



Research paper

Rotational spectrum of the pentafluoroethane-argon van der Waals complex

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ARTICLE INFO

Article history:

Received 22 September 2017

In final form 9 November 2017

Available online 11 November 2017

Keywords:

Van der Waals interaction

Rotational spectroscopy

Pulsed jet

Freons

ABSTRACT

Rotational spectra of the van der Waals complex of pentafluoroethane-argon and its two ^{13}C isotopes in nature abundance have been investigated by pulsed jet Fourier transform microwave spectroscopy. The Ar atom lies in the symmetry plane of pentafluoroethane, with a distance of 4.05 Å from its center of mass. The dissociation energy has been estimated to be 3.2 kJ/mol with a pseudodiatom approximation.

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1. Introduction

Cryogenic environment can lead a quite large fraction of molecules exist as stable complexes bound primarily with a rare gas (RG) atom by weak van der Waals interaction. Such complexes are amenable to be investigated, especially with high resolution rotational spectroscopic technique, which has revealed itself to be particularly effective in study such anisotropic intermolecular potentials.

Normally with aromatic molecules, the RG atom firmly links to one side of the ring and van der Waals motions do not generate observable splittings of rotational transitions. This is the case, for instance, of complexes of pyridine-RG (RG = He, Ne, Ar, Kr and Xe) [1–7] and benzene-RG (RG = Ne, Ar, Kr and Xe) [8–11]. Instead, when a RG atom is linked to an open chain molecule, such as dimethyl ether-RG (RG = Ne, Ar, Kr and Xe) [12–18], the resulted complexes often display rotational transitions with tunneling splittings. These splittings are useful to quantify the barriers to the inversions of RG atoms.

Freons are often taken as prototypes for studying different kinds of noncovalent intermolecular interactions, such as the van der Waals interaction, weak hydrogen bond [19], halogen bond [20,21], lone pair $\cdots\pi$ interaction [22,23], etc.. It has been noted that the number of fluorine and chlorine atoms as well as the length of carbon skeleton in freons can dramatically affect the topologies of intermolecular interactions and the internal dynamics. For van der Waals interactions, in going from CH_2F_2 to CH_2FCl , i.e. replacing one fluorine with a chlorine atom, a considerable decrease of the

inversion splittings has been observed: 193.74, 79.19 and 39.32 MHz for CH_2F_2 -Ar [24], CH_2F_2 -Kr [25] and CH_2F_2 -Xe [26], whilst 2.92, 0.63 and 0.14 MHz for CH_2FCl -Ar [27], CH_2FCl -Kr [28] and CH_2FCl -Xe [29], respectively. For CH_2Cl_2 , the inversion splittings become smaller: only 6.89 MHz for CH_2Cl_2 -Ne [30], and even not observable for CH_2Cl_2 -Ar [31]. Apart from these asymmetric freons, the complexes of symmetric freons CHF_3 [32] and CF_3Cl [33] with Ar usually display spectra of an asymmetric top, in which the Ar atom almost T-shaped with respect to the C–H/Cl bond.

If considering the carbon skeleton, scarce data are available for the van der Waals complex formed between an ethane halide and a RG atom. CH_3CHF_2 can be taken as one of hydrogen atom replaced by methyl group. In such way, the molecular symmetry is reduced. The Ar atom has been found, according to the free jet absorption millimeter-wave spectroscopic investigation, to *eclipse* one of the methyl hydrogens in the symmetryless geometry of the complex and close to the $-\text{CHF}_2$ group [34]. Doubling due to a tunneling motion of Ar between two equivalent positions has also been observed. How an additional CF_3 group, instead of $-\text{CH}_3$, would affect the spectrum feature of the van der Waals complex captured our interest. Herein, the rotational spectrum of the van der Waals complex formed between pentafluoroethane (HFC-125 , CF_3CHF_2) and Ar has been studied by using the pulsed jet Fourier transform microwave (FTMW) spectroscopic technique. The results are reported below.

2. Experimental

Rotational spectra were measured by using a highly integrated pulsed jet FTMW spectrometer (coaxially oriented beam-resonator

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arrangement, COBRA-type [35]) at Chongqing University covering 2.0–20.0 GHz [36].

A mixture of 1.5% CF_3CHF_2 (commercial sample) in Ar was expanded at the pressure of 0.3 MPa through the solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity. Each rotational line is split into two components due to the Doppler effect. The rest frequencies were 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. Theoretical calculations

In order to have a reliable starting conformation, we first ran some theoretical calculations. DFT and *ab initio* methods with different basis sets were performed for the full geometry optimizations and harmonic frequency calculations by using the Gaussian09 program package [37]. The shapes of six plausible conformers are reported in Table 1. Different levels of theory obtained different results: MP2/6-311++G(2df,2pd), MP2/6-311++G(3df,3pd) and MP2/aug-cc-pVTZ suggest that conformer **VI** with a small value of imaginary frequency not to be a real minimum. MP2/6-311++G(d,p) gives an energy order quite different from others. The details of the theoretical results are summarized in the Supplementary Materials. We finally choose the M06-2X/aug-cc-pVTZ results to be used through this paper since it has the best agreement with the experimental values among all the levels of theory we performed.

