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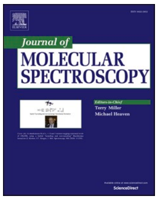

The microwave spectra and molecular structures of (*Z*)-1-chloro-3,3,3-trifluoropropene and its gas-phase heterodimer with the argon atom

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A B S T R A C T

The microwave spectra of (*Z*)-1-chloro-3,3,3-trifluoropropene and its gas-phase heterodimer with the argon atom in the 5.6 to 18.1 GHz frequency range are first observed and assigned using broadband, chirped pulse, Fourier transform microwave (FTMW) spectroscopy. Subsequent analysis of higher-resolution spectra obtained between 5 and 21 GHz with a narrowband, Balle-Flygare FTMW instrument provides spectroscopic constants, including nuclear quadrupole coupling constants, for five isotopologues of the propene molecule and two isotopologues of the complex with argon. Structural parameters obtained from these spectra show the existence of an intramolecular hydrogen bond between one of the fluorine atoms of the trifluoromethyl group and the hydrogen atom on the adjacent carbon atom. No evidence is seen for internal rotation of the trifluoromethyl group. The location of the argon atom in the heterodimer is consistent with the expectation that it will be positioned so to interact with the greatest number of heavy atoms, and in particular, the polarizable chlorine atom.

1. Introduction

Following our exploration of the manner in which a haloethylene interacts with a simple protic acid [1], we have begun to examine the larger halopropene systems by adding a fluoromethyl (CH_nF_{3-n}) group to the haloethylenes. Our purpose is to observe how different functional groups compete and/or cooperate with each other in intermolecular interactions. The introduction of additional F atoms both provides additional nucleophilic sites to potentially interact with a protic acid and affects the electron density distribution in the rest of the molecule. By combining our findings on haloethylene complexes and halopropene complexes, we seek to obtain a deeper understanding into the intricate balance of intermolecular forces.

Here, we turn to (*Z*)-1-chloro-3,3,3-trifluoropropene, which is the result of replacing an H atom of vinyl chloride, or equivalently, the F atom of (*Z*)-1-chloro-2-fluoroethylene with a CF_3 group. These two ethylenes (along with another notable exception, *cis*-1,2-difluoroethylene [2,3]) behave differently from the majority of fluoroethylenes that contain at least one H atom in their interactions with protic acids such as HF, HCl, and HCCH. For the majority of complexes studied so far, the binding mode of the acid to vinyl fluoride [4–7], 1,1-difluoroethylene [8–10], *trans*-1,2-difluoroethylene [11,12], and 1,1,2-trifluoroethylene [13–15] is independent of acid identity. Specifically, the binding of the acid is to an F, H pair across the double bond for the first three fluoroethylenes, and to a geminal F, H pair for 1,1,2-trifluoroethylene. For vinyl chloride [16–19] and (*Z*)-1-chloro-2-fluoroethylene [20,21], however, the binding modes are different for different acids. By placing a CF_3 substituent *cis* to the Cl atom, we wish to investigate how differently (*Z*)-1-chloro-3,3,3-trifluoropropene interacts with protic acids from its two ethylene counterparts. First, however, we need to characterize the rotational spectra of this propene, and, because we use argon as a carrier gas in our system, the argon complex of the propene. This is a necessary first step to facilitate the searches for and analyses of the propene-acid complexes. Furthermore, the structure of the propene thus determined will be foundational to future work, and the structure of the argon complex will inform us how it interacts via dispersion interactions.

2. *Ab initio* calculations

Our experimental work is guided by theory at the MP2/6–311++G (2d,2p) level with GAUSSIAN 16 [22]. We start by determining the ease of internal rotation of the CF_3 group in (*Z*)-1-chloro-3,3,3-trifluoropropene and thereby, the possible structures of the molecule.

