Journal of Molecular Spectroscopy 280 (2012) 97–103

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Molecular structure of the argon-(*Z*)-1-chloro-2-fluoroethylene complex from chirped-pulse and narrow-band Fourier transform microwave spectroscopy

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ARTICLE INFO

Article history:
Available online 7 June 2012

Keywords:
Microwave spectroscopy
Molecular structure
Nuclear quadrupole coupling
Z-1-chloro-2-fluoroethylene
Argon complex
Chirped pulse

ABSTRACT

Broadband chirped pulse, Fourier transform microwave spectra in the 6–18 GHz region are obtained for the ^{35}Cl and ^{37}Cl isotopomers of the complex formed between argon and (*Z*)-1-chloro-2-fluoroethylene. Analysis of the spectra provides predictions of rotational transition frequencies for the two singly substituted ^{13}C isotopomers of Ar-^{35}ClHCCHF sufficient to narrow the search range required for observation in a more sensitive, narrow band cavity Fourier transform instrument. Only a non-planar structure with the argon atom maximizing the number of its contacts with preferably heavy atoms is consistent with the rotational constants for all four isotopomers, and no evidence of tunneling between the two equivalent minima on either side of the ethylene plane is found. Rotational transitions for four isotopomers of (*Z*)-1-chloro-2-fluoroethylene itself, appearing in the broadband spectrum, are analyzed to determine the complete chlorine nuclear quadrupole coupling tensor for this molecule, and when these are combined with the hyperfine constants determined for the complex with argon, the sign ambiguity of the measured off-diagonal tensor components is removed.

1. Introduction

To examine the effects that changes in electron distribution in a molecule have upon the manner in which it interacts with another molecule, we have been conducting a systematic investigation of a series of molecular complexes formed between protic acids and ethylenes substituted with fluorine and/or chlorine atoms. The complexes we have studied and reported thus far are 1,1-difluoroethylene-H*X* (*X* = F [1], CCH [2]), 1,1,2-trifluoroethylene-H*X* (*X* = F [3], Cl [4], CCH [5]), *trans*-1,2,-difluoroethylene-HF [6], and 1-chloro-1-fluoroethylene-H*X* (*X* = F [7], CCH [8]). Additional species currently under investigation include vinyl chloride-HF, (*E*)-1-chloro-2-fluoroethylene-HF, and (*E*)-1-chloro-1,2-difluoroethylene-HF. These complexes are planar, with the protic acid functioning as a donor in a hydrogen bond to a halogen on the substituted ethylene, and also forming a secondary interaction involving the nucleophilic portion of the acid and a hydrogen atom of the ethylene subunit. The number and the type of substituents on the ethylene subunit can have significant effects on the nature of intermolecular interactions, causing not only changes in the values of the geometric parameters, but also different modes of bonding (across or at one end of the double bond). Additionally, a competition between electrostatics and steric effects must be considered in interpreting the structures of these complexes.

While we were searching for the spectra of two additional complexes in this series, *cis*-1,2-difluoroethylene-HF and vinyl chloride-HF, we discovered many transitions that do not belong to these species complicating our attempts to obtain the desired spectra. These lines were attributed to Ar-*cis*-1,2-difluoroethylene [9] and Ar-vinyl chloride [10], formed via complexation with the argon carrier gas. In both cases, Ar lies on one side of the ethylene plane, and the complexes exhibit tunneling motion.

Indeed, the interactions between argon and three other fluorine-substituted ethylenes, vinyl fluoride, 1,1-difluoroethylene, and 1,1,2-trifluoroethylene, have been previously studied by the Legon group [11]. In each case, the complex is non-planar, and argon is located at a position that maximizes the number of its contacts with heavy atoms. Apparently, this position reflects a fine balance between attractive dispersion interactions with the heavy atoms and hard sphere repulsion. It is interesting to note that the distance between Ar and the F atoms that it contacts remains very constant, ranging between 3.45 and 3.55 Å. Additionally, as is the case with Ar-vinyl chloride, tunneling splitting is observed in the spectrum of Ar-vinyl fluoride.

In view of the richness of the structural and dynamical information that can be obtained by using argon as a structureless probe of the electronic distribution away from the molecular plane of a substituted ethylene, we turn to Ar-(*Z*)-1-chloro-2-fluoroethylene. Our results, reported below, will allow a comparison of how

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0022-2852/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jms.2012.05.008

changing a fluorine atom in *cis*-1,2-difluoroethylene to chlorine will affect the interaction of the substituted ethylene with argon. During our search for the complex, we have also obtained the spectra of four isotopomers of the (*Z*)-1-chloro-2-fluoroethylene monomer in the 6–18 GHz region, complementing the previous 15–25 GHz [12] and 26.5–40 GHz [13] studies of the ^{35}Cl and ^{37}Cl isotopomers and the 50–150 GHz study of the two ^{13}C-containing isotopomers [14]. Our work allows us to determine more precisely the chlorine quadrupole coupling constants in these isotopomers.

2. *Ab initio* calculations for the argon complex

The interaction potential between Ar and (*Z*)-1-chloro-2-fluoroethylene is determined using *ab initio* calculations at the MP2/6-311++G(2d,2p) level performed with Gaussian 09 [15]. The structure of the ethylene subunit is fixed at its ground-state, experimental configuration [16], and the coordinate system employed to locate the position of argon is shown in Fig. 1. The origin is placed at the center of the C=C bond, with the plane of the molecule defining the *xz* plane. The positive *x* axis points towards the halogen atoms and the positive *z* axis points along the C=C double bond towards the fluorine atom. The position of argon is specified using spherical polar coordinates: *R*, the length of the vector from the origin to the Ar atom, and θ and ϕ, the polar and azimuthal angles of the vector. Initially a relaxed potential scan, shown in Fig. 2, was performed in which the polar angle, θ, was scanned in 10° steps from 0° to 180° while both *R* and ϕ were allowed to vary. Three minima were found in this manner, near $\theta = 10°$, 80°, and 160°, and additional points obtained in the vicinity of each. An analogous scan with ϕ stepped in 10° increments and *R* and θ allowed to vary confirmed these results and provided no additional information.

