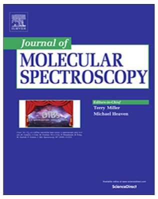
Journal of Molecular Spectroscopy 374 (2020) 111379

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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



The microwave spectra and molecular structures of (*E*)-1,3,3,3-tetrafluoropropene and its complex with the argon atom

Mark D. Marshall *, Helen O. Leung, Olivia Febles, Alexandra Gomez

Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, MA 01002-5000, United States

ARTICLE INFO

Article history:
Received 13 September 2020
Accepted 8 October 2020
Available online 15 October 2020

Keywords:
Intermolecular interactions
Microwave spectroscopy
Rotational spectroscopy
Molecular structure

ABSTRACT

The microwave spectra of four isotopologues of (*E*)-1,3,3,3-tetrafluoropropene, which has been proposed as a refrigerant alternative with a low global warming potential and also finds use as a foaming agent, and additionally the spectra of four isotopologues of the complex formed between argon and (*E*)-1,3,3,3-tetrafluoropropene are obtained in the 5.3–21.1 GHz region using a combination of broadband chirped pulse and Balle-Flygare cavity Fourier transform microwave spectroscopy. The argon atom is determined to occupy a position out of the symmetry plane of the tetrafluoropropene where it can interact most strongly with the in-plane fluorine atom of the fluoromethyl group and carbon atom C1. This contrasts to the previously studied argon-2,3,3,3-tetrafluoropropene complex where the argon atom interacts most strongly with an out-of-plane fluorine atom and that attached to the olefinic carbon.

1. Introduction

Through a systematic study of gaseous heterodimer complexes formed between simple protic acids (such as HF, HCl, and HCCH) and ethylenes substituted with 1–3 fluorine atoms, much information regarding the nature of interactions between these species has been revealed [1]. For the acid complexes of vinyl fluoride [2–4], 1,1-difluoroethylene [5–7], and *trans*-1,2-difluoroethylene [8,9], it has been observed that each of the three acids binds to an F, H pair across the C=C bond instead of a geminal F, H pair connected to the same C atom (this latter configuration is absent in 1,1-difluoroethylene). This binding mode is a result of favorable steric factors resulting from placing the acid across the double bond even though electrostatically the H atom geminal to an F atom, in contrast to the one located *cis* to the F atom, is more positive and can interact more strongly with the nucleophilic portion of the acid. For 1,1,2-trifluoroethylene, even though both *cis* and geminal F, H pairs are available, the three acids all bind to the geminal pair [10–12]. In these cases, the binding is driven by electrostatic factors: the acids interact with the most nucleophilic F atom in the ethylene subunit, which is geminal to the only H atom. As a result, the binding of the acid necessarily takes place at one end of the double bond. Finally, in the case of *cis*-1,2-difluoroethylene, only geminal F, H pairs are available. In fact, HCCH does bind to one of these pairs [13], but HCl adopts an entirely different mode in which the zero-point motion in the complex samples interactions between the HCl and the two F atoms [14]. With this body of knowledge in hand, we are proceeding to increase the complexity of the olefinic subunit by turning to propenes. We choose initially to add a –CF_3 group to vinyl fluoride at different locations relative to the F atom. With the heavy F atoms, it is unlikely that –CF_3 will exhibit internal rotation. Our goal is to discern how –CF_3 affects the nucleophilicity of the F atom bonded to one of the ethylenic C atoms, whether all the F atoms in CF_3 are equally nucleophilic, and if these atoms furnish additional binding sites to protic acids. The observation of binding modes differing from those observed for vinyl fluoride, 1,1-difluoroethylene, and *trans*-1,2-difluoroethylene would add much to the understanding of the nature of intermolecular interactions.

To prepare for work on acid complexes, it is useful to obtain the structures of the individual propene molecules and understand their electronic distribution by using the argon atom as a probe. We have already studied 2,3,3,3-tetrafluoropropene [15] (where the –CF_3 group and the F atom are connected to the same ethylenic C) and its argon complex [16]. Here, we report our work on (*E*)-1,3,3,3-tetrafluoropropene, where the –CF_3 group is *trans* to the F atom in the propene, and the complex of this molecule with argon.

(*E*)-1,3,3,3-tetrafluoropropene is one of a series of hydrofluoroolefins (HFOs) that have been proposed as replacement refrigerants on the basis of their relatively short atmospheric lifetime that results in a lowering of their global warming potential. Several of these HFOs also find use as foam blowing agents. Computational

---

* Corresponding author.
E-mail addresses: mdmarshall@amherst.edu (M.D. Marshall), hleung@amherst.edu (H.O. Leung).

https://doi.org/10.1016/j.jms.2020.111379
0022-2852/

studies have explored the structures, responses to external fields [17], decomposition pathways [18], and condensed phase dynamics [19,20] of these HFOs and experimental results are available for the kinetics of the reaction of (*E*)-1,3,3,3-tetrafluoropropene and (*Z*)-1,3,3,3-tetrafluoropropene with OH radicals [21] and of the shock-wave induced reaction with HF for (*E*)-1,3,3,3-tetrafluoropropene and 2,3,3,3-tetrafluoropropene [18].

2. *Ab initio* calculations

We use *ab initio* calculations at the MP2/6–311++G(2d,2p) level with GAUSSIAN 16 [22] to guide our experimental search for and assignments of rotational transitions for (*E*)-1,3,3,3-tetrafluoropropene and its argon complex. We begin with the structure and atom numbering scheme of the propene shown in Fig. 1, where all but two of the F atoms (F3 and F4) connected to C3 are in the same plane. To explore the structure of the molecule without restricting any portion of it to be planar, we change the F2-C3-C2-C1 dihedral angle while optimizing all other structural parameters. Because of the symmetry of the CF_3 group, the dihedral angle need not cover the entire 360°, but a scan from 0° to 120° is sufficient. This is conducted in steps of 10° and the potential energy plot is displayed in Fig. 2. The minimum energy structure is at 0° (and equivalently at ±120° when another F atom in the CF_3 group assumes the same position as that occupied by F2 at 0°). The barrier to this motion is greater than 730 cm^{-1}, too high for $-CF_3$ to display any effects of internal rotation. The optimized structure indeed has a symmetry plane, with F3 and F4 lying on different sides of it. The bond lengths and bond angles are listed in Table 1 and the atom coordinates in the principal axis system can be found in the supplementary material. This configuration allows an intramolecular hydrogen bond of 2.4295 Å between F2 and H1 and a bifurcated hydrogen bond to H2 formed with F3 and F4, each having an interaction length of 2.7109 Å. These interactions, especially the short F2–H1 bond, no doubt contribute to the large barrier to internal rotation of the $-CF_3$ group. The *A*, *B*, *C* rotational constants for the optimized structure are 5326, 1460, 1434 MHz, respectively, and the dipole moment components along the *a*, *b*, *c* inertial axes are likewise 1.15, 0.07, 0.00 D. We therefore expect the propene to be a (very) near prolate asymmetric top with strong *a* type rotational transitions and much weaker *b* type transitions; no *c* type transitions are allowed.

