transform microwave spectrometer. Only one set of rotational transitions belonging to the lowest energy conformer has been observed and assigned, although theoretical calculations suggest six stable conformers that might be observed. The observed conformer, according to the experimental evidence from two isotopologues (^{35}Cl and ^{37}Cl), adopts a configuration in which the argon atom is located, close to the —CF_2Cl top, between the CCF and CCCl planes (the dihedral angle $\angle ArCCCl$ is 65.2°). The distance between argon atom and the center of mass of CH_3CF_2Cl is 3.949(2) Å. The dissociation energy, with pseudo diatomic approximation, is evaluated to be 2.4 kJ mol^{-1}.

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1. Introduction

Pulsed jet Fourier transform microwave (FTMW) spectroscopy has proved itself to be particularly suitable to characterize the van der Waals interaction between rare gas (RG) atoms and organic molecules: they are stable species in a supersonic jet. In general, complexes with aromatic molecules are relatively rigid, this is the case for pyridine-RG (RG = He, Ne, Ar, Kr and Xe) [1–5] and benzene-RG (RG = Ne, Ar, Kr and Xe) [6–9]. The RG atom is firmly located at one side of the ring and van der Waals motions do not generate any observable tunneling fine structure of rotational transitions. On the other hand for open chain molecules, the resulting complexes such as dimethyl ether-RG (RG = Ne, Ar, Kr and Xe) [10–13] often display rotational transitions with tunneling splittings, which are useful to quantify the inversion barriers to large amplitude motions (LAM) of RG atoms.

Considerable attention has been drawn to the freon-bearing complexes to decode different kinds of noncovalent intermolecular interactions [14–17]. Particularly, the enormous variety in the different species of freons allow us getting insight into how the number of halogen atoms and the carbon skeleton presented in freons affect the topologies of intermolecular interactions and internal dynamics. For van der Waals complexes, in going from CH_2F_2-RG [17–19] to CH_2FCl-RG [20–22] (RG = Ar, Kr and Xe), a considerable decrease of the inversion splittings has been observed: 193.74, 79.19 and 39.32 MHz *versus* 2.92, 0.63 and 0.14 MHz for complexes of Ar, Kr, and Xe, respectively. For CH_2Cl_2, the inversion splittings becomes only 6.89 MHz for CH_2Cl_2-Ne [23], and

even not observable for CH_2Cl_2-Ar [24]. Apart from these asymmetric freons, the complexes of symmetric freons CHF_3 [25] and CF_3Cl [26] with Ar, in which Ar is almost T-shaped with respect to the C-H/Cl bond, usually display spectra of asymmetric tops, without observable tunneling splittings.

Scarce data are available for the van der Waals complexes formed between ethane halides and RG atoms. CH_3CHF_2 can be considered as arising from replacing a hydrogen atom in CH_2F_2 by a methyl group. The free jet absorption millimeter-wave spectroscopic investigation suggests Ar to eclipse one of the methyl hydrogens in the symmetry less geometry of the complex and close to the —CHF_2 group. Doublets of rotational transitions due to a tunneling motion of Ar between two equivalent positions have also been observed [27]. Herein, the rotational spectrum of the van der Waals complex between 1-chloro-1,1-difluoroethane (HFC-142b, CH_3CF_2Cl) and Ar has been studied by using the technique of pulsed jet FTMW spectroscopy. The results are reported below.

2. Experimental

Rotational spectra of CH_3CF_2Cl-Ar were measured using the highly integrated pulsed jet FTMW spectrometer [28] (of COBRA-type [29]) built at Chongqing University, covering 2.0–20.0 GHz [30].

Molecular clusters were generated in a supersonic expansion, under conditions optimized for the formation of the CH_3CF_2Cl-Ar complex. About 2% CH_3CF_2Cl (commercial sample, purity>97%) in argon at a stagnation pressure of ~0.4 MPa expanded through a solenoid valve (Parker-General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity. The spectral line positions were determined after

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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 spectral 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.

3. Results and Discussion

3.1. Theoretical Calculations

Full geometry optimizations of the CH_3CF_2Cl-Ar complex were performed at the MP2/aug-cc-pVTZ level of theory [31] employing of the Gaussian 09 suite [32]. Harmonic frequency calculations at the same level confirmed six conformers to be real minima, whose shapes and relative zero-point corrected energies (ΔE_0) are given in Fig. 1.

At the global minimum (conformer I), Ar is located, close to -CF_2Cl, between the CCF and CCCl planes. The other five conformers all have Ar located in the symmetric plane of CH_3CF_2Cl, lying slightly higher in energy. The calculated spectroscopic parameters useful for the assignment of rotational spectrum as well as the dissociation energies are summarized in Table 1.