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Using the atom labeling system shown in Fig. 1, we take one of the F atoms and scan the dihedral angle it forms with C-3, C-2, C-1 from 0° to 360° in steps of 10° while optimizing all other structural parameters. The resulting potential energy curve (Fig. 1), not surprisingly, shows the three-fold symmetry of the molecule. Each of the three equivalent equilibrium structures has a symmetry plane that contains all but two of the F atoms (Fig. 1), and the values for the structural parameters are listed in Table 1. The F atom residing in the symmetry plane, F-1. is only 2.4453 Å from H-2, a favorable interaction length for an intramolecular hydrogen bond, and the distance between each out-of-plane F atom and the Cl atom is 3.2108 Å, equivalent to the sum of the van der Waals radii of the two atoms [23]. (The atomic positions in the inertial axis system of the molecule are available as Supporting Information.) Each potential maximum corresponds to a structure where the planar F atom is 2.9265 Å from the Cl atom, with the other two F atoms forming bifurcated hydrogen bonds, each with a length of 2.6364 Å, with H-2. Thus, this configuration suffers from steric crowding between F and Cl and contains weaker hydrogen bonds. Because the barrier to internal rotation, 266 cm^{-1} (3.18 kJ mol^{-1}), is relatively high, we do not expect the CF_3 group to rotate freely. In the presence of the symmetry plane, the *c*-component of the dipole moment for the equilibrium structure of the molecule vanishes, but the values for the *a*- and *b*-components are quite large: 1.185 and 2.481 D, respectively. The values for the *A*, *B*, and *C* rotational constants are 4376, 1377, and 1284 MHz.

To explore the possible configurations of the Ar-(*Z*)-1-chloro-3,3,3-trifluoropropene complex, we use the inertial axis system of the propene as a reference, and optimize the distance between Ar and the origin (the center of mass of the propene), *R*, while scanning the polar angle (θ, formed between *R* and the *c* axis) from 5° to 175° and the azimuthal angle (ϕ, formed by the *a* axis and the projection of *R* onto the *a*-*b* plane) from 0° to 360°, each in 10° increments. The resulting interaction potential energy contour (Fig. 2) is symmetrical about the symmetry plane of the propene, that is, $\theta = 90°$, and shows five unique minima. The structures corresponding to these minima are then optimized (Fig. 3), labeled in order of increasing energy as Isomers (a) – (e). The more significant intermolecular distances are indicated in the figures, and the distances between Ar and the heavy atoms are listed in Table 2. The atomic positions for each isomer in its inertial axis system are available as Supporting Information.

Of the five isomers of the argon complex, four of them, Isomers (b) – (e) have argon residing in the symmetry plane of the propene. They are 79 – 133 cm^{-1} higher in energy than Isomer (a), or when corrected for zero-point energies, 81 – 136 cm^{-1} higher than that for Isomer (a), where Ar is located out of the symmetry plane (Table 3). The two equivalent global minima in the potential energy contour (Fig. 2), both labeled (a), represent Ar located on one side or the other of the symmetry plane. These configurations are equivalent (in fact, are mirror images of each other) and are not distinguishable spectroscopically.

Table 1

Structural parameters for (*Z*)-1-chloro-3,3,3-trifluoropropene obtained using *ab initio* calculations and from a structure fit to the moments of inertia of five isotopologues of the molecule.[a]

	Theory	Experiment[b]
C-1–C-2 / Å	1.3321	1.3384(62)
C-1–H-1 / Å	1.0769	[1.0769]
C-1–C1 / Å	1.7260	1.7111(27)
C-2–H-2 / Å	1.0779	[1.0779]
C-2–C-3 / Å	1.4938	1.4909(32)
C-3–F-1 / Å	1.3470	[1.3470]
C-3–F-2 / Å	1.3445	[1.3445]
C-3–F-3 / Å	1.3445	[1.3445]
∠H-1C-1C-2 / °	121.14	[121.14]
∠ClC-1C-2 / °	124.86	124.57(18)
∠H-2C-2C-1 / °	118.85	[118.85]
∠C-3C-2C-1 / °	124.88	124.87(23)
∠F-1C-3C-2 / °	109.77	109.9504(44)
∠F-2C-3C-2 / °	112.52	112.6970[c]
∠F-3C-3C-2 / °	112.52	112.6970[c]
∠F-1C-3C-2C-1 / °	180.00	[180.00]
∠F-2C-3C-2C-1 / °	60.57	[60.57]
∠F-3C-3C-2C-1 / °	−60.57	[−60.57]

[a] Except for F-2 and F-3, all atoms are planar in the theoretical equilibrium structure and are fixed as such for the experimental average structure.