To explore the interaction potential between (*E*)-1,3,3,3-tetrafluoropropene and argon, we place the origin of a coordinate system at the center of mass of the optimized propene structure, and assign the *x*, *y*, *z* axes to be, respectively, the *a*, *b*, *c* inertial axes of the propene. The position of Ar is specified by its polar angle with respect to this axis system: *R* is the distance between Ar and the origin, θ is the polar angle formed between *R* and the *z* axis, and ϕ is the azimuthal angle formed by the *x* axis and the projection of *R* onto the *x*-*y* plane (Fig. 3). Because the molecule has a plane of symmetry, it is only necessary to sample θ for just one side of the plane; thus, the value of θ is scanned from 5° to 85° and that of ϕ from 0° to 360°, both in 10° increments, while allowing *R* to optimize. The resulting interaction potential is shown in Fig. 3. Three minima, labeled (a)–(c), are identified and optimized, and the corresponding structures are in Fig. 4. While argon is not in the plane of symmetry of the propene in Structure (a), it does lie in the plane for Structures (b) and (c). The rotational constants, dipole moment components, and relative energies of these structures are listed in Table 2. We have discovered that rotational constants calculated in this manner typically match well with experimental rotational constants for the isomer we ultimately

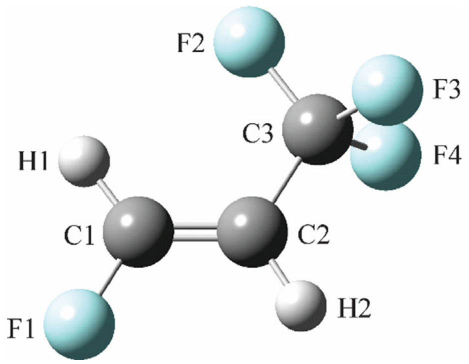


Fig. 1. The (*E*)-1,3,3,3-tetrafluoropropene molecule with the atom numbering scheme. All atoms except F3 and F4 are in the same plane. This is the starting configuration for optimizing the structure of the molecule, and indeed, as confirmed through *ab initio* calculations, the optimized structure is also planar. Atom colors: C, dark gray; H, light gray; F, light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

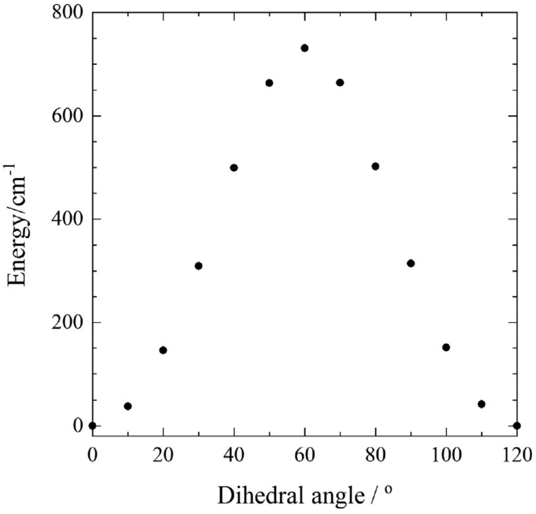


Fig. 2. A relaxed scan of the F2-C3-C2-C1 dihedral angle in (*E*)-1,3,3,3-tetrafluoropropene from 0° to 120° in steps of 10°.

Table 1
Structural parameters for the global minimum configuration of (*E*)-1,3,3,3-tetrafluoropropene obtained using *ab initio* calculations and from a structure fit to the moments of inertia of four isotopologues of the molecule.

	Theory	Experiment[a]
C1–C2/Å	1.3266	1.3279(44)
C2–C3/Å	1.4834	1.4660(39)
C1–F1/Å	1.3388	1.3388
C1–H1/Å	1.0773	1.0773
C2–H2/Å	1.0775	1.0775
C3–F2/Å	1.3459	1.3459
C3–F3/Å	1.3475	1.3475
C1–F4/Å	1.3475	1.3475
∠F1C1C2/°	121.0242	122.33(22)
∠H1C1C2/°	125.6360	125.6360
∠H2C2C1/°	121.5735	121.5735
∠C3C2C1/°	121.1747	121.74(37)
∠F2C3C2/°	112.6097	112.87(29)[b]
∠F3C3C2/°	111.2772	111.54(13)[b]
∠F4C3C2/°	111.2772	111.54(13)[b]
∠F3C3C2C1/°	120.6148	120.6148
∠F4C3C2C1/°	−120.6148	−120.6148

[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 F3C3C2 and F4C3C2 are fixed to the same value, which in turn is fixed to be 1.3325° smaller than the F2C3C2 angle, as suggested by the *ab initio* result.

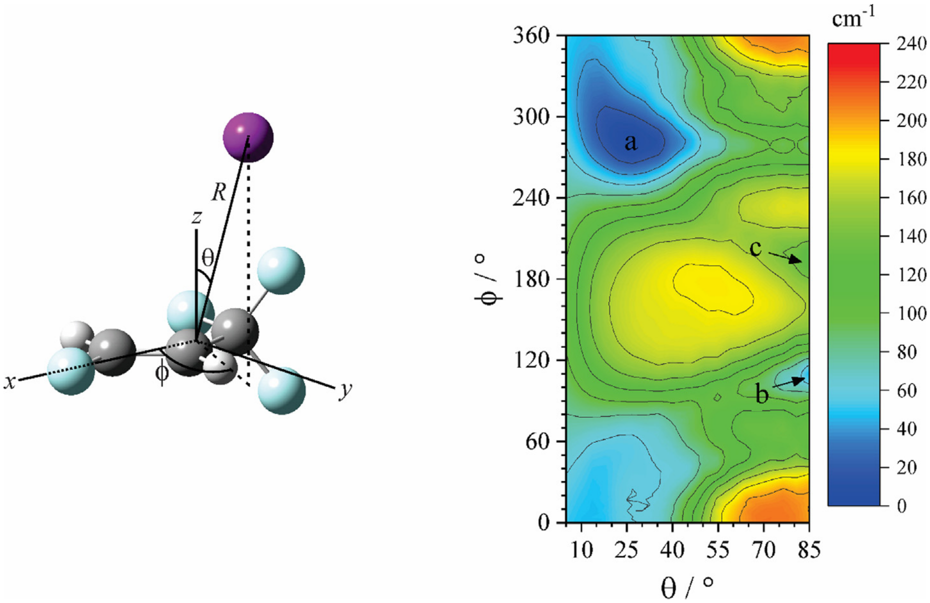


Fig. 3. Left: the spherical polar coordinate system used to locate Ar with respect to (*E*)-1,3,3,3-tetrafluoropropene. The *x*, *y*, and *z* axes are the *a*, *b*, and *c* axes for the propene, with the origin at its center of mass. *R* is the distance between Ar and the origin, and θ and ϕ are, respectively, the polar and azimuthal angles formed by *R* and the coordinate system. Right: a contour plot of the potential energy as a function of the angles with *R* optimized. Three minima are located, and the geometry is optimized at each. The corresponding structures are shown in Fig. 4. Atom colors: C, dark gray; H, light gray; F, light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

