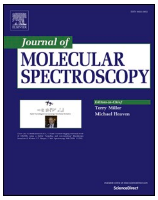
Journal of Molecular Spectroscopy 381 (2021) 111520

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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



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

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A R T I C L E I N F O

Keywords:
Intermolecular interactions
Microwave spectroscopy
Rotational spectroscopy
Molecular structure

A B S T R A C T

The microwave spectra of four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene, and additionally, the spectra of two isotopologues of the complex formed between argon and (*E*)-1-chloro-1,2-difluoroethylene are obtained in the 5.6–18.1 GHz region using broadband chirped pulse Fourier transform microwave spectroscopy. The argon atom is determined to occupy a position out of the symmetry plane of the haloethylene where it can interact most strongly with the fluorine atom and the chlorine atom located geminal to each other as well as the π electron density at the end of the double bond on carbon atom C-1. As in the previously studied argon-2-chloro-1,1-difluoroethylene complex, the argon atom interacts most strongly with a fluorine atom and the chlorine atom regardless of whether they are located geminal or *cis* to each other.

1. Introduction

Intermolecular interactions between two molecules necessarily result from a delicate and complicated balance between attractive and repulsive forces. In particular, our studies of haloethylene-protic acid complexes have shown that the most stable structure of each species results from a balance between electrostatic and steric requirements [1]. These complexes are typically planar, with both the electropositive and the electronegative portions of the acid (HF, HCl, or HCCH) interacting with a halogen-hydrogen pair located either *cis* to each other or connected to the same C atom in the haloethylene subunit. These acids, therefore, are effective in seeking out favorable binding sites in the haloethylene plane. To have a more complete understanding of haloethylenes, especially how they may participate in intermolecular interactions in a nonplanar fashion, we need to probe the electron density distribution and steric environment away from the molecular plane. As noted by the Legon group in the study of the argon complexes of vinyl fluoride, 1,1-difluoroethylene, and 1,1,2-trifluoroethylene [2], argon prefers to be in a position that maximizes its contact with heavy atoms. This can be better achieved if argon binds to a haloethylene away from its plane. Furthermore, this location can inform us of the site in the haloethylene that can provide the strongest dispersion interactions.

When interacting with dihaloethylenes where the two halogen atoms are located *cis* to each other, such as *cis*-1,2-difluoroethylene and (*Z*)-1-chloro-2-fluoroethylene, argon is able to interact with all the heavy atoms by residing in the XCCY cavity away from the haloethylene plane (X and Y represent the two relevant halogen atoms). Tunneling motion is observed for Ar-*cis*-1,2-difluoroethylene [3], but is quenched when one of the F atoms is replaced by Cl [4]. The binding motif remains unchanged for the two Ar-trihaloethylene complexes, Ar-1,1,2-trifluoroethylene [2] and Ar-2-chloro-1,1-difluoroethylene [5]; namely, argon is in the FCCF cavity and the FCCCl cavity, respectively. A comparison between these complexes and their dihaloethylene counterparts just described shows that the F atom not participating in the intermolecular interaction pulls Ar closer to the C-1 side (which are connected to two F atoms) of the cavity, weakening the interaction that Ar forms with C-2 and the halogen connected to it. The findings for Ar-2-chloro-1,1-difluoroethylene begs the question: what if the Cl atom is located on C-1 instead of C-2? That is, what is the structure of Ar-(*E*)-1-chloro-1,2-difluoroethylene? Would Ar bind in the FCCF cavity because it could interact with four heavy atoms, or would the large number of electrons of Cl draw Ar to the FCCl cavity? The work reported here serves to address these questions.

The haloethylene under consideration here, (*E*)-1-chloro-1,2-difluoroethylene, was previously studied in the 11–48 GHz region of the microwave spectrum by Ogata [6]. The rotational transitions for each of the most abundant and ^{37}Cl-containing isotopologues were fitted to three rotational constants, centrifugal distortion constants in the

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https://doi.org/10.1016/j.jms.2021.111520
Received 3 July 2021; Received in revised form 10 August 2021; Accepted 16 August 2021

notation of Kivelson and Wilson (τ's) [7,8], and the diagonal components of the chlorine nuclear quadrupole coupling constants. Before embarking on the exploration of the Ar-(*E*)-1-chloro-1,2-difluoroethylene complex, it is helpful for us to first characterize the haloethylene monomer in our spectral range. We report here the spectral data for 4 isotopologues. With spectral resolution higher than that of the previous work, we are able to determine the spectroscopic constants more precisely, and we also express the centrifugal distortion constants in the now more commonly used Watson notation [9]. Furthermore, we are better able to establish the structure of the molecule, which we will use to determine the structure of the complex with argon.

2. *Ab initio* calculations

Before assigning the spectra for the isotopologues of (*E*)-1-chloro-1,2-difluoroethylene and its argon dimer, we use *ab initio* calculation at the MP2/6–311++G(2d,2p) level with GAUSSIAN 16 [10] to locate the potential minima for these species. The labeling scheme for the haloethylene is shown in Fig. 1. To clearly distinguish the atoms without confusion, we use C_a and C_b to represent C-1 and C-2, respectively, and the F atoms attached to C-1 and C-2 are accordingly F_a and F_b. The optimized structural parameters for the haloethylene are listed in Table 1, together with the rotational constants and the nonzero components of the chlorine nuclear quadupole coupling tensor for the most abundant isotopologue. (The positions of the atoms in the principal coordinate system are available as supplementary material.) The predicted structure is planar, and as such, it has no dipole moment along the *c* inertial axis. The magnitudes of μ_a and μ_b are 0.72 and 1.53 D (1 D = 3.33564×10^{-30}C·m), respectively. We thus expect stronger *b* type transitions in the rotational spectrum than *a* type transitions.