[b] 1σ standard deviations in the parameters are given in parentheses. The parameters placed in square brackets are fixed to the *ab initio* values.

[c] Because of symmetry, the bond angles, ∠F-2C-3C-2 and ∠F-3C-3C-2, are restricted to have the same value, which is 2.7466° greater than the ∠F-1C-3C-2 angle, as given by ab initio calculation.

Because argon interacts solely via dispersion interaction, the most favorable interactions it forms involve polarizable heavy atoms (the most polarizable atom of the propene here is Cl) and π electrons. Isomer (a) is the only structure that shows argon interacting with 4 heavy atoms, including the Cl atom and the ethylenic π bond; thus, it is reasonable that it is the most stable isomer. In Isomers (b) – (d), argon interacts with fewer heavy atoms, and not simultaneously with the Cl atom and both carbon atoms connected by the double bond. [It is worth

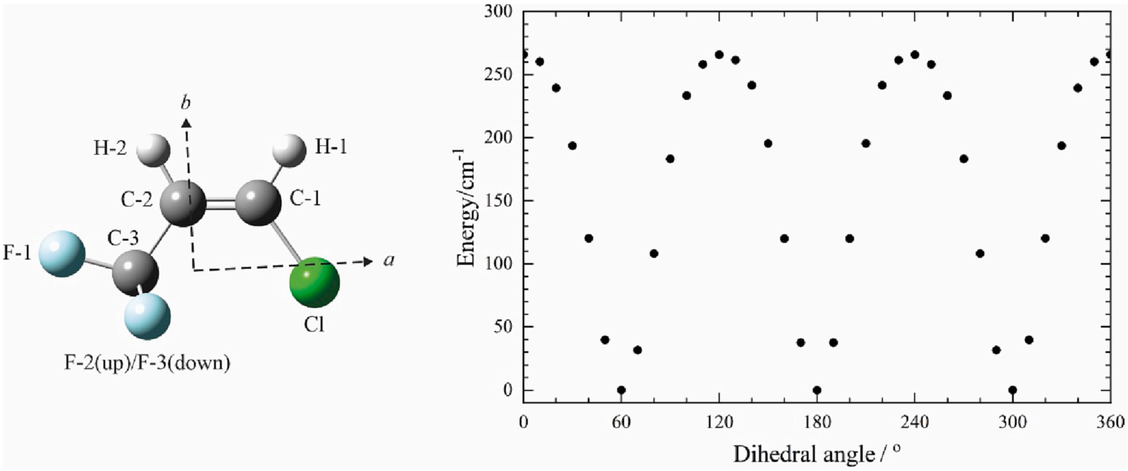


Fig. 1. A relaxed scan of the dihedral angle formed by one of the F atoms, C-3, C-2, and C-1 in (*Z*)-1-chloro-3,3,3-trifluoropropene. The angle is scanned from 0° to 360° in steps of 10°. There are three equivalent minima, each corresponds to a structure with a symmetry plane (formed by the *a* and *b* inertial axes) containing all the atoms except two F atoms. The atom labeling scheme of one of these equivalent, equilibrium, structures is shown, with the out-of-plane F atoms labeled as F-2 and F-3. Atom colors: C, dark gray; H, light gray; Cl, green; 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.)