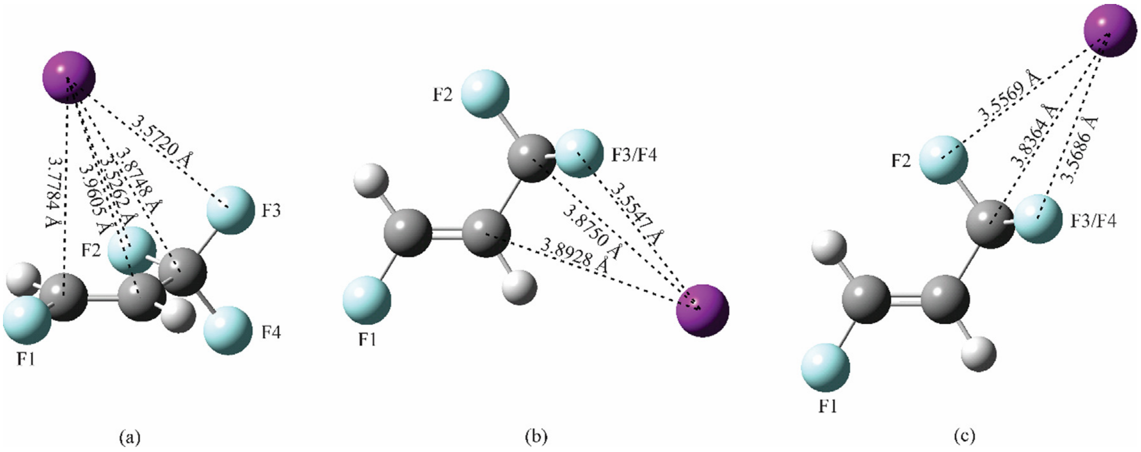


Fig. 4. The optimized structures (without BSSE correction) corresponding to the three minima found in the potential scan for Ar-(*E*)-1,3,3,3-tetrafluoropropene, arranged in order of increasing energy. The more important intermolecular interactions are indicated using dashed lines. Note that in (b) and (c), Ar forms an interaction to F4 (located directly underneath F3 and thus not visible) identical to that to F3. Atom colors: C, dark gray; H, light gray; F, light blue; Ar: purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Rotational constants, dipole moment components, and relative equilibrium and zero-point corrected energies for three isomers of Ar-(*E*)-1,3,3,3-tetrafluoropropene obtained from *ab initio* calculations at the MP2/6–311++G(2d,2p) level without and with BSSE correction.

	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction
	Structure (a)		Structure (b)		Structure (c)	
A/MHz	1463	1474	1712	1661	4697	4670
B/MHz	1001	916	778	738	526	492
C/MHz	672	635	591	562	516	483
$\|\mu_a\|$/D	0.325	0.359	0.641	0.585	1.143	1.134
$\|\mu_b\|$/D	1.060	1.058	0.864	0.914	0.281	0.291
$\|\mu_c\|$/D	0.044	0.046	0.000	0.000	0.000	0.000
E_{equil}[a,b]/cm^{-1}	0.0	0.0	36.4	14.2	111.4	63.7
E_{zpe}[a,c]/cm^{-1}	0.0	0.0	38.6	13.2	104.0	57.7

[a] The energy of the most stable isomer is set to 0 for the structures computed respectively with and without BSSE correction.

[b] The equilibrium energy is determined by using the global minimum theoretical structure of (*E*)-1,3,3,3-tetrafluoropropene.

[c] A full relaxation of the complex geometry, include the structural parameters of (*E*)-1,3,3,3-tetrafluoropropene, is used to compute the equilibrium energy and the zero-point corrected energy. A counterpoise calculation is then performed using this optimized structure, and the BSSE corrected energy is computed as $E_{\text{zpe}} - E_{\text{equil}} + E_{\text{BSSE}}$.

observe, but that basis set superposition error (BSSE) can sometimes affect the energy ordering of the isomers and also provides rotational constants that agree less well with experiment. Nevertheless, we proceed to optimize each of the three isomers with the BSSE correction included [23], and report the energy, together with the rotational constants and dipole moment components in Table 2. Finally, we explore the effects of zero-point energy by fully relaxing the structure of each isomer and calculating a harmonic correction. The sero-point corrected energy, E_{zpe}, is also reported in Table 2, and we estimate the BSSE correction for this fully relaxed geometry, reporting the energy corrected for both BSSE and zero-point energy. The atomic coordinates of three structures, with and without BSSE correction, and those with fully relaxed structures, are given in the supplementary material. The different sets of computation all indicate that Structure (a) has the lowest energy. When BSSE correction is not considered, it is more stable than Structure (b) by at least 36 cm^{-1} with or without consideration of zero-point energy correction. The difference decreases to 13.2–14.2 cm^{-1} when BSSE correction is made. Because of the delicate nature of intermolecular interactions, we do not expect theoretical calculations, at least at the level we employ, to definitively identify the lowest energy species; thus, we keep both structures, (a) and (b), in mind when we search for the spectrum of Ar-(*E*)-1,3,3,3-tetrafluoropropene. Structure (c) is significantly higher in energy than Structure (a), by 57.7–111.4 cm^{-1}, and is likely not observable under our experimental conditions.

To gain insight into the energy ordering of the three isomers, we label those Ar-heavy distances in Fig. 4 that are no more than approximately 10% longer than the sum of the van der Waals radii of the two atoms. (The following radii are used: Ar, 1.88 Å; F, 1.47 Å; C, 1.70 Å [24].) There are 5 such interactions in Structures (a) and 4 each in Structures (b) and (c). Specifically, Ar interacts with two F atoms in each of Structures (a) and (b), and with three F atoms in Structure (c). The shortest, and therefore the strongest, Ar–F interaction is in Structure (a), with a length of 3.5262 Å. All other Ar–F interactions in the three structures are between 3.56 and 3.57 Å and likely to have equivalent strengths. The shortest Ar–C interaction is also in Structure (a), with a length of 3.7784 Å. In fact, Ar is positioned to interact with both C1 and C2 in that isomer, indicating that there is an interaction with the polarizable π cloud. This is not the case for Structures (b) and (c) where Ar can only interact with C2 and C3. It appears then Structure (a) allows argon to interact with more heavy atoms (and the π bond formed by C1 and C2), rendering it more stable than the other isomers.

The rotational constants of Structures (a) and (b) are very different; consequently, they should give significantly different rotational spectra. Each one should have stronger *b* type transitions than *a* type transitions, and very weak [Structure (a)] or no [Structure (b)] *c* type transitions.

3. Experiment

The rotational spectra of (*E*)-1,3,3,3-tetrafluoropropene and its argon complex are obtained simultaneously using a sample of 1% of the propene (SynQuest Laboratories) in argon at a backing pressure of 1–2 atm. We use two Fourier transform microwave spectrometers for this work: a broadband chirped pulse (5.6–18.1 GHz) spectrometer [15,25,26] and a narrow band, Balle-Flygare Fourier transform microwave (5–21 GHz) spectrometer [25,27]. Both utilize 0.8-mm diameter pulsed nozzles; two for the broadband and one for the narrow band instrument. We first collect the spectra with the broadband spectrometer. The sample is polarized using a chirped microwave polarization pulse of 4 μs duration and 20–25 W of power. The resulting free induction decay (FID) is digitized at 50 Gs s^{-1} for 10 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 typically operate at 4 Hz, although this is reduced to 0.8 Hz for overnight operation. Approximately 400,000 FIDs are averaged for each segment, and as described previously [25], the average is Fourier transformed to give a frequency domain spectrum with a resolution element of 23.84 kHz and typical line widths (FWHM) of 225 kHz. We are able to assign strong *a* type transitions for the most abundant species of (*E*)-1,3,3,3-tetrafluoropropene and three isotopologues singly substituted with naturally occurring ^{13}C, as well as *b* type transitions of the most abundant Ar-(*E*)-1,3,3,3-