Although the spectroscopic constants from Ogata's previous work [6] would have been the more appropriate starting point, we did not initially have access to that manuscript. Thus, we used the predicted spectroscopic constants to identify and assign the rotational spectra for four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene and determine its structure, as detailed below. With the experimental determined planar structure defining the *x-z* plane and the center of the C=C bond as the origin (Fig. 2), the position of Ar can be described by the spherical polar coordinates *R*, θ, and ϕ, indicating, respectively, its distance from the origin and the polar and azimuthal angles of *R*. To probe the interaction energies between the two subunits, we carry out a relaxed scan where θ varies from 5° to 175° and ϕ from 0° to 180°, both in 10° increments while allowing *R* to optimize. Because of the planar symmetry of the haloethylene, it is unnecessary to sample ϕ from 180° to 360°. The resulting potential energy contour diagram is shown in Fig. 2. There is only one significant energy minimum, which upon optimization gives the corresponding position of $R = 3.67$ Å (1 Å = 10^{-10} m), θ = 71.00°, ϕ = 80.90°. (The positions of the atoms in the principal coordinate system are available as supplementary material.) This places Ar in the FCCl cavity, as shown in Fig. 3. The distance between Ar and each atom in the haloethylene, together with the rotational constants and the chlorine nuclear quadrupole coupling constants of the most abundant isotopologue of the complex are listed in Table 2. The magnitudes of the dipole moment components along the *a*, *b*, and *c* inertial axes are, respectively, 0.39, 0.78, and 1.46 D. We therefore expect *c* type transitions to be the strongest and *a* type transitions to be the weakest.

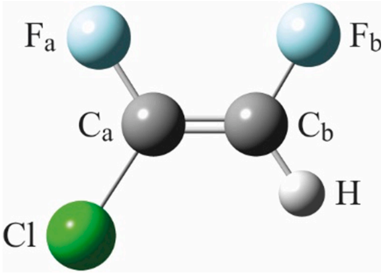

Fig. 1. The atom labeling scheme for (*E*)-1-chloro-1,2-difluoroethylene. Atom colors: C, dark gray; H, light gray; F, light blue; Cl, green.

Table 1
Structural parameters for the global minimum configuration of (*E*)-1-chloro-1,2-difluoroethylene obtained using *ab initio* calculations and from a structure fit to the moments of inertia of four isotopologues of the molecule. Also listed are the rotational constants and nuclear quadrupole constants for the most abundant isotopologue from the theoretical prediction and determined by experiment.

	Theory	Experiment[a]
C_a–C_b/Å	1.3297	1.3329(51)
C_a–F_a/Å	1.3290	1.3290
C_a–Cl/Å	1.7160	1.6989(30)
C_b–F_b/Å	1.3415	1.3415
C_b–H/Å	1.0741	1.0741
$\angle F_aC_aC_b$/°	122.1349	121.86(25)[b]
$\angle ClC_aC_b$/°	123.1120	123.221(81)
$\angle F_bC_bC_a$/°	120.5234	120.25(25)[b]
$\angle HC_bC_a$/°	123.4539	123.4539
A/MHz	9087.5	9126.19775(29)
B/MHz	2438.6	2461.051639(83)
C/MHz	1922.7	1936.697418(77)
χ_{aa}/MHz	−64.2	−67.8147(17)
χ_{bb}/MHz	28.6	29.9713(21)
χ_{cc}/MHz	35.6	37.8434(21)
$\lvert\chi_{ab}\rvert$/MHz	26.3	28.62(17)

[a] 1σ standard deviations in the parameters are given in parentheses. The parameters without uncertainties are fixed to the *ab initio* values.

[b] The angles $F_aC_aC_b$ and $F_bC_bC_a$ are fitted with their difference fixed to the the value suggested by the *ab initio* result; specifically, the former being greater than the latter by 1.61°.

3. Experiment

Preliminary rotational spectra of (*E*)-1-chloro-1,2-difluoroethylene and its argon complex were obtained over several years utilizing both the narrow band, Balle-Flygare Fourier transform microwave (FTMW) spectrometer [4,11] and the broadband chirped pulse instrument [4,5,12] in our laboratories and several sets of experimental conditions. However, the best quality data were obtained on the broadband instrument during a search for the complex of (*E*)-1-chloro-1,2-difluoroethylene with hydrogen fluoride using a sample of 1% of an (*E/Z*) mixture of the ethylene (SynQuest Laboratories, lot Q186-135) and 1% HF in argon at a backing pressure of 1 atm, and all the data used in the analysis that follows came from those spectra. For these final spectra, after expanding the gas mixture through two pulsed valves, each with a 0.8 mm diameter nozzle, the sample is polarized using a chirped microwave polarization pulse of 4 μs duration and 20–25 W of power. Three separately acquired segments of 4.0 or 4.5 GHz bandwidth are obtained by mixing the output of an arbitrary waveform generator with carrier frequencies of 10.6, 14.6, or 18.6 GHz (generated using phase locked dielectric resonator oscillators) and isolating the lower sideband. The resulting free induction decay (FID) is digitized at 50 Gs s^{-1} for 20 μs beginning 0.5 μs after the end of the excitation pulse. Ten FIDs are collected during each 800 μs opening of the pulsed valves, which operate at 4 Hz. 1,575,000–1,701,000 FIDs are averaged for each segment, and as described previously [4], the average is Fourier transformed to give a frequency domain spectrum with a resolution element of 11.92 kHz and typical line widths (FWHM) of 125 kHz. This allows us to assign line centers with an estimated measurement uncertainty of 5–10 kHz. Some of the earlier spectra obtained at higher resolution (~1–2 kHz) with the narrow band instrument showed evidence of magnetic hyperfine splitting, likely either a F–F spin–spin interaction or F spin-rotation interactions, but this was not apparent in the lower resolution spectra used in the final analysis.

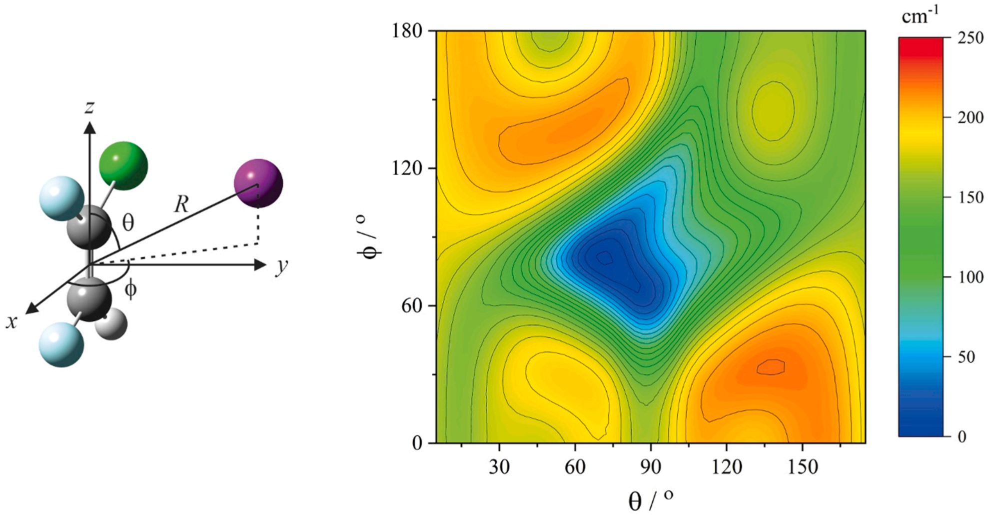

Fig. 2. Left: the coordinate system used to define the position of Ar with respect to (*E*)-1-chloro-1,2-difluoroethylene. The orgin is the center of the C=C bond, with the haloethylene lying in the *x*-*z* plane, and *R*, θ, and ϕ are the spherical polar coordinates of Ar. Right: a contour plot of the potential energy as a function of the angles with *R* optimized. Atom colors: C, dark gray; H, light gray; F, light blue; Cl, green; Ar, purple.