The relative zero-point corrected energies (ΔE_0), rotational constants (A , B and C), dipole moment components (μ_a , μ_b and μ_c) and dissociation energies (E_D) of all six conformers are listed in Table 1. In the global minimum (**I**), Ar is located in its symmetry plane of CF_3CHF_2 and on the same side of hydrogen atom. When Ar is slightly out of the symmetry plane (Conformer **II**), the energy is just 1 cm^{-1} higher than **I**. Both conformers **III** and **IV** have Ar along the C–C bond, which are a bit higher in energy. Conformer **V** and **VI** with Ar on the opposite side of hydrogen atom lie 39 and 79 cm^{-1} higher in energy with respect to conformer **I**. Taking the dipole moment components into account, all six conformers are plausible to be observed in the pulsed jet.

4. Rotational spectrum

Following predictions from the theoretical results, the preliminary search was covered the frequency region where the

μ_a – R type rotational transitions with $J:5 \leftarrow 4$ of all six conformers would fall. Only one set of transitions has been measured, as shown in Fig. 1 for a part of the spectrum with $J:5 \leftarrow 4$, which has been assigned to conformer **I**. Then the measurements of μ_a – R type transitions have been extended to the J_{lower} from 4 to 12, with K_a up to 5, and to 24 weaker μ_b type transitions, from which the rotational constants A , B and C can be well determined. No μ_c type transition was observed, in accord with the zero value of this dipole moment component.

All the 103 measured line frequencies (available in Supplementary Materials) have been fitted by using the Pickett's SPFIT computer program [38] with the S reduction in the I' representation [39]. The obtained rotational and centrifugal distortion constants are reported in the first column of Table 2.

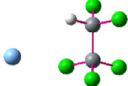
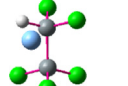
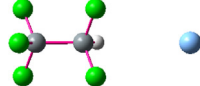
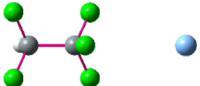
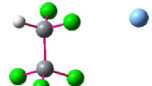
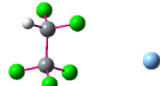
After a first structural adjustment, it was possible to assign spectra of two ^{13}C isotopologues of conformer **I** in natural abundance (about $\sim 1\%$). The obtained spectroscopic parameters are also summarized in Table 2. Due to much smaller number of lines (see in Supplementary Materials) that could be measured, the values of centrifugal distortion constants have been fixed at the corresponding ones of the parent species.

In spite of a careful search, no transition belonging to the other conformers was detected. This could be due to the conformational relaxation to the most stable conformer in the pulsed jet. It has been, indeed, shown that such kind of conformational relaxation takes place easily when the interconversion barrier is smaller than $2kT$ (where T is the absolute temperature prior to the expansion) [40]. $2kT$ is about 415 cm^{-1} at 298.15 K, the pre-expansion temperature in our case.

5. Conformation assignment

Concerning the conformational assignment, the comparison between the theoretical and experimental rotational constants did not give us a clear idea. It can only exclude the possibilities of conformers **III** and **IV**. The planar moments of inertia $P_{gg} = \sum_i m_i r_i^2$ ($g = a, b$ and c) supply information on the mass distributions along principal axes of this complex. In Table 3, the corresponding values of P_{gg} calculated from experimental and theoretical rotational constants of conformers **I**, **II**, **V** and **VI** are summarized, which provide evidence in favor of the conformational assignment to the form **I**. In addition, the fact that no μ_c type transitions were observed, confirmed the assignment to conformer **I**, accordingly to the zero value of μ_c dipole moment component.

Table 1
M06-2X/aug-cc-pVTZ shapes and spectroscopic parameters of the six more stable forms of the complex $\text{CF}_3\text{CHF}_2\text{-Ar}$.

			
$\Delta E_0/\text{cm}^{-1}$	0 ^a	1	8
$E_D/\text{kJ mol}^{-1}$	1.9	1.8	1.8
$A, B, C/\text{MHz}$	2105, 812, 740	2249, 824, 717	3311, 637, 616
$\mu_a, \mu_b, \mu_c/\text{D}$	–1.6, 0.7, 0.0	–1.2, 0.0, –1.1	0.9, 0.0, –1.3
			
$\Delta E_0/\text{cm}^{-1}$	23	39	79
$E_D/\text{kJ mol}^{-1}$	1.6	1.4	0.9
$A, B, C/\text{MHz}$	3564, 689, 656	2409, 828, 788	2193, 782, 692
$\mu_a, \mu_b, \mu_c/\text{D}$	0.5, 0.0, –1.5	–1.1, 1.2, 0.0	–1.2, 0.5, 1.0

^a The absolute energies is $E_0 = -1103.580180 E_h$.

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