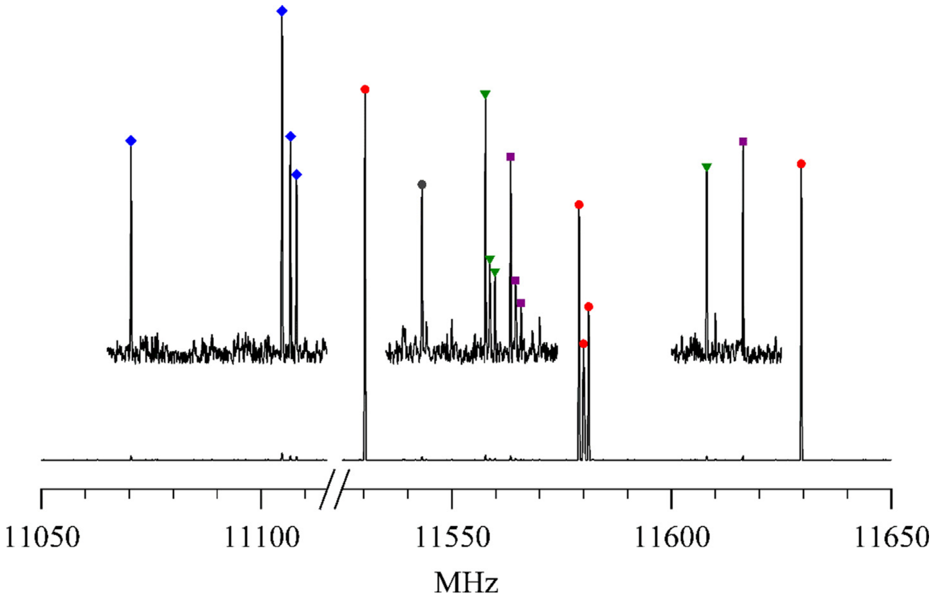


Fig. 5. A 600 MHz portion of the chirped pulse spectrum obtained by expanding 1% (*E*)-1,3,3,3-tetrafluoropropene in Ar. The upper trace is magnified 50× and displayed in three portions. Transitions due to the most abundant (*E*)-1,3,3,3-tetrafluoropropene and its ^{13}C1-, ^{13}C2-, and ^{13}C3-containing isotopologues are marked, respectively, by red circles, gray circles, purple squares, and green triangles. Those due to the most abundant Ar-(*E*)-1,3,3,3-tetrafluoropropene are marked by blue diamonds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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

	CF_3CHCHF	$CF_3CH^{13}CHF$	$CF_3^{13}CHCHF$	$^{13}CF_3CHCHF$
A	5353.38188(17)	5348.38084(29)	5336.98768(62)	5353.84542(42)
B	1459.930976(37)	1449.143013(36)	1458.558485(65)	1457.223057(52)
C	1435.112941(35)	1424.336258(34)	1432.620607(64)	1432.490001(50)
$D_J/10^{-3}$	0.08629(21)	0.08712(30)	0.08769(54)	0.08694(43)
$D_{JK}/10^{-3}$	2.7296(11)	2.6916(12)	2.6728(22)	2.7232(16)
$D_K/10^{-3}$	−1.279(13)	[−1.279][b]	[−1.279][b]	[−1.279][b]
$d_1/10^{-6}$	0.535(81)	[0.535][b]	[0.535][b]	[0.535][b]
$d_2/10^{-6}$	1.973(20)	2.06(21)	2.20(37)	1.77(30)
No. of rotational transitions	120	48	47	50
No. of *a* type	46	44	44	46
No. of *b* type	74	4	3	4
J range	0–14	0–7	1–7	0–7
K_a range	0–5	0–5	0–5	0–5
rms/kHz	1.57	0.49	0.88	0.72

[a] 1σ standard deviations in the parameters are given in parentheses.
[b] Fixed at the value appropriate to the most abundant isotopologue.

tetrafluoropropene complex consistent with Structure (a). An example of these transitions is shown in Fig. 5. The J = 4–3 *a* type transition with K_a = 0, 1, and 2 for the most abundant isotopologue of (*E*)-1,3,3,3-tetrafluoropropene can readily be identified, some of the transitions for each of the ^{13}C-containinig isotopologues are also in this region. Additionally, four *b* type transitions due to the argon complex can also be seen. These transitions are similar in intensity to the *a* type transitions of the ^{13}C isotopologues of the propene.

To better resolve some of the transitions and to record weaker transitions, we turn to the narrow band instrument. We are also able to collect the spectra for three isotopologues of the argon complex singly substituted with naturally occurring ^{13}C. The signals are collected in the time domain, and after background correction, they are digitized for 1024 data points and zero-filled to a 2048-point record length before Fourier transformation to give a frequency domain signal with a resolution element of 4.8 kHz. Occasionally, to resolve close-lying transitions, twice the number of data points are collected and zero-filled. No *c*-type transitions are observed for the propene or for its argon complex. All analyses below are done with transition frequencies measured using the narrow band instrument.

4. Results

4.1. Spectral analysis

4.1.1. (E)-1,3,3,3-tetrafluoropropene

We have observed and assigned 120 rotational transitions, both *a* and *b* type, for the most abundant isotopologue of (*E*)-1,3,3,3-tetrafluoropropene, sampling *J* from 0 to 14 and K_a from 0 to 5. Although *b* type transitions are significantly weaker, in accord with *ab initio* calculation, the number density of the most abundant species allows us to observe 74 of them. This is not the case for the minor isotopologues singly substituted with ^{13}C; significantly fewer *b* type transitions are observed for each of them but the number of *a* type transitions remains similar to that for the most abundant species. In the end, 47–50 rotational transitions are observed for these three species, sampling *J* from 0 or 1 to 7 and K_a from 0 to 5.

Because the asymmetry parameter of each isotopologue is −0.987 (a value obtained after the rotational constants have been determined), it is almost a prolate symmetric top. Thus, its spectrum is analyzed using the Watson *S*-reduced Hamiltonian [28] in the I^r representation. Using Pickett's nonlinear SPFIT program [29], we determine 3 rotational constants for all species, 5 quartic centrifugal distortion constants for the most abundant species and 3 for each of the minor isotopologues. The rms deviation of each fit is between 0.5 and 1.6 kHz. The spectroscopic constants are in Table 3, and tables of observed and calculated transition frequencies with assignments for all isotopologues studied are in the supplementary material.

4.1.2. Ar-(E)-1,3,3,3-tetrafluoropropene

The asymmetry parameter for each of the isotopologues of Ar-(*E*)-1,3,3,3-tetrafluoropropene is between −0.195 and −0.179 (calculated from the rotational constants presented later); thus, the complex is very asymmetric. We have observed 336 *a* and *b* type transitions for the most abundant isotopologue, and sampled *J* from 1 to 15, K_a from 0 to 10, K_c from 0 to 15. For the three ^{13}C-containing species, we have only observed 43–45 *a* type transitions for each. The absence of *b* type transitions for these isotopologues is commensurate with the small theoretical dipole moment component along the *b* axis reported earlier and with the low population density of these species. Nevertheless, the transitions still sample a relatively large range of *J* (2–10), K_a (0–6), and K_c (0–10). The spectrum for each species is analyzed using the Watson *A*-reduced Hamiltonian [28] in the I^r representation and Pickett's nonlinear SPFIT program [29]. For each species, we have determined 3 rotational constants and 5 quartic centrifugal distortion constants. Additionally, for the most abundant isotopologue, we also determine 7 sextic centrifugal distortion constants (Table 4). The rms deviation of each fit is between 0.8 and 1.1 kHz. Tables of observed and calculated transition frequencies with assignments for all isotopologues studied are in the supplementary material.