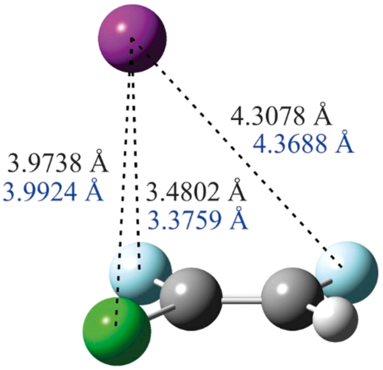

Fig. 3. The structure of Ar-(*E*)-1-chloro-1,2-difluoroethylene. The theoretical bond lengths (black) are on top whereas the experimental values (blue) are in the bottom. Atom colors: C, dark gray; H, light gray; F, light blue; Cl, green; Ar, purple.

Table 2
The distances between Ar and the atoms in (*E*)-1-chloro-1,2-difluoroethylene obtained using *ab initio* calculations and from a structure fit to the moments of inertia of two isotopologues of the complex. Also listed are the rotational constants and nuclear quadrupole constants for the most abundant isotopologue from theoretical predication and determined by experiment.

	Theory	Experiment[a]
Ar–C$_a$/Å	3.5111	3.51664(50)
Ar–C$_b$/Å	3.9388	4.0213(40)
Ar–F$_a$/Å	3.4802	3.3759(21)
Ar–F$_b$/Å	4.3078	4.3688(89)
Ar–Cl/Å	3.9738	3.9924(73)
Ar–H/Å	4.4561	4.5967(33)
A/MHz	1968.5	1994.00782(72)
B/MHz	1228.7	1218.15549(24)
C/MHz	893.9	883.86951(27)
χ_{aa}/MHz	34.85	37.1417(62)
χ_{bb}/MHz	−63.61	−67.8212(62)
χ_{cc}/MHz	28.76	30.6795(64)
$\lvert\chi_{bc}\rvert$/MHz	24.79	26.91(32)
$\lvert\chi_{ab}\rvert$/MHz	3.34	–
$\lvert\chi_{ac}\rvert$/MHz	0.79	–

[a] 1σ standard deviations in the parameters are given in parentheses.

4. Results

4.1. Spectral analysis

4.1.1. (E)-1-chloro-1,2-difluoroethylene

For the most abundant and ^{37}Cl containing isotopologues of (*E*)-1-chloro-1,2-difluoroethylene, we have observed, respectively, 66 and 54 rotational transitions (both *a* and *b* type) consisting of 419 and 335 chlorine nuclear quadrupole hyperfine components. As predicted by *ab initio* calculations, the *b* type transitions are typically stronger than those of *a* type. In the previous work, Ogata observed 22 and 16 rotational transitions for the same two species, most of which consist of the 4 strongest quadrupole hyperfine components for each transition. Nine of the 66 rotational transitions we observed for the most abundant isotopologue were also observed in the previous work [6], with three rotational transitions in common for the ^{37}Cl species. Although Ogata [6] was able to sample transitions in a higher frequency region, we sample higher *J* and K_a values. Namely, for (*E*)-CF^{35}ClCHF, $J = 0$–16, $K_a = 0$–5 here versus $J = 0$–8, $K_a = 0$–3 reported by Ogata, and for (*E*)-CF^{37}ClCHF, $J = 0$–14, $K_a = 0$–4 here versus $J = 0$–10, $K_a = 0$–4 reported by Ogata. Fig. 4a shows an 60 MHz portion of the spectrum from our work illustrating the $1_{10} - 1_{01}$ transitions of these species. Additionally, we have also observed 31 *a* and *b* type transitions for each of the naturally occurring ^{13}C isotopologues, albeit sampling smaller *J* and K_a ranges (0–8 and 0–2, respectively).

The spectrum for each of the 4 isotopologues of (*E*)-1-chloro-1,2-difluoroethylene is assigned with the aid of Kisiel's AABS package [13,14] and analyzed using the Watson *A*-reduced Hamiltonian [9,15] in the I^r representation, with the inclusion of the chlorine nuclear quadrupole coupling interaction, using Pickett's nonlinear SPFIT program [16]. The rotational constants, 5 quartic centrifugal distortion constants, and the nonzero elements of the chlorine nuclear quadrupole coupling tensor are determined and listed in Table 3. With an asymmetry parameter, κ, approximately equal to −0.85 (see below), the molecule is sufficiently far removed from the symmetric top limit for satisfactory use of the *A* reduction. Because the diagonal elements of the quadrupole coupling tensor satisfy the Laplace condition ($\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$), only two of them can be determined, and we choose them to be χ_{aa} and $\chi_{bb} - \chi_{cc}$. Additionally, because the molecule is planar (as shown by the value of the inertial defect discussed below in Section 4.2.1), the only nonzero off-diagonal component of the coupling tensor is χ_{ab}. The rms deviation of each fit is less than 5.5 kHz,