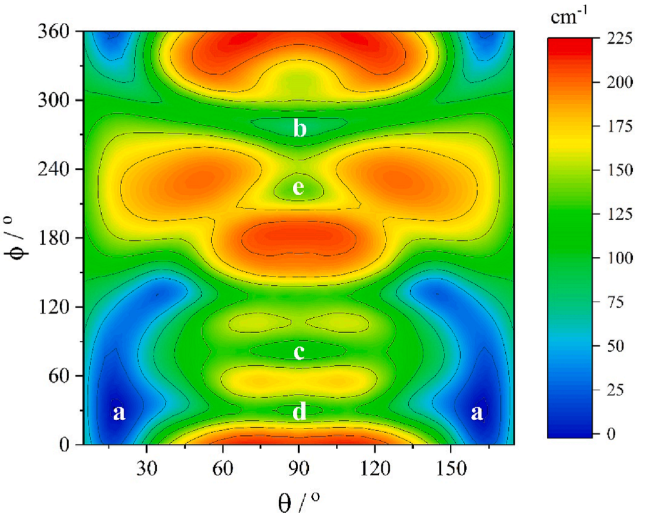


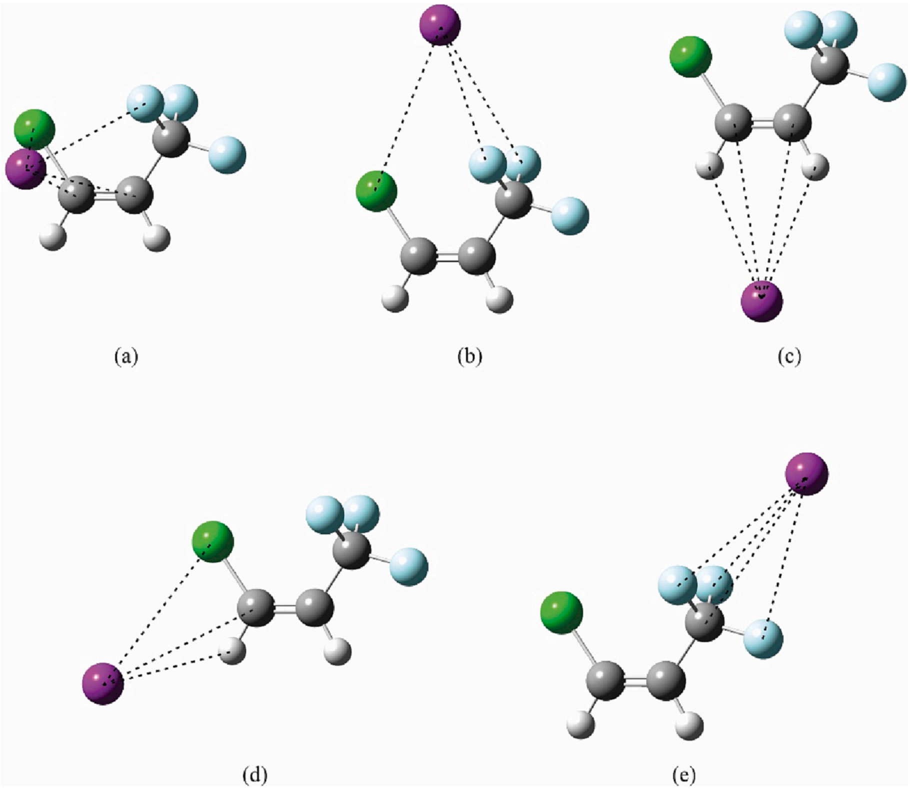
Fig. 2. A contour plot of the potential energy describing the interaction between argon and (*Z*)-1-chloro-3,3,3-trifluoropropene. The position of the argon atom is specified with respect to the inertial axis system of the propene (Fig. 1). The distance, *R*, between argon and the center of mass of the axis system forms a polar angle (θ) with the *c* axis and its projection in the *a*-*b* plane of the propene forms an azimuthal angle (ϕ) with respect to the *a* axis. The value of *R* is optimized at each pair of values for θ and ϕ. Five unique minima are identified in the contour plot.