4.2. Structure determination

4.2.1. (E)-1,3,3,3-tetrafluoropropene

Because three of the ^{13}C-containing isotopologues contain a single substitution in the most abundant species, we are able to determine the Kraitchman coordinates [30] of the three C atoms given in Table 5. A Kraitchman analysis does not take into account the difference in vibrational motions upon isotopic substitution. As a result, when the value of a coordinate is close to 0, it is either not well determined or appears as a nonphysical value. Indeed, the *c* coordinates of C1 and C2 are very small, with values similar to their respective uncertainties, confirming that these two atoms are indeed in the *a-b* plane, as suggested by *ab initio* calculation. Additionally, the *b* and *c* coordinates of C3 are nonphysical, indicating that this atom lies on the *a* axis. The co-planarity of the three C

Table 4

Spectroscopic constants (in MHz, unless otherwise noted) for four isotopologues of Ar-(*E*)-1,3,3,3-tetrafluoropropene.[a,b]

	Ar–CF$_3$CHCHF	Ar–CF$_3$CH^{13}CHF	Ar–CF$_3^{13}$CHCHF	Ar–^{13}CF$_3$CHCHF
A	1463.663690(38)	1451.85387(12)	1460.498388(94)	1461.842530(90)
B	985.434872(22)	984.87771(19)	982.79178(15)	982.92249(14)
C	662.465335(17)	659.898961(61)	661.002477(49)	660.946061(47)
$\Delta_J/10^{-3}$	1.90800(21)	1.8953(17)	1.8951(13)	1.9056(13)
$\Delta_{JK}/10^{-3}$	9.39057(80)	9.4007(63)	9.4439(49)	9.2415(47)
$\Delta_K/10^{-3}$	−9.51431(73)	−9.5781(48)	−9.6468(38)	−9.2982(36)
$\delta_J/10^{-3}$	0.63299(11)	0.63074(81)	0.62680(63)	0.63338(61)
$\delta_K/10^{-3}$	6.41127(53)	6.3928(49)	6.4217(40)	6.3607(38)
No. of rotational transitions	336	45	43	45
No. of *a* type	110	0	0	0
No. of *b* type	226	45	43	45
J range	1–15	2–10	2–10	2–10
K_a range	0–10	0–6	0–6	0–6
K_c range	0–15	0–10	0–10	0–10
rms/kHz	0.75	1.10	0.86	0.84

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

[b] Additional centrifugal constants, all in Hz, are determined for the most abundant isotopologue: Φ_J = −0.03326(97), Φ_{JK} = −0.2071(49), Φ_{KJ} = 0.456(12), and Φ_K = −0.0461(87), ϕ_J = −0.01397(48), ϕ_{JK} = −0.1638(34), and ϕ_K = 0.2539(86), and are fixed at these values for the 3 minor isotopologues.

Table 5

The coordinates of the carbon atoms in (*E*)-1,3,3,3-tetrafluoropropene determined from a Kraitchman analysis and a structure fit of four isotopologues.

	a/Å	*b*/Å	*c*/Å
(i) Substitution coordinates[a,b]			
C1	1.60924(93)	−0.2987(50)	0.021(72)[c]
C2	0.5706(26)	0.5388(28)	0.040(37)[c]
C3	−0.8073(19)	nonphysical	nonphysical
(ii) From structure fit[d]			
C1	1.61051(87)	−0.28709(85)	0.0000
C2	0.5707(37)	0.5388(52)	0.0000
C3	−0.80864(20)	0.04205(40)	0.0000

[a] Costain errors [33] 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. The *c* coordinates of C1 and C2 are not well determined and thus, no signs are assigned.

[c] The coordinate is poorly determined, suggesting that the atom lies in the *a-b* plane. No attempt is made to assign it a relative sign.

[d] The *c* coordinates of the C atoms are fixed to 0 in the structure fit.

atoms can further be verified by the practically identical values of $P_{cc} = \sum m_i c_i^2$ for all 4 isotopologues: 44.2087, 44.2091, 44.2102, and 44.2038 u Å^2, respectively, for the most abundant species and isotopologues with ^{13}C substitution in the C1, C2, and C3 positions. For the other coordinates, although the Kraitchman analysis gives only absolute values, we can use physically reasonable bond lengths to assign relative signs to them.

We determine the average structure of (*E*)-1,3,3,3-tetrafluoropropene by fitting 5 geometric parameters to 12 moments of inertia of the isotopologues using Kisiel's STRFIT program [31]. The parameters are the bond lengths of C1–C2 and C2–C3, and the bond angles, F1C1C2, C1C2C3, and F2C3C2. Furthermore, the bond angles F3C3C2 and F4C3C2 are restricted to have the same value which is 1.3325° smaller than the F2C3C2 angle, as given by *ab initio* calculation. All other parameters are fixed to their *ab initio* values. The rms deviation is 0.0060 u Å^2. We attempted other fits that involve adjusting the positions of the F atoms, but the one reported here gives the lowest rms deviation (and no significant correlations between the parameters). The coordinates of the C atoms from the fit are listed in Table 5 (coordinates of all atoms are available in the supplementary material). They agree excellently with the corresponding Kraitchman coordinates, differing by only 0.001–0.01 Å. The bond lengths are bond angles calculated using Kisiel's EVAL program [32] are listed in Table 1.

4.2.2. Ar-(E)-1,3,3,3-tetrafluoropropene

We once again carry out a Kraitchman analysis for the three C atoms, this time in the Ar-(*E*)-1,3,3,3-tetrafluoropropene complex and the coordinates are listed in Table 6. All coordinates are well determined except for the *c* coordinate of C3; the unphysical value indicates that this atom lies in the *a-b* inertial plane of the complex. Fixing the structure of the propene at its average structure as determined experimentally in the previous section, we need only 3 geometric parameters to locate argon. A fit of these parameters to 12 moments of inertia of the 4 isotopologues gives a relatively large deviation of fit (0.1047 u Å^2), the greatest contribution to this deviation comes from the moments of inertia for the ^{13}C2 isotopologue, which are not as well reproduced by the fit as those of the other isotopologues. This can be clearly shown by fitting the position of Ar to the 6 moments of inertia of the most abundant and ^{13}C1-containing isotopologues or to the 9 moments of inertia of these two species plus the ^{13}C3-containing isotopologue. The rms deviation of these two fits are, respectively, 0.0194 and 0.0236 u Å^2.

An inspection of the rotational constants for the ^{13}C2- and ^{13}C3-containing isotopologues shows that they are very similar: the cor-

Table 6

The coordinates of the carbon atoms in Ar-(*E*)-1,3,3,3-tetrafluoropropene determined from a Kraitchman analysis, a structure fit of four isotopologues, and *ab initio* calculation.

	a/Å	*b*/Å	*c*/Å
(i) Substitution coordinates[a,b]			
C1	0.4703(32)	−1.65960(90)	0.2587(58)
C2	1.0766(14)	−0.7305(21)	−0.4705(32)
C3	1.1480(13)	0.6643(23)	nonphysical[c]
(ii) From structure fit to all four isotopologues			
C1	0.4488(20)	−1.65864(37)	0.2258(14)
C2	1.1907(33)	−0.75248(86)	−0.4002(27)
C3	1.15633(70)	0.66445(80)	−0.02562(22)
(iii) From *ab initio* calculation[d]			
C1	0.4294	−1.6757	0.2632
C2	1.0452	−0.7588	−0.4741
C3	1.1629	0.6341	−0.0324

[a] Costain errors [33] 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 coordinates are assigned using physically reasonable atomic distances.