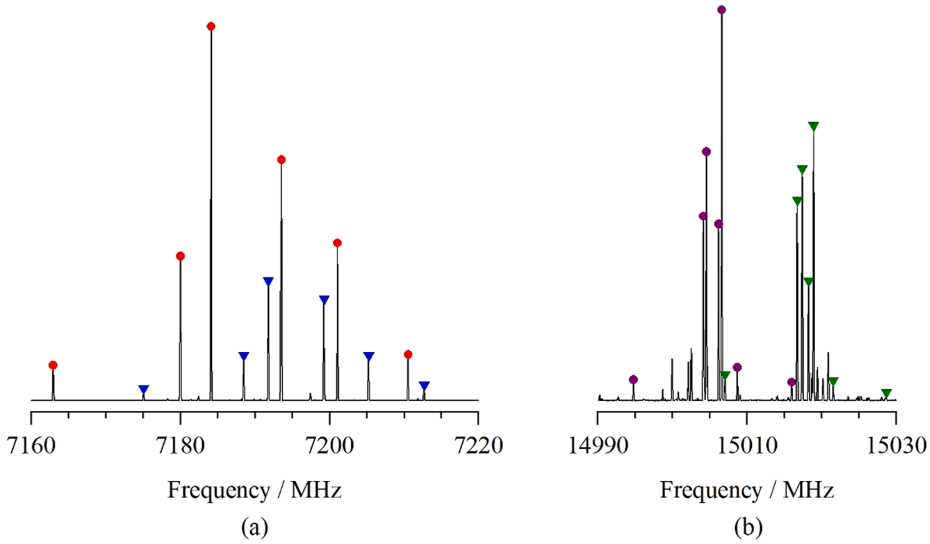

Fig. 4. (a) The nuclear quadrupole hyperfine components for the $1_{10} - 1_{01}$ transitions for (*E*)-CF^{35}ClCHF (red circles) and (*E*)-CF^{37}ClCHF (blue triangles). (b) The nuclear quadrupole hyperfine components for the *c*-type asymmetry doublet $4_{40} - 3_{30}$ (purple circles)/$4_{41} - 3_{31}$ (green triangles) for Ar-(*E*)-CF^{35}ClCHF. The unmarked transitions (all but one of them) are also of Ar-(*E*)-CF^{35}ClCHF and assigned as $9_{27} - 8_{35}$, $7_{44} - 6_{43}$, and the *b*-type asymmetry doublet $4_{41} - 3_{30}/4_{40} - 3_{31}$.

Table 3
Spectroscopic constants (in MHz, unless otherwise noted) for four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene.[a]

	(*E*)-CF^{35}ClCHF	(*E*)-CF^{37}ClCHF	(*E*)-^{13}CF^{35}ClCHF	(*E*)-CF^{35}Cl^{13}CHF
A	9126.19775(29)	9091.71546(41)	9124.5264(11)	9034.6940(10)
B	2461.051639(83)	2397.56052(11)	2461.20714(26)	2449.85653(21)
C	1936.697418(77)	1895.656934(97)	1936.72083(38)	1925.64078(36)
$\Delta_J/10^{-3}$	0.22961(70)	0.21582(93)	0.2239(61)	0.2231(38)
$\Delta_{JK}/10^{-3}$	2.3536(71)	2.1862(97)	2.325(43)	2.327(49)
$\Delta_K/10^{-3}$	19.4289(72)	19.716(15)	19.35(26)	17.87(32)
$\delta_J/10^{-3}$	0.05105(23)	0.04800(49)	0.0500(15)	0.0508(14)
$\delta_K/10^{-3}$	1.7022(95)	1.591(20)	1.794(96)	1.496(95)
χ_{aa}[b]	−67.8147(17)	−53.7564(21)	−67.8203(35)	−67.5377(34)
χ_{bb}[b]	29.9713(21)	23.9315(25)	29.9780(40)	29.6944(38)
χ_{cc}[b]	37.8434(21)	29.8249(25)	37.8423(39)	37.8433(37)
$\lvert\chi_{ab}\rvert$	28.62(17)	21.19(47)	27.75(46)	28.95(24)
No. of rotational transitions	66	54	31	31
No. of *a* type	19	17	12	12
No. of *b* type	47	37	19	19
No. of hyperfine components	419	335	153	163
J range	0–16	0–14	0–8	0–8
K_a range	0–5	0–4	0–2	0–2
rms/kHz	4.77	5.32	5.49	5.37

[a] 1σ standard deviations in the parameters are given in parentheses.

[b] The nuclear quadrupole coupling constants of chlorine are fitted as $1.5\chi_{aa}$ and $(\chi_{bb}-\chi_{cc})/4$, and the Laplace condition is used to calculate the individual hyperfine constants.

commensurate with the resolution of the chirped pulse spectrometer. Tables of observed and calculated transition frequencies with assignments for all 4 isotopologues are in supplementary material. It is satisfying that the rotational constants and diagonal nuclear quadrupole coupling constants for the most abundant and ^{37}Cl isotopologues determined here and those by Ogata [6] agree to within 3σ reported by that work. (Small differences in the rotational constants are to be expected as a result of the different reductions of the centrifugal distortion Hamiltonian used, and Ogata did not report values of χ_{ab} for these species.)

4.1.2. Ar-(E)-1-chloro-1,2-difluoroethylene

We have observed 201 and 111 rotational transitions for the most abundant and ^{37}Cl-containing isotopologues, respectively, of Ar-(*E*)-1-chloro-1,2-difluoroethylene representing 796 and 428 chlorine nuclear quadrupole hyperfine components. The *J* and K_a ranges are fairly large; specifically, $J = 1$ to at least 9 and $K_a = 0$ to at least 5. As predicted theoretically, *c* type transitions are generally the most intense. Fig. 4b shows a 40 MHz region in which two transitions due to the most abundant species are observed.

As with the monomer, the spectra of each of the two isotopologues of Ar-(*E*)-1-chloro-1,2-difluoroethylene are analyzed using AABS [13,14], the Watson *A*-reduced Hamiltonian [9,15] in the I^r representation with the inclusion of the chlorine nuclear quadrupole coupling interaction, and Pickett's nonlinear SPFIT program [16]. This time, to satisfactorily fit the transitions for the most abundant isotopologue, we have to include centrifugal distortion constants of orders higher than quartic; specifically, 11 sextic and octic constants are determined. This is not too surprising upon comparing the values of the quartic centrifugal distortion constants for this species (Table 4) with those for two other argon-chlorofluoroethylenes, Ar-CH^{35}ClCF$_2$ [5] and Ar-(*Z*)- CH^{35}ClCHF [4]. While the values of Δ_J and δ_J for all three species are of similar magnitude, the magnitudes of Δ_{JK}, Δ_K and δ_K for Ar-(*E*)-CF^{35}ClCHF are 6–14 times greater than the corresponding values for the other two

Table 4
Spectroscopic constants (in MHz, unless otherwise noted) for two isotopologues of Ar-(*E*)-1-chloro-1,2-difluoroethylene.[a]

