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The microwave spectra and molecular structures of 2-chloro-1,1-difluoroethylene and its complex with the argon atom

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ABSTRACT

The microwave spectra of six isotopologues each of 2-chloro-1,1-difluoroethylene and its argon complex are obtained in the 5.6–20.5 GHz region using a combination of broadband chirped pulse and Balle–Flygare cavity Fourier transform microwave techniques. The structure of the halogen substituted ethylene has been determined using a combination of theory and experiment. Argon is found to form a nonplanar complex with this haloethylene, locating in the ClCCF cavity, which maximizes its interactions with the heavy atoms in the ethylene subunit. A combined analysis of the chlorine quadrupole coupling constants of the monomer and of the complex allows the sign of the only nonzero off-diagonal component of the quadrupole coupling tensor for the monomer to be determined; thus, the complete tensor for the monomer has been derived.

1. Introduction

The investigation of complexes formed between halogen-substituted ethylenes and protic acids has so far produced a wealth of information regarding the nature of intermolecular interactions that take place in the plane of each ethylene subunit [1–4] (Ref. [1] summarizes the structural parameters of 9 fluoroethylene-protic acid complexes). As we increase our understanding of the electronic distribution in the ethylene plane through these studies, we concurrently turn to argon to probe the electron density away from the plane to obtain a more complete description of the entire molecule.

Unlike the protic acid-haloethylene complexes, argon-haloethylene complexes are non-planar. Those formed by argon with vinyl fluoride, 1,1-difluoroethylene, and 1,1,2-trifluoroethylene have been studied by the Legon group [5]. Of these three species, Ar-vinyl fluoride exhibits tunneling splitting in the rotational spectrum. A similar splitting is also observed for Ar-vinyl chloride [6], and work is currently underway to unravel the motion that is involved. In the Ar-vinyl chloride complex, both *ab initio* theory and experiment point towards two possible nonplanar structures, with argon binding either in the ClCH cavity or in the ClCCH cavity. Interestingly, when a second fluorine atom is added to vinyl fluoride or to vinyl chloride in the position *cis* to the original halogen, the internal dynamics of the resulting argon complexes are different. Ar locates in the FCCF cavity of *cis*-1,2-difluoroethylene and interconversion tunneling motion is once again detected [7], but the motion is quenched in Ar-(*Z*)-1-chloro-2-fluoroethylene where argon binds in the ClCCF cavity [8]. The mode of binding of these complexes shows argon maximizes its contacts with preferably heavy atoms, consistent with the suggestion of Kisiel et al. [5]. Here we focus our work on a system where yet another fluorine atom is present, Ar-2-chloro-1,1-difluoroethylene.

Before we can gain insight into the interactions between Ar and 2-chloro-1,1-difluoroethylene, however, we need to know the structure of the 2-chloro-1,1-difluoroethylene monomer. The microwave spectra of two isotopologues, $CF_2CH^{35}Cl$ and $CF_2CH^{37}Cl$, have been previously studied by Jenkins and Sugden [9] in the 19–25 GHz region and by Leal et al. in the 12–225 GHz region [10]. Additionally, to determine the off-diagonal element of the ^{35}Cl quadrupole coupling tensor, Stone and Flygare measured 8 rotational transitions of the $CF_2CH^{35}Cl$ isotopologue in the 9.9–24.1 GHz region [11]. These studies, however, are insufficient to determine the structure of 2-chloro-1,1-difluoroethylene. Thus, we undertake a microwave study of six isotopologues and derive an average structure for the substituted ethylene, which we report below. The monomeric structure enables us to determine the structure of Ar-2-chloro-1,1-difluoroethylene and compare it with

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Ar-(*Z*)-1-chloro-2-fluoroethylene to examine the effect of the second fluorine. Comparison with Ar-1,1,2-trifluoroethylene provides the opportunity to explore the effect of changing a fluorine substituent to chlorine.

2. *Ab initio* calculations for the argon complex

The interaction potential between Ar and 2-chloro-1,1-difluoroethylene is determined using a*b initio* calculations at the MP2/6-311G++(2d,2p) level performed with GAUSSIAN 09 [12]. The structure of the ethylene subunit is fixed at its ground-state, experimental configuration, as reported in Section 4.2.1 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 ethylene subunit defining the *xz* plane. The positive *z* axis points along the C=C double bond towards the fluorine atoms, with the positive *x* axis perpendicular to it and pointing towards the Cl atom side of the molecule. 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. A relaxed potential scan 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. Two minima were located, and θ was scanned in 2.5° steps in the vicinity of each (Fig. 2). A scan with ϕ stepped in 10° increments for each value of θ confirms these results and provides no additional information.

The minimum near $\theta = 160°$ is 102 cm^{-1} higher in energy than the global minimum; the corresponding structure is not expected to be observable under our experimental conditions, and thus, it is not considered further. The structure corresponding to the global minimum is optimized to give $R = 3.6140$ Å, $\theta = 80.86°$, and $\phi = 69.97°$ (Fig. 3) and the rotational constants, *A*, *B*, *C*, are respectively, 1924, 1291, and 891 MHz. Argon is in the cavity formed by the carbon atoms and the F and Cl located *cis* to each other. The predicted dipole moment components are $\mu_a = 0.34$ D, $\mu_b = 0.01$ D, and $\mu_c = 1.10$ D.