[c] The coordinate is poorly determined, suggesting that the atom lies in the *a-b* plane.

[d] The average structure of (*E*)-1,3,3,3-tetrafluoropropene is used in a calculation (MP2/6-311++G(2d,2p), without BSSE correction) to determine these coordinates in the argon complex with Structure (a).

Table 7
The argon-heavy atom bond lengths resulting from structural fits of the moments of inertia of different number of Ar-(*E*)-1,3,3,3-tetrafluoropropene isotopologues.

	All 4 isotopologues	Most abundant & ^{13}C1-containing	Most abundant, ^{13}C1- & ^{13}C3-containing
Ar–C1/Å	3.7814(19)	3.78113(50)	3.78090(49)
Ar–C2/Å	4.1068(33)	4.10854(86)	4.10877(85)
Ar–C3/Å	3.91750(77)	3.91784(20)	3.91780(20)
Ar–F1/Å	4.6118(28)	4.61265(73)	4.61267(72)
Ar–F2/Å	3.2725(75)	3.2686(20)	3.2677(20)
Ar–F3/Å	3.8322(69)	3.8360(18)	3.8368(18)
Ar–F4/Å	5.1899(32)	5.18918(87)	5.18892(86)
rms/u Å^2	0.1047	0.0194	0.0236

responding *A*, *B*, and *C* constants for these species differ by 1.34, 0.13, and 0.06 MHz from each other (Table 4). To ensure that we did not mis-assign the rotational constants to the wrong isotopologues, we turn to theory for guidance. For better comparison between experiment and theory, we use the average structure – instead of the equilibrium structure employed earlier – of (*E*)-1,3,3,3-tetrafluoropropene here to calculate the global minimum structure of its argon complex at the MP2/6–311++(2d,2p) level. The theoretical coordinates of C1, C2, and C3 are listed in Table 6 and the Kraitchman coordinates of these atoms agree well with them (the corresponding pairs of coordinates differ by 0.004–0.04 Å). The coordinates of the C atoms from a structure fit to all 4 isotopologues also show a similar agreement with *ab initio* calculation except for the *a* and *c* coordinate of C2, where they differ by 0.14 and 0.07 Å, respectively. Indeed, this is in accord with our finding that the moments of inertia of the ^{13}C2 species are not as well fitted.

We are confident that we did not mistakenly attribute the rotational constants to the wrong isotopologues. To examine how the three structural fits differ, it is useful to inspect the Ar-heavy atom distances (calculated using Kisiel's EVAL program [32]) (Table 7). The corresponding distances derived from a fit to all 4 isotopologues agree with those from the other two fits to within 0.005 Å, suggesting that all 3 fits are comparable. Seeing no reason to exclude the moments of inertia of the ^{13}C2 isotopologue, we proceed to use structural results from all 4 species, which are also presented graphically in Fig. 6 in two views (the atomic coordinates are available in the supplementary material). It is evident that the zero-point motion in the ^{13}C2 species is more different from the other isotopologues, but it is not clear why.

5. Discussion

We have determined the structure of (*E*)-1,3,3,3-tetrafluoropropene. It is remarkable that the *B* and *C* rotational constants corresponding to the experimental, average structure agree with those derived theoretically for the equilibrium structure to 1 MHz or better. The experimental *A* constant is 27 MHz greater than the theoretical value, but this is merely 0.5% of the constant. These excellent agreements indicate that the molecule (at least the heavy atom frame) is likely quite rigid.

Ab initio calculation also serves well as a guide in the assignment of the Ar-(*E*)-1,3,3,3-tetrafluoropropene spectrum (Table 2). The experimental *A* rotational constant, 1463.663690(38) MHz, agrees excellently that that predicted theoretically (1463 MHz, without BSSE correction) for Structure (a), while the *B* and *C* experimental constants are only 16 and 10 MHz (corresponding to 1.6%

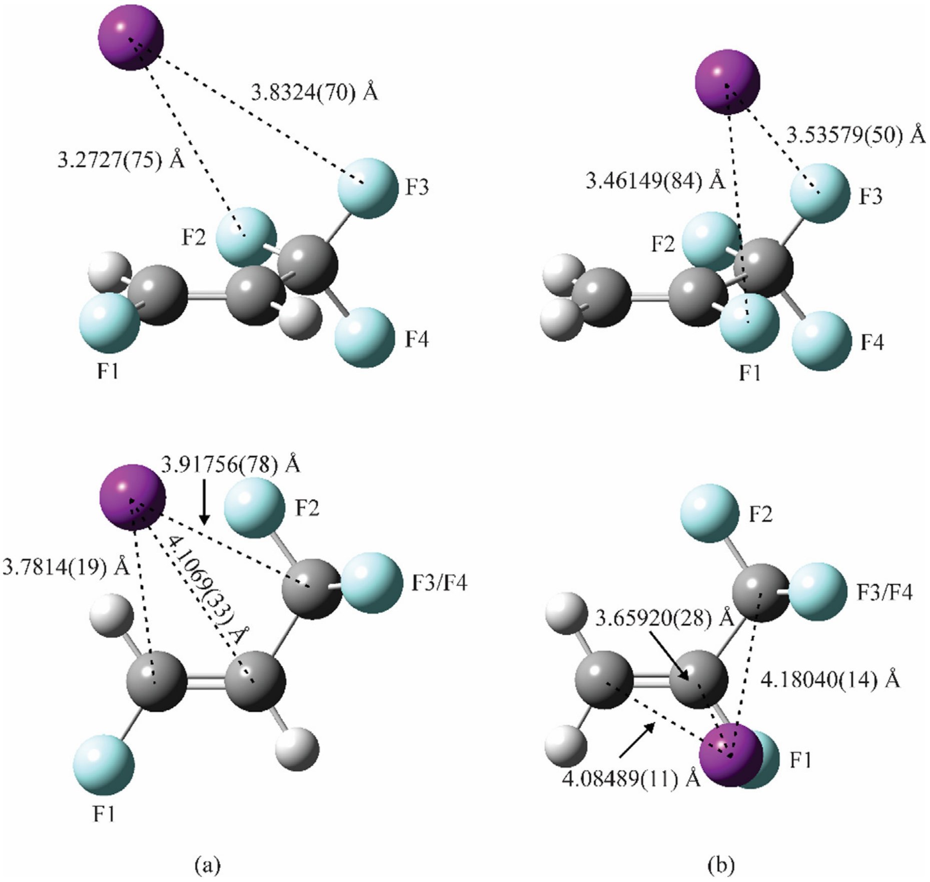


Fig. 6. In two views, the experimental structure of (a) Ar-(*E*)-1,3,3,3-tetrafluoropropene (this work) and (b) Ar-2,3,3,3-tetrafluoropropene (Ref. [16]). The lower set of figures show the propenes lying in their respective planes of symmetry.

and 1.4% of the values of these constants, without BSSE correction) greater than the corresponding theoretical values. The experimental constants do not agree quite as well with the theoretical values predicted for Structure (a) when BSSE correction is taken: the differences being 10, 69, and 27 MHz (1%, 7%, and 4% of the corresponding constants). These theoretical values (without or with BSSE correction) are determined using the equilibrium structure of (*E*)-1,3,3,3-tetrafluoropropene. When the average structure of the propene is used to determine the structure of the argon complex corresponding to Structure (a), the rotational constants are greater than the corresponding ones calculated using the equilibrium structure, but by no more than 2–3 MHz with or without BSSE correction. Thus, the calculation without BSSE correction predicts the experimental constants better, regardless whether we use the equilibrium or average structure for the propene.