	Ar−(*E*)-CF^{35}ClCHF	Ar−(*E*)-CF^{37}ClCHF
A	1994.00782(72)	1949.6964(12)
B	1218.15549(24)	1211.39554(36)
C	883.86951(27)	872.11146(40)
$\Delta_J/10^{-3}$	4.7544(24)	4.2382(39)
$\Delta_{JK}/10^{-3}$	212.236(42)	199.801(82)
$\Delta_K/10^{-3}$	−207.550(58)	−193.379(93)
$\delta_J/10^{-3}$	1.6502(17)	1.3903(30)
$\delta_K/10^{-3}$	122.766(52)	114.350(98)
$\Phi_{JK}/10^{-3}$	0.2054(15)	0.1596(14)
$\Phi_{KJ}/10^{-3}$	−0.2120(45)	−0.0977(62)
$\Phi_K/10^{-3}$	0.0132(37)	[0.0132][b]
$\phi_{JK}/10^{-3}$	0.1060(11)	0.0813(15)
$\phi_K/10^{-3}$	0.4716(50)	0.4725(83)
$L_{JJK}/10^{-6}$	−0.127(14)	[−0.127][b]
$L_{JK}/10^{-6}$	−3.82(11)	−3.665(59)
$L_{KKJ}/10^{-6}$	9.28(24)	[9.28][b]
$L_K/10^{-6}$	−5.48(15)	−7.118(78)
$l_{KJ}/10^{-6}$	−2.350(67)	−2.204(88)
$l_K/10^{-6}$	−1.63(21)	−2.55(17)
χ_{aa}[c]	37.1417(62)	29.2475(78)
χ_{bb}[c]	−67.8212(62)	−53.6691(75)
χ_{cc}[c]	30.6795(64)	24.4217(75)
$\lvert\chi_{bc}\rvert$	26.91(32)	21.12(45)
$\chi_{bb-cc,JK}/10^{-3}$	0.171(11)	0.114(27)
No. of rotational transitions	201	111
No. of *a* type	45	30
No. of *b* type	71	36
No. of *c* type	85	45
No. of hyperfine components	796	428
J range	1–10	1–9
K_a range	0–7	0–5
rms/kHz	12.77	10.71

[a] 1σ standard deviations in the parameters are given in parentheses.
[b] Fixed at the value appropriate to the most abundant isotopologue.
[c] The nuclear quadrupole coupling constants of chlorine are fitted as $1.5\chi_{aa}$ and $(\chi_{bb}-\chi_{cc})/4$, and the Laplace condition is used to calculate the individual hyperfine constants.

species, signifying that the intermolecular bond in Ar-(*E*)-CF^{35}ClCHF is much “floppier”. The argon complex is even further removed from the symmetric top limit ($\kappa \approx -0.4$) than the parent haloethylene, suggesting that the large number of centrifugal distortion constants is not a consequence of using the *A* reduction. Indeed, test fits utilizing the *S* reduction [9,17] required additional higher order constants and resulted in a slightly larger rms deviation. An additional effect of the floppy bond is that the effective value of $\chi_{bb}-\chi_{cc}$, $(\chi_{bb}-\chi_{cc})_{\text{eff}}$, has a dependence on *J* and *K*; namely, $(\chi_{bb}-\chi_{cc})_{\text{eff}} = (\chi_{bb}-\chi_{cc}) + (\chi_{bb}-\chi_{cc})_{JK}J(J+1)K^2$, although no such dependence is observed for χ_{aa}. We are also able to determine one off diagonal element of the chlorine quadrupole coupling tensor, χ_{bc}. The rotational constants, centrifugal distortion constants, and chlorine nuclear quadrupole hyperfine components are listed in Table 4. For the ^{37}Cl-containing species, only 8 sextic and octic centrifugal distortion constants can be determined. The rms deviation of each fit is less than 13 kHz; although this is greater than that for each of the isotopologue for (*E*)-1-chloro-1,2-difluoroethylene, this value is still within one-tenth of a line width. Tables of observed and calculated transition frequencies with assignments for the two isotopologues of the argon complex are in supplementary material.

4.2. *Structure determination*

4.2.1. *(E)-1-chloro-1,2-difluoroethylene*

For each of the four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene, the value of the asymmetry parameter is approximately −0.85, and the inertial defect is 0.22 μÅ^2, indicating that this is a planar asymmetic top molecule with small in-plane vibrational motions. Because only two of three moments of inertia are independent for a planar species, we fit the average structure of the molecule to 8 moments of inertia of the isotopologues using Kisiel’s STRFIT program [18]. We tried using all three possible sets of two moments of inertia in each isotopologue to fit various combinations of geometric parameters. In the end, using I_a and I_c from each isotopologue allows the parameters to be uncorrelated. In addition to fitting the $C_a{=}C_b$ and C_a–Cl bond lengths and the ClC_aC_b angle, we are able to restrict the difference between the $F_aC_aC_b$ and $F_bC_bC_a$ angles to its *ab initio* value, and thus fitting these two angles as a unit. These geometric parameters are reported in Table 1, and the rms deviation is 0.0076 μÅ^2. The coordinates of each atom in the principal axis system of the most abundant isotopologue of the haloethylene are available as supplementary material.

The isotopic data also allow us to determine the Kraitchman substitution coordinates for (*E*)-1-chloro-1,2-difluoroethylene. Because each of the three minor isotopologues contains a single substitution in the most abundant species, we are able to determine the Kraitchman substitution coordinates [19] of the Cl and C atoms (Table 5). For C_b and Cl, the agreement between the coordinates derived from a Kraitchman analysis and the average structure (also in Table 5) is excellent, differing no more than 0.002 Å. Because a Kraitchman analysis ignores differences in zero point motions upon isotopic substitution, the fact that C_a lies almost on the *b* axis [the magnitude of its *a* coordinate is 0.0304(29) Å in the average structure] renders its substitution coordinate ill-determined and thus it appears nonphysical; its *b* substitution and average coordinates do agree to within 1.5 times the uncertainty of the former.