3. Experiment

Spectra for six isotopologues each of the 2-chloro-1,1-difluoroethylene monomer and Ar-2-chloro-1,1-difluoroethylene complex

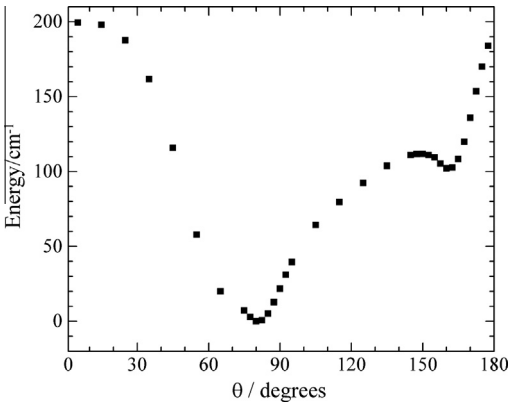

Fig. 2. A relaxed potential scan for Ar-2-chloro-1,1-difluoroethylene in which *R* and ϕ are optimized and θ is varied in 10° steps, calculated at the MP2/6-311G++(2d, 2p) level. Additional points are obtained in the vicinity of two minima.

are collected. The species are the most abundant isotopologues, those singly substituted with ^{37}Cl, ^{13}C, and D, and the doubly substituted species containing D and ^{37}Cl. All nondeuterated species are studied in natural abundance and the deuterated species using a sample of CF_2CDCl synthesized by Prof. Norman Craig of Oberlin College. Because 4 isotopologues of the 2-chloro-1,1-difluoroethylene monomer and the ^{35}Cl and ^{37}Cl isotopologues of Ar-2-chloro-1,1-difluoroethylene are present in relatively large quantities, their spectra are collected using a broadband chirped pulse Fourier transform microwave (CP-FTMW) spectrometer operating in the 5.6–18.1 GHz region. For the rest of the species, because of low number density (Ar—$^{13}CF_2CH^{35}Cl$ and Ar—$CF_2^{13}CH^{35}Cl$) or additional, small hyperfine splitting ($CF_2CD^{35}Cl$, $CF_2CD^{37}Cl$, and their argon complexes), spectra are collected using a narrow band Balle–Flygare cavity Fourier transform microwave spectrometer in the 6.0–20.5 GHz region.

Both the chirped pulse [8,13] and the Balle–Flygare spectrometers [8,14] have been previously described. The only new feature is that a second pulsed nozzle has been added to the chirped pulse spectrometer, which effectively doubles the signal-to-noise ratio

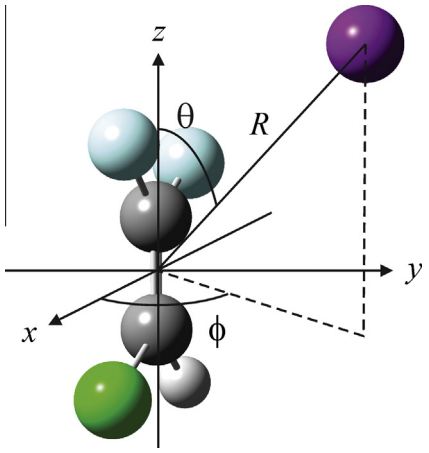

Fig. 1. The coordinate system used to define the position of Ar with respect to the 2-chloro-1,1-difluoroethylene molecule. The origin is the center of the C=C bond with the plane of the molecule defining the *xz* plane. *R* is the distance of Ar from the origin and θ and ϕ are, respectively, the polar and azimuthal angle of *R*. The carbon atoms are dark gray, the hydrogen atom is light gray, fluorine atoms are 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.)

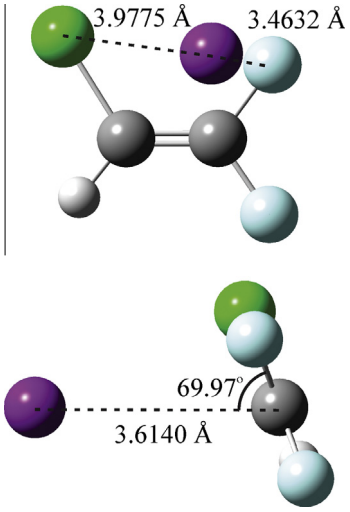

Fig. 3. Two views of the optimized structure corresponding to the global minimum found in the relaxed potential scan for Ar-2-chloro-1,1-difluoroethylene showing chemically relevant geometric parameters. Ar—Cl and Ar—F distances are given in the top view. In the bottom view, the values of *R* and ϕ, as defined in Fig. 1 are shown. The carbon atoms are dark gray, the hydrogen atom is light gray, fluorine atoms are 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.)