Based on the sums of van der Waals radii for Ar–F (3.35 Å) and Ar–C (3.58 Å), the experimental structure of Ar-(*E*)-1,3,3,3-tetrafluoropropene (Fig. 6) indicates that Ar interacts strongly with F2 and moderately with C1. The location of Ar also allows it to interact, though not as strongly, with F3, C2, and C3, with corresponding interaction lengths of 14%, 15%, and 9% longer than the respective van der Waals contact. Ar, indeed, is positioned to interact with a maximum of heavy atoms (and the π cloud formed by C1 and C2) in the propene, but the locations of F1 and F4 are too far away to form any significant interactions.

It is useful to compare the structure of Ar-(*E*)-1,3,3,3-tetrafluoropropene with Ar-2,3,3,3-tetrafluoropropene [16] where the F atom connected directly to the ethylenic C is in a different location (Fig. 6). In this latter species, Ar is located out of the symmetry plane of the propene at a position practically above F1, interacting with two F atoms (F1 and F3) and three C atoms (C1, C2, and C3). Both Ar–F interactions are only 3% and 6% longer than van der Waals contact; thus, they should be relatively strong. Ar also interacts strongly with C2 (2% longer than Ar–C van der Waals contact) and more weakly with C1 (thus with the π cloud formed by C1 and C2) and C3 (14% and 17% longer than the van der Waals contact). Once again, Ar is located to interact with a maximum of heavy atoms in the propene.

To compare the electron density distribution of the two propenes, we mapped the electrostatic potential of each onto its total electron density surface (Fig. 7). It is interesting to note that when the F atom connected to an ethylenic C, it is much less nucleophilic when it is *trans* to the CF_3 group [in (*E*)-1,3,3,3-tetrafluoropropene] than when it is geminal (in 2,3,3,3-tetrafluoropropene) while the same time, the F atoms in the CF_3 group are more nucleophilic for the former than the latter. The CF_3 group, therefore, can withdraw electron density easier from a F atom when they are *trans* to each other, suggesting the importance of hyperconjugation in (*E*)-1,3,3,3-tetrafluoropropene in channeling electron density to the highly electronegative CF_3 group. Within the CF_3 group, the F atom in the symmetry plane is less nucleophilic for each propene. Once again, hyperconjugation likely plays a role in siphoning off its electron density.

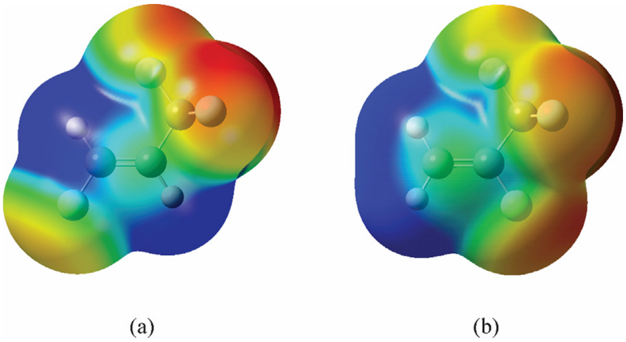


Fig. 7. The electrostatic potentials of (a) (*E*)-1,3,3,3-tetrafluoropropene and (b) 2,3,3,3-tetrafluoropropene mapped onto their respective total electron density surfaces. The same value of electron density and identical color scales are used for the two surfaces. Blue color represents positive electrostatic potential and red, negative electrostatic potential. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The electrostatic potential surfaces suggest that these propenes are indeed interesting binding partners for a protic acid. Because the F bonded to C2 in 2,3,3,3-tetrafluoropropene is quite nucleophilic and has an electropositive H atom *cis* to it, it is likely that a protic acid would bind to this propene in a similar manner as that observed in vinyl fluoride, 1,1-difluoroethylene, and *trans*-1,2-difluoroethylene. On the other hand, the F atom bonded to C1 in (*E*)-1,3,3,3-tetrafluoropropene is the least nucleophilic F atom in that propene, but F2 and F3 (or equivalently F4) are rather nucleophilic. These can furnish binding sites for a protic acid. F2 locates very close to H1: as a result, if an acid were to bind in the molecular plane, the hydrogen bond may not need to deviate much from linearity (compared to fluoroethylene complexes) to interact with H1, but of course, the binding need not occur in the symmetry plane. If the binding were to F3 (or F4), then the acid cannot be in the symmetry plane. An exploration of the acid binding mode in (*E*)-1,3,3,3-tetrafluoroproene would therefore furnish much information regarding intermolecular interactions.

6. Conclusion

The microwave rotational spectra for four isotopologues of (*E*)-1,3,3,3-tetrafluoropropene have obtained and assigned along with those of the argon complexes for these same four isotopologues. Rotational constants obtained from the analysis of the spectra in combination with results from *ab initio* quantum chemistry calculations are used to determine the average structure of (*E*)-1,3,3,3-tetrafluoropropene, which is then used to determine the location of the argon atom in the heterodimer. The argon is found to occupy a position out of the symmetry plane of (*E*)-1,3,3,3-tetrafluoropropene in a spot where it can interact all three carbon atoms (more so with C1 and C3 than C2), the in-plane fluorine atom and one of the two equivalent out-of-plane fluorine atoms. (Of course, there is an equivalent binding site on the other side of the (*E*)-1,3,3,3-tetrafluoropropene symmetry plane, in which the argon atom would be interacting with the alternate out-of-plane fluorine atom.) In contrast to the structure found for Ar-2,3,3,3-tetrafluoropropene [16], there is no significant interaction with the fluorine atom directly attached to an olefinic carbon (C1 in the present case, C2 for 2,3,3,3-tetrafluoropropene). This indicates a preference for locating near the C3 end of the molecule closer to the –CF_3 group. It appears that the argon atom seeks to maximize the number of heavy atom contacts it can make so to enhance the opportunity for dispersion interactions with the greater number of polarizable electrons, including those in the π bond. It should be noted that in the case of Ar-2,3,3,3-tetrafluoropropene, the argon atom locates in a region of relatively negative electrostatic potential in the propene [16], while in the present case, it occupies a position that has a positive electrostatic potential. Being a non-polar species, the argon atom can respond equally well to both directions of polarization-induced moments while seeking to maximize dispersion interactions.

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.2020.111379.

References

[1] H.O. Leung, M.D. Marshall, Exploring the forces contributing to non-covalent bonding by microwave spectroscopy and structural characterization of gas-phase heterodimers of protic acids with haloethylenes, J. Phys. Chem. A 123 (2019) 10846–10861.