4.2.2. *Ar-(E)-1-chloro-1,2-difluoroethylene*

The two isotopologues of Ar-(*E*)-1-chloro-1,2-difluoroethylene are more asymmetric than their haloethylene monomer, with asymmetry parameters of −0.40 and −0.37 for the most abundant and ^{37}Cl-containing isotopologue, respectively. Using the atomic coordinates of (*E*)-1-chloro-1,2-difluoroethylene derived above, we determine 4 possible locations of Ar in Ar-(*E*)-1-chloro-1,2-difluoroethylene that can equally well reproduce the experimentally determined rotational constants of the most abundant isotopologue of the argon complex. These positions are all 3.352 Å from the haloethylene plane, with each set of *a* and *b* coordinates differing from each other only in their signs, and Fig. 5 shows their projections onto the *a*-*b* inertial plane of (*E*)-CF^{35}ClCHF. The isotopic dependence of the experimental rotational constants is used to determine which of four possibilities represents the actual geometry. Moments of inertia are calculated for the four locations of the argon atom indicated in Fig. 5 but using the mass of ^{37}Cl. Upon this substitution of ^{37}Cl for ^{35}Cl, the resulting rotational constants for each possible location of Ar are listed in Table 6 for Ar-(*E*)-CF^{37}ClCHF, and location i is seen to reproduce the experimental rotational constants of this isotopologue the best, to within 0.3 MHz. Other locations of Ar give at least

Table 5
The coordinates of the carbon and chlorine atoms in (*E*)-1-chloro-1,2-difluoroethylene determined from a Kraitchman analysis and a structure fit of four isotopologues.

	a/Å	*b*/Å
(i) Substitution coordinates[a,b]		
C_a	nonphysical	−0.101(15)
C_b	0.9702(15)	0.7538(20)
Cl	−1.66572(90)	0.3335(45)
(ii) From structure fit		
C_a	−0.0304(29)	−0.12361(58)
C_b	0.9719(21)	0.7551(40)
Cl	−1.6672(15)	0.3315(22)

[a] Costain errors[24] in the parameters are given in parentheses.
[b] Although only the absolute values of the substitution coordinates can be determined from the Kraitchman analysis, the relative signs for the *a* and *b* coordinates are assigned using physically reasonable atomic distances.

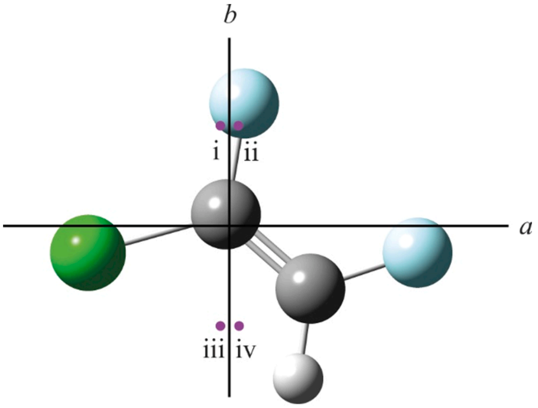

Fig. 5. Four possible locations (i – iv) of Ar, marked in purple circles and projected onto the *a*-*b* inertial plane of haloethylene, that reproduce the experimentally determined rotational constants of the ^{35}Cl isotopologue of Ar-(*E*)-1-chloro-1,2-difluoroethylene. Only location (i) also provides satisfactory agreement with the experimentally determined rotational constants of the ^{37}Cl isotopologue. Atom colors: C, dark gray; H, light gray; F, light blue; Cl, green.

Table 6
The rotational constants of Ar−(*E*)-CF^{37}ClCHF for each possible location of Ar shown in Fig. 5. Each location is expressed in the inertial axis system of (*E*)-CF^{35}ClCHF, where $c = 3.352$ Å for all locations.

Ar location	a/Å	b/Å	A/MHz	B/MHz	C/MHz
i	−0.106	1.185	1949.4	1211.3	871.8
ii	0.106	1.185	1954.1	1208.3	871.2
iii	−0.106	−1.185	1949.0	1213.7	873.4
iv	0.106	−1.185	1952.0	1211.4	872.7

one rotational constant that differs from the corresponding experimental value by more than 2 MHz. Indeed, this is consistent with the theoretical finding that Ar is located in the FCCl cavity.

Assuming the structure of the haloethylene does not change upon complexation, the average structure of Ar-(*E*)-1-chloro-1,2-difluoroethylene is then determined by fitting the Ar–C$_a$ distance, the ArC$_a$C$_b$ angle, and the ArC$_a$C$_b$F$_b$ dihedral angle to the 3 moments of inertia of each isotopologues. The fit has an rms error of 0.0802 μ Å^2. The distance between Ar and each atom in the haloethylene is calculated using Kisiel's EVAL program [13,20] and listed in Table 2. The coordinates of each atom in the principal axis system of the most abundant isotopologue of the complex are available as supplementary material. Using the principal axis system of the haloethylene monomer given in Fig. 5, the position of argon is at $a = -0.1149$ Å, $b = 1.1811$ Å. The c coordinate signifies the distance between Ar and the haloethylene plane, and it is 3.3528 Å. These coordinates are very similar to those determined above using only the most abundant species, and because here they are derived from two isotopologues, they represent a better average position for Ar.

For completeness, we have also calculated the Kraitchman substitution coordinates for Cl: $|a| = 1.0222(15)$ Å, $|b| = 1.69326(89)$ Å, and $|c| = 0.3115(48)$ Å. A comparison with the Cl coordinates from the structure fit [$a = 1.0350(75)$ Å, $b = 1.7138(25)$ Å, and $c = 0.24304(45)$ Å] shows that the values of the a and b coordinates calculated from both methods agree well, to within 0.02 Å. The larger difference (0.07 Å) between the values of the c coordinate is a reflection of the zero point vibrational motion of the soft intermolecular bond with argon.

4.2.3. Chlorine nuclear quadrupole coupling constants

Aside from the sign of the χ_{ab} component, we have determined the complete chlorine nuclear quadrupole coupling tensor for each isotopologue of (*E*)-1-chloro-1,2-difluoroethylene. These experimental, average values agree well with theoretical, equilibrium values, as illustrated in Table 1 for the most abundant species. Diagonalization of the tensor for (*E*)-CF^{35}ClCHF gives the principal quadrupole coupling constants, which are, labeling in order of increasing magnitude, χ_{xx}, χ_{yy}, and χ_{zz}, respectively, 37.7309, and 37.8434, and −75.5741 MHz. Here, the x and z principal electric field gradient axes lie in the molecular plane while the y axis is the same as the inertial c axis, that is, perpendicular to the molecular plane. The z axis forms an angle of 15.17° with the a inertial axis, which is almost the same as the angle of 15.54° between the C–Cl bond and the a axis. Thus, the z axis lies practically along the C–Cl bond. The magnitude of the asymmetry parameter for the nuclear quadrupole coupling constants, $|\eta| = \left|\left(\chi_{xx} - \chi_{yy}\right)/\chi_{zz}\right|$, is 0.0015, indicating that the charge about the z electric field gradient axis deviates little from a cylindrical distribution.