3.2. Rotational Spectra

Preliminary trial searches were aimed at detecting μ_c-type R-branch transitions of conformer I, which were expected to be the most intense ones. The transition $6_{24} \leftarrow 5_{14}$ was first identified, as shown in Fig. 2, based on their ^{35}Cl ($I = 3/2$) nuclear quadrupole hyperfine structure (hfs) pattern. From 31 measured μ_c-type transitions, including the Q-branch, rotational constants were well determined. Then, the assignment was extended to some strong μ_b- and weaker μ_a- type transitions. No splitting due to the tunneling motion of Ar between two equivalent minima was observed. Compared to the case of CH_3CHF_2-Ar [27], replacing the H atom with Cl in -CHF_2 seems to dramatically affect the internal dynamics of Ar. Further conclusion rationalizing the anomeric effect of freons on the tunneling motion of Ar cannot be drawn, since too few examples of van der Waals complexes of ethane halides with rare gas atoms are available so far.
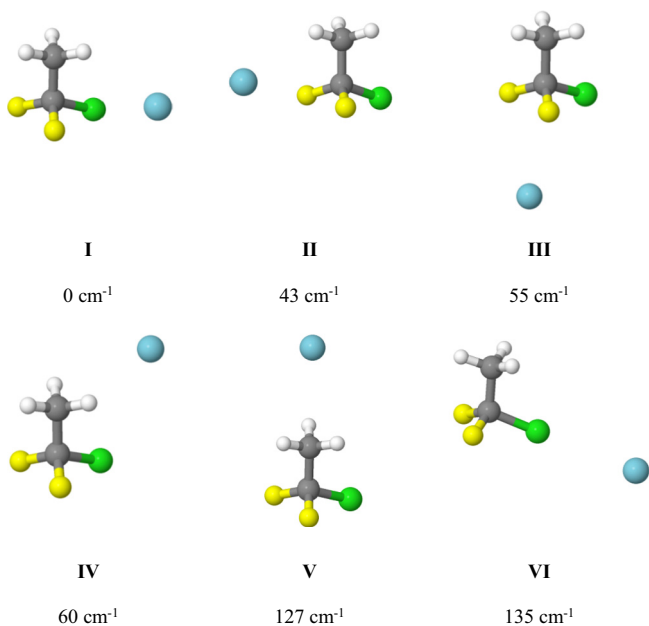
Table 1
MP2/aug-cc-pVTZ spectroscopic parameters of the six plausible conformers of CH_3CF_2Cl-Ar.

	I	II	III	IV	V	VI
E_D/kJ mol^{-1}	4.0	3.5	3.4	3.3	2.9	2.8
A/MHz	3212	5113	3268	3533	3506	5243
B/MHz	977	780	1031	791	563	589
C/MHz	879	772	915	733	532	586
μ_a/D	0.6	0.3	2.2	1.5	−2.2	0.6
μ_b/D	−0.8	2.1	−0.4	−1.6	0.3	2.1
μ_c/D	1.8	0	0	0	0	0
χ_{aa}/MHz	29.24	−62.53	31.26	10.90	12.24	−66.31
$(\chi_{bb}-\chi_{cc})$/MHz	−96.47	−2.70	−96.34	−75.93	−77.48	1.18

Towards the lower frequency range side of each observed transition, a weaker set of transitions were observed, belonging to the ^{37}Cl isotopologue. The intensities of these transitions were about 1/3 of those of the parent ^{35}Cl species, consistent with the relative natural abundance of the two isotopes.

All the measured frequencies (available in the Supplementary material) were fitted with Pickett's SPFIT program [33] by direct diagonalization of the Hamiltonian consisting of Watson's "S" reduced semirigid-rotor Hamiltonian [34] in the I^r representation, augmented by the hyperfine contribution:

$$H = H_R + H_{CD} + H_Q \tag{1}$$

where H_R represents the rigid-rotor Hamiltonian, the centrifugal distortion contributions are included by H_{CD}, while H_Q is the operator associated with the nuclear quadrupole interaction of ^{35}Cl (or ^{37}Cl) with the overall rotation. The obtained spectroscopic constants are reported in Table 2.

After a careful search, no lines belonging to the other five conformers could be identified, despite the very small energy differences according to the theoretical results. This is likely due to the conformational relaxation to the most stable conformer upon supersonic expansion. Such relaxation takes place easily when the interconversion barrier is smaller than $2kT$ [35], where T is the temperature before supersonic expansion.

3.3. Conformational Assignment

The experimental values of rotational and quadrupole coupling constants in Table 2 are close to those of conformers I and III in Table 1. Aiding the conformational assignment, the planar moments of inertia $P_{gg} = \Sigma_i m_i g_i^2$ ($g = a$, b and c) supply information on the mass distributions along principal axes of the complex. The corresponding planar moments of inertia from experimental and theoretical rotational constants for conformer I and III are summarized in Table 3, which provide
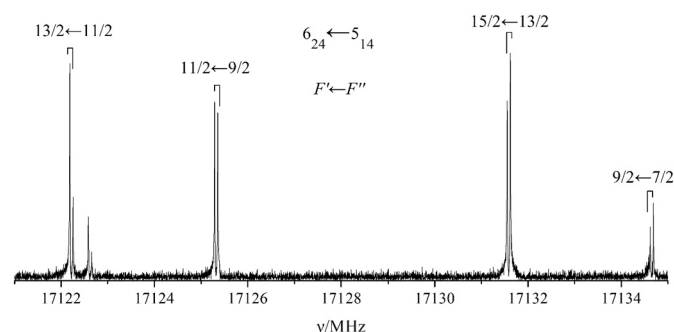

Fig. 1. MP2/aug-cc-pVTZ shapes of CH_3CF_2Cl-Ar and their relative zero-point corrected energies. The absolute energy $E_0 = -1264.022144$ E$_h$.

I — 0 cm^{-1} · II — 43 cm^{-1} · III — 55 cm^{-1} · IV — 60 cm^{-1} · V — 127 cm^{-1} · VI — 135 cm^{-1}

Fig. 2. The $6_{24} \leftarrow 5_{14}$ rotational transition of $CH_3CF_2{}^{35}Cl$-Ar. The Doppler doubling, indicated by the bracket for every component of this transition, is an instrumental artifact.