[2] G.C. Cole, A.C. Legon, A characterisation of the complex vinyl fluoride$\cdots$hydrogen fluoride by rotational spectroscopy and ab initio calculations, Chem. Phys. Lett. 400 (4-6) (2004) 419–424.

[3] Z. Kisiel, P.W. Fowler, A.C. Legon, Rotational spectrum, structure, and chlorine nuclear quadrupole tensor of the vinyl fluoride-hydrogen chloride dimer, J. Chem. Phys. 93 (1990) 3054–3062.

[4] A.J. Fillery-Travis, A.C. Legon, L.C. Willoughby, Characterisation by rotational spectroscopy of a hydrogen-bonded dimer formed between H_2O and HCN, Chem. Phys. Lett. 98 (4) (1983) 369–372.

[5] H.O. Leung, M.D. Marshall, T.L. Drake, T. Pudlik, N. Savji, D.W. McCune, Fourier transform microwave spectroscopy and molecular structure of the 1,1-difluoroethylene–hydrogen fluoride complex, J. Chem. Phys. 131 (2009) 204301.

[6] Z. Kisiel, P.W. Fowler, A.C. Legon, Investigation of the rotational spectrum of the hydrogen-bonded dimer $CF_2CH_2\cdots HCl$, J. Chem. Soc., Faraday Trans. 88 (23) (1992) 3385–3391.

[7] H.O. Leung, M.D. Marshall, Rotational spectroscopy and molecular structure of the 1,1-difluoroethylene-acetylene complex, J. Chem. Phys. 125 (2006) 154301.

[8] H.O. Leung, M.D. Marshall, B.K. Amberger, Fourier transform microwave spectroscopy and molecular structure of the *trans*-1,2-difluoroethylene–hydrogen fluoride complex, J. Chem. Phys. 131 (2009) 204302.

[9] H.O. Leung, M.D. Marshall, Finding the better fit: The microwave spectrum and sterically preferred structure of *trans*-1,2-difluoroethylene-hydrogen chloride, J. Phys. Chem. A 122 (2018) 8363–8369.

[10] H.O. Leung, M.D. Marshall, Rotational spectroscopy and molecular structure of 1,1,2-trifluoroethylene and the 1,1,2-trifluoroethylene-hydrogen fluoride complex, J. Chem. Phys. 126 (2007) 114310.

[11] H.O. Leung, M.D. Marshall, M.R. Ray, J.T. Kang, Rotational spectroscopy and molecular structure of the 1,1,2-trifluoroethylene−hydrogen chloride complex, J. Phys. Chem. A 114 (41) (2010) 10975–10980.

[12] H.O. Leung, M.D. Marshall, W.T. Cashion, V.L. Chen, Rotational spectroscopy and molecular structure of the 1,1,2-trifluoroethylene-acetylene complex, J. Chem. Phys. 128 (2008) 064315.

[13] H.O. Leung, M.D. Marshall, Exploring the sterically disfavored binding of acetylene to a geminal olefinic hydrogen-fluorine atom pair: the microwave spectrum and molecular structure of *cis*-1,2-difluoroethylene–acetylene, J. Chem. Phys. 152 (2020) 034303.

[14] H.O. Leung, M.D. Marshall, L.H. Yoon, The importance of a good fit: The microwave spectra and molecular structures of *trans*-1,2-difluoroethylene-hydrogen chloride and *cis*-1,2-difluoroethylene-hydrogen chloride, The 72nd International Symposium on Molecular SpectroscopyUrbana-Champaign, IL, 2017.

[15] M.D. Marshall, H.O. Leung, B.Q. Scheetz, J.E. Thaler, J.S. Muenter, A chirped pulse Fourier transform microwave study of the refrigerant alternative 2,3,3,3-tetrafluoropropene, J. Mol. Spectrosc. 266 (1) (2011) 37–42.

[16] H.O. Leung, M.D. Marshall, M.A. Wronkovich, The microwave spectrum and molecular structure of Ar-2,3,3,3-tetrafluoropropene, J. Mol. Spectrosc. 337 (2017) 80–85.

[17] Y. Liang, F. Wang, Q. Sun, Y. Zhai, Molecular structural and electrical properties of trans-1,3,3,3-tetrafluoropropene and 2,3,3,3-tetrafluoropropene under external electric fields, Comput. Theor. Chem. 1120 (2017) 79–83.

[18] A. Matsugi, K. Takahashi, Thermal decomposition of 2,3,3,3- and *trans*-1,3,3,3-tetrafluoropropenes, J. Phys. Chem. A 121 (26) (2017) 4881–4890.

[19] G. Raabe, Molecular dynamics studies on liquid-phase dynamics and structures of four different fluoropropenes and their binary mixtures with R-32 and CO_2, J. Phys. Chem. B 118 (1) (2014) 240–254.

[20] G. Raabe, Molecular modeling of fluoropropene refrigerants, J. Phys. Chem. B 116 (19) (2012) 5744–5751.

[21] N. Zhang, L. Chen, J. Mizukado, H. Quan, H. Suda, Rate constants for the gas-phase reactions fo (*Z*)-$CF_3CH{=}CHF$ and (*E*)-$CF_3CH{=}CHF$ with OH radicals at 253–328 K, Chem. Phys. Lett. 621 (2015) 78–84.

[22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, F. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16, Wallingford, CT, 2016.

[23] S.F. Boys, F. Bernardi, The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors, Mol. Phys. 19 (4) (1970) 553–566.

[24] A. Bondi, van der Waals volumes and radii, J. Phys. Chem. 68 (3) (1964) 441–451.

[25] M.D. Marshall, H.O. Leung, C.E. Calvert, Molecular structure of the argon-(*Z*)-1-chloro-2-fluoroethylene complex from chirped-pulse and narrow-band Fourier transform microwave spectroscopy, J. Mol. Spectrosc. 280 (2012) 97–103.

[26] H.O. Leung, M.D. Marshall, J.P. Messinger, G.S. Knowlton, K.M. Sundheim, J.C. Cheung-Lau, The microwave spectra and molecular structures of 2-chloro-1,1-difluoroethylene and its complex with the argon atom, J. Mol. Spectrosc. 305 (2014) 25–33.

[27] H.O. Leung, D. Gangwani, J.-U. Grabow, Nuclear quadrupole hyperfine structure in the microwave spectrum of Ar–N_2O, J. Mol. Spectrosc. 184 (1) (1997) 106–112.

[28] J.K.G. Watson, Aspects of quartic and sextic centrifugal effects on rotational energy levels, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, Elsevier Scientific Publishing, Amsterdam, 1977, pp. 1–89.

[29] H.M. Pickett, The fitting and prediction of vibration-rotation spectra with spin interactions, J. Mol. Spectrosc. 148 (2) (1991) 371–377.

[30] J. Kraitchman, Determination of Molecular Structure from Microwave Spectroscopic Data, Am. J. Phys. 21 (1) (1953) 17–24.

[31] Z. Kisiel, Least-squares mass-dependence molecular structures for selected weakly bound intermolecular clusters, J. Mol. Spectrosc. 218 (1) (2003) 58–67.

[32] Z. Kisiel, PROSPE - Programs for ROtational SPEctroscopy, http://info.ifpan.edu.pl/~kisiel/prospe.htm (accessed April 26, 2020).

[33] C.C. Costain, Determination of molecular structures from ground state rotational constants, J. Chem. Phys. 29 (4) (1958) 864–874.