Even though the sign of the χ_{ab} component for (*E*)-CF^{35}ClCHF cannot be determined from the rotational spectrum, and indeed depends on the directions chosen for the positive directions of the a and b axes, nevertheless, if there is no significant electric field gradient perturbation when the molecule is complexed with Ar, and given a specific choice of directions for the axes, the sign can be derived by realizing that the nuclear quadrupole coupling tensor for the haloethylene is related to that for its Ar complex by a simple rotation. This is the same as the rotation matrix that transforms the inertial axis system for (*E*)-CF^{35}ClCHF into that for Ar–(*E*)-CF^{35}ClCHF. By so doing, we find that a negative sign of the χ_{ab} component for the configuration of the monomer as drawn in Fig. 5 and with axes chosen to give the coordinates in the supplementary material can best reproduce the nuclear quadrupole components for the dimer. Specifically, the rotation gives, for Ar–(*E*)-CF^{35}ClCHF, the diagonal quadrupole coupling components of 37.7197, −69.0607, and 31.3410 MHz. These differ from the experimental values by 1.6%, 1.8%, and 2.2%, respectively. Additionally, it gives a positive sign for the χ_{bc} component for the complex with the configuration shown in Fig. 3 and with axes chosen to give the coordinates in the supplementary material. The signs of the off-digaonal components, χ_{ab} for the minor (*E*)-CFClCHF isotopologues and χ_{bc} for the minor Ar–(*E*)-CF^{37}ClCHF isotopologue are the same as the corresponding ones for the most abundant species.

5. Discussion

Our work is well guided by theory. The experimental rotational constants differ from the corresponding theoretical constants by no more than 0.9% for (*E*)-CF^{35}ClCHF and 1.3% for Ar–(*E*)-CF^{35}ClCHF. Nevertheless, these translate to differences of 14–39 MHz and 10–26 MHz, respectively (Tables 1 and 2). Without the broadband spectrometer, we would need to cover large search ranges to locate the rotational transitions. The nuclear quadrupole coupling constants are also well predicted; the corresponding experimental and theoretical values differ by no more than 8.1% for both species.

Because no additional naturally occurring isotopes of F exists, and we do not have available the deuterated (*E*)-1-chloro-1,2-difluoroethylene monomer, the H and F positions are fixed to *ab initio* values when we derive a structure for the molecule. The excellent agreements between experimental and theoretical rotational constants clearly extend to the corresponding structures. The experimental, average C$_a$–C$_b$ and C$_a$–Cl bond lengths agree with the theoretical, equilibrium ones to 0.003 Å and 0.017 Å, respectively, and the experimental and theoretical values of ∠ClC$_a$C$_b$ agree to 0.11° (Table 1). Using the experimental structure of the haloethylene, we have located the position of argon in Ar-(*E*)-1-chloro-1,2-difluoroethylene. The distance between Ar and each atom in the haloethylene determined experimentally agrees with its theoretical counterpart within 0.006–0.104 Å for the heavy atoms. The difference increases to 0.141 Å for the H atom.

Here, we examine the structural parameters for Ar-trihaloethylenes (Fig. 6a-c), their dihalo counterparts after the removal of a geminal halogen atom, leaving two halogen atoms *cis* to each other (Fig. 6d&e), and Ar-1,1-difluoroethylene (Fig. 6f), where the two F atoms are

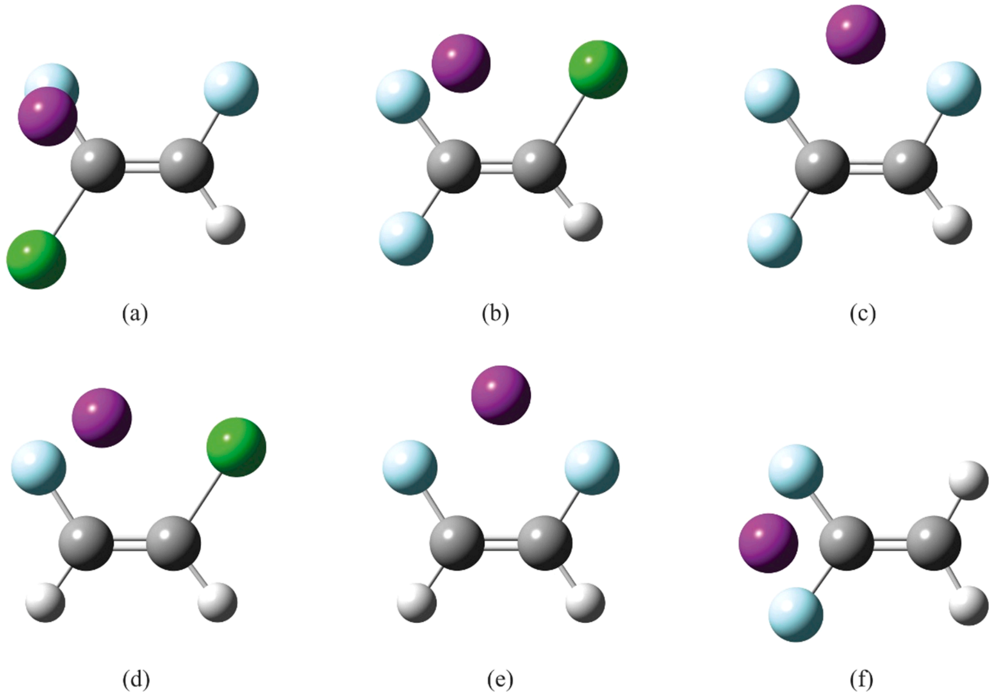

Fig. 6. The structure of six Ar-haloethylene complexes with the haloethylene planes lying on the page: (a) Ar-(*E*)-1-chloro-1,2-difluoroethylene (this work), (b) Ar-2-chloro-1,1-difluoroethylene [5], (c) Ar-1,1,2-trifluoroethylene [2], (d) Ar-(*Z*)-1-chloro-2-fluoroethylene [4], (e) Ar-*cis*-1,2-difluoroethylene [3], and (f) Ar-1,1-difluoroethylene [2]. Atom colors: C, dark gray; H, light gray; F, light blue; Cl, green; Ar, purple.

geminal. Although the trihaloethylenes offer two possible cavities, XCCY and XCY, for Ar to reside, the dihaloethylenes offer only one, either XCCY or XCY. For the argon complexes of (*Z*)-1-chloro-2-fluoroethylene [4] and *cis*-1,2-difluoroethylene [3] where Ar resides in the XCCY cavity, Ar interacts with each F atom with a length of 3.46–3.47 Å. Upon the addition of another F atom to these haloethylenes to give 2-chloro-1,1-difluoroethylene [5] and 1,1,2-trifluoroethylene [2], Ar still binds in the XCCY cavity, with the range of Ar–F interaction length expanding to 3.43–3.53 Å (Table 7), signifying that when Ar interacts simultaneously with two C atoms and at least one F atom, this is an optimal interaction length. The Ar–Cl interaction length is 3.85 Å in Ar-(*Z*)-1-chloro-2-fluoroethylene, which increases to 3.89 Å in Ar-2-chloro-1,1-difluoroethylene.