Optimized geometries were obtained for the three minima found in the relaxed potential scans, corresponding to three distinct structures of Ar-(*Z*)-1-chloro-2-fluoroethylene. The polar coordinates of the argon position, the relative energies, and the rotational constants of these structures are listed in Table 1 and displayed in Fig. 3 with chemically relevant geometric parameters. The two higher energy structures (Fig. 3a and b) are both planar: each with Ar at one end of the double bond. Argon interacts with H, F, and C-2 (the distance between Ar and C-2 is 3.806 Å) in isomer (a), but with H, Cl, and C-1 (the distance between Ar and C-1 is 3.912 Å) in isomer (b). The non-planar, global minimum structure, isomer (c), shows argon interacting with a greater number of heavy atoms, as would be expected from the conclusions of Kisiel et al. [11]: F, Cl, C-1, and C-2 (Ar—C-1: 3.813 Å and Ar—C-2: 3.658 Å). The two planar isomers, (a) and (b), are 131.9 cm^{-1} and 74.7 cm^{-1}, respectively, higher in energy than the non-planar species and should not be observable under our molecular beam conditions. We therefore expect to see only isomer (c). The predicted dipole moment components for this isomer are $\mu_a = 0.38$ D, $\mu_b = 0.75$ D, and $\mu_c = 2.06$ D.

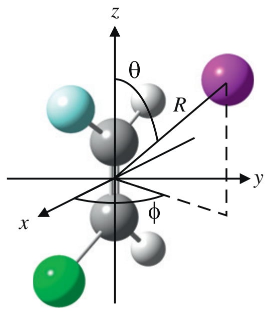

Fig. 1. The coordinate system used to define the position of Ar with respect to the (*Z*)-1-chloro-2-fluoroethylene molecule. The origin is the center of the C=C bond with the plane of the molecule defining the *xz* plane. *R* is the distance of Ar from the origin and θ and ϕ are respectively the polar and azimuthal angle of *R*. The carbon atoms are dark gray, hydrogen atoms are light gray, the fluorine atom is light blue, the chlorine atom is green, and the argon atom is purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

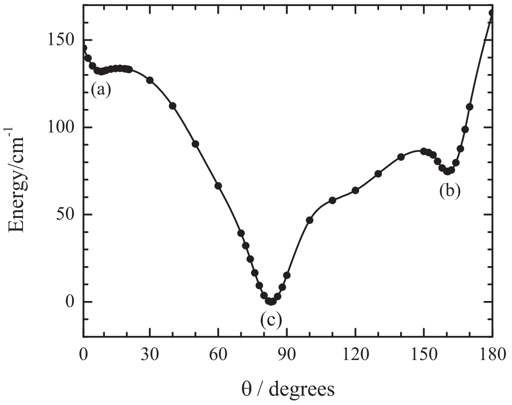

Fig. 2. A relaxed potential scan for Ar-(*Z*)-1-chloro-2-fluoroethylene in which *R* and ϕ are optimized and θ is varied in 10° steps, calculated at the MP2/6-311++G(2d, 2p) level. Additional points are obtained in the vicinity of the three minima for which structures are shown in Fig. 3.

Table 1
Polar coordinates of the positions of Ar, relative energies and rotational constants of three isomers of Ar-(*Z*)-1-chloro-2-fluoroethylene (shown in Fig. 3) calculated using Gaussian 09 at the MP2/6-311++G(2d,2p) level.

	Isomer (*a*)	Isomer (*b*)	Isomer (*c*)
Relative energy (cm^{-1})	131.9	74.7	0
R (Å)	4.454	4.526	3.678
θ (°)	8.6	160.5	83.1
ϕ (°)	180.1	180.0	65.8
A (MHz)	16114	6338	3231
B (MHz)	626	788	1396
C (MHz)	603	701	1099

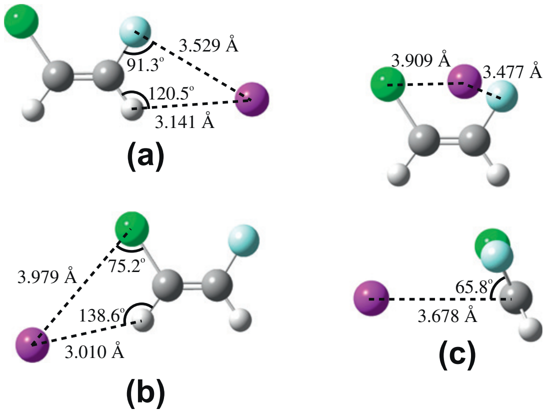

Fig. 3. Optimized structures corresponding to the three minima found in the relaxed potential scan for Ar-(*Z*)-1-chloro-2-fluoroethylene showing chemically relevant geometric parameters. Isomers (a) and (b) are planar, and isomer (c) for which two views are shown is non-planar. Atom–atom distances and bond angles are given as indicated for isomers (a), (b), and the top view of isomer (c). In the bottom view of this latter structure, the values of *R* and ϕ, as defined in Fig. 1 are shown. The carbon atoms are dark gray, hydrogen atoms are light gray, the fluorine atom is light blue, the chlorine atom is green, and the argon atom is purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)