Table 7

The distances between argon and atoms forming the cavity in which it resides for 6 Ar-haloethylene complexes and their calculated binding energies. A similar table is available in Reference [5] for 4 of the species. Ar in each complex resides in a FCCY or FCY cavity, where Y represents the appropriate halogen.

	Ar–F/Å	Ar–C/Å	Ar–C/Å	Ar–Y/Å	Binding Energy[e]/kJ mol^{-1}
Ar–(*E*)-CFClCHF	3.3759 (21)	3.51664 (50)	–	3.9924 (73)	1.9
Ar–CF_2CHCl[a]	3.4348 (31)	3.6390 (14)	3.8264 (13)	3.8895 (34)	2.0
Ar–CF_2CHF[b]	3.4543	3.7097	3.7497	3.5262	1.5
Ar–(*Z*)-CHFCHCl[c]	3.4578 (25)	3.7567 (15)	3.9014 (15)	3.8458 (28)	1.9
Ar–*cis*-CHFCHF[d]	3.4732 (14)	3.7926 (16)	3.7926 (16)	3.4732 (14)	1.5
Ar–CF_2CH_2[b]	3.5525	3.5609	–	3.5525	1.4

[a] Reference [5].

[b] Reference [2].

[c] Reference [4].

[d] Reference [3].

[e] Calculated at the MP2/6–311++G(2d,2p) level of theory and corrected for basis set superposition error using the experimental average geometry as reported in the indicated reference.

The binding mode observed for Ar-(*E*)-1-chloro-1,2-difluoroethylene is different. Ar prefers the FCCl cavity to the FCCF cavity. In fact, this XCY interaction has been previously observed in Ar-1,1-difluoroethylene where Ar interacts with each F atom with a length of 3.55 Å [2]. This value is similar to the Ar–F interaction length of 3.43–3.53 Å mentioned earlier. In Ar-(*E*)-1-chloro-1,2-difluoroethylene, however, the Ar–F disance of 3.3759(21) Å is noticely shorter and is close to the sum of the van der Waals radii of Ar and F of 3.35 Å [21]. The Ar–Cl distance is 3.9924(73) Å, longer than those observed in Ar-(*Z*)-1-chloro-1,2-difluoroethylene and Ar-2-chloro-1,1-difluoroethylene by at least 0.1 Å. On the other hand, the Ar–C_a distance of 3.51664(50) Å is the shortest observed among the aforementioned complexes, which have Ar–C distances ranging from 3.64 to 3.90 Å when Ar is in the XCCY cavity but closer to that in Ar-1,1-difluoroethylene (3.56 Å). It therefore appears that by interacting with only 3 heavy atoms (F_a, C_a, Cl), argon can lengthen the interaction with Cl somewhat to achieve shorter interaction distances to the F and C atoms to maximize interaction energy. A comparsion between Ar-(*E*)-1-chloro-1,2-difluoroethylene and Ar-2-chloro-1,1-difluoroethylene shows that in the presence of two F and one Cl atoms in the haloethylene, the argon binding site depends on where the heavy Cl atom is. When it is located *cis* to a F atom, as in 2-chloro-1,1-difluoroethylene, argon resides in the FCCCl cavity. On the other hand, when Cl is geminal to a F atom, as in (*E*)-1-chloro-1,2-difluoroethylene, argon binds in the FCCl cavity. The interaction energy of Ar with C_b and F_b is apparently outweighed by that with the more polarizable Cl.

Indeed, the stronger binding to the Cl atom can be seen through a comparison of the binding energies of argon to each haloethylene. These have been calculated at the experimentally determined average geometry for each using the MP2/6–311++G(2d,2p) model chemistry in GAUSSIAN 16 [10] employed for all calculations here and corrected for basis set superposition error [22,23]. Although this level of theory cannot be expected to give quantitatively accurate values, that is not the point here, but rather to discern trends among the species. The results are presented in Table 7. All four argon complexes with ethylenes that contain only fluorine subsitutions give a result of 1.4–1.5 kJ mol^{-1}, the addition or substitution of a single chlorine atom increases the calculated binding energy by 0.5 kJ mol^{-1}.

6. Conclusion

The microwave spectra for two isotopologues (^{35}Cl and ^{37}Cl) of the gas-phase heterodimer formed between (*E*)-1-chloro-1,2-difluoroethylene and argon have been obtained and analyzed. Additionally, the spectra for four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene itself have been obtained in a different frequency range and at higher resolution than in earlier work [6], and have been analyzed using a modern and now commonly-used reduction of the centrifugal distortion Hamiltonian. The complete nuclear quadrupole coupling tensor for the (*E*)-1-chloro-1,2-difluoroethylene monomer has been determined, allowing the transformation into its principal axis system and shows that the electron charge distribution is very nearly cylindrical about the C–Cl bond.

The values of and the isotopic dependence of the rotational constants obtained from the analysis of the spectra of the two isotopologues of Ar-(*E*)-1-chloro-1,2-difluoroethylene show that the argon atom lies out of the plane of the haloethylene in what has been called the triatomic FCCl cavity. This differs from previously characterized argon-trihaloethylene species that had the argon in the four-atomic FCCF or FCCCl cavity where it could interact with two carbon atoms and two halogens. Indeed, quantum chemistry calculations indicate that binding to the FCCCl cavity is not a minimum on the argon-(*E*)-1-chloro-1,2-difluoroethylene interaction potential surface. Presumably the greater polarizability of the chlorine atom skews the balance of attractive forces away from the configuration predicted by the previous suggestion that argon binds in a manner to maximize its contacts with heavy atoms [2].

CRediT authorship contribution statement

Helen O. Leung: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Mark D. Marshall:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Aaron T. Bozzi:** Formal analysis, Investigation. **Jonah R. Horowitz:** Formal analysis, Investigation. **Andres C. Nino:** Formal analysis, Investigation. **Hannah K. Tandon:** Formal analysis, Investigation. **Leonard Yoon:** Formal analysis, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This material is based on work supported by the National Science Foundation under Grant No. CHE-1856637.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jms.2021.111520.

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