mentioning that there are Ar-H interactions in Isomers (c) and (d), with lengths between 3.0 and 3.1 Å.] Although Isomer (e) has 4 Ar-heavy atom interactions, none of them involve Cl or the doubly-bonded carbon atoms. These isomers are easily distinguishable spectroscopically: the rotational constants of Isomers (c) – (e) are very different from those of Isomers (a) and (b) (Table 3). The similarity of the constants for Isomers (a) and (b) – differing only between 2% and 4% – is not a concern because their dipole moment components are very different. While the spectrum of Isomer (a) should have all three types of transitions, with *c*-type predicted to be much stronger than *a*- and *b*-types because the *c*-component of the dipole moment is more than twice as large as each of the other two components. On the other hand, Isomer (b) should have strong *a*- and *b*-type transitions; *c*-type transitions should be absent because the complex possesses a symmetry plane (Table 3). Additionally, the chlorine nuclear quadrupole coupling constants for these two isomers are different (see Supporting Information). Consequently, they have different spectral signatures.

We have found in our work that the energy ordering of isomers can change upon correcting for basis set superposition error (BSSE). Thus, we also optimize the five isomers of the Ar-(*Z*)-1-chloro-3,3,3-trifluoropropene complex with the correction [24]. Interestingly, Isomer (d) no longer corresponds to a potential minimum. The interaction lengths between argon and the heavy atoms in the propene for the other 4 isomers with BSSE correction are listed in Table 2. In each case, the distance between Ar and a heavy atom becomes longer by 2% – 7% with the correction, and the values of the rotational constants, dipole moment components, and relative energies of the isomers are shown in Table 3. (The atomic positions and nuclear quadrupole coupling constants for each species in its inertial axis system are available as Supporting Information). The energy ordering of the isomers does not change, but Isomers (b) and (c) are now almost isoenergetic. With the additional inclusion of zero-point correction, Isomers (b) and (c) are still very close in energy, but the ordering does switch. Nevertheless, Isomer (a) remains the most stable structure, more than 57 cm^{-1} lower in energy than the other isomers. Under our experimental conditions, it is therefore likely that we can only observe Isomer (a), but we are mindful to look for other possible isomers.

3. Experiment

Initial spectroscopic work on (*Z*)-1-chloro-3,3,3-trifluoropropene and its argon complex is carried out using a broadband, chirped-pulse


(a) (b) (c)

(d) (e)

Fig. 3. The optimized structures (without BSSE correction) corresponding to the minima found in the potential scans displayed in Fig. 2. Argon is in the symmetry plane of the propene in all isomers expect Isomer (a). The more important intermolecular interactions (arbitrarily chosen to have a distance no more than 15% greater than the sum of the van der Waals radii of the respective atoms) are indicated using dashed lines. Atom colors: C, dark gray; H, light gray; Cl, green; 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

Interaction lengths in Ångstroms between Ar and heavy atoms in five isomers of Ar-(*Z*)-1-chloro-3,3,3-trifluoropropene obtained from *ab initio* calculations. The experimental results come from a fit to the moments of inertia of two isotopologues of the complex.

	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction
	Isomer (a)		Isomer (b)		Isomer (c)	
Ar–C-1	3.717	3.819	5.051	5.209	3.878	3.997
Ar–C-2	3.901	4.042	5.100	5.280	3.886	4.010
Ar–C-3	4.250	4.421	4.169	4.358	5.281	5.403
Ar-Cl	3.928	4.013	3.897	4.019	5.488	5.601
Ar–F-1	4.975	5.150	5.129	5.318	5.494	5.606
Ar–F-2	3.476	3.654	3.552	3.733	6.071	6.192
Ar–F-3	5.288	5.451	3.552	3.733	6.071	6.192
	Isomer (d)[a]		Isomer (e)		Experiment	
Ar–C-1	3.872	–	6.197	6.419	3.6172(58)	
Ar–C-2	5.112	–	5.323	5.561	3.8388(67)	
Ar–C-3	6.374	–	3.829	4.067	4.28922(52)	
Ar-Cl	3.953	–	6.158	6.341	3.9044(19)	
Ar–F-1	7.434	–	3.573	3.822	5.0145(28)	
Ar–F-2	6.669	–	3.554	3.765	3.6007(60)	
Ar–F-3	6.669	–	3.554	3.765	5.3421(31)	

[a] The structure corresponding to isomer (d) is not at a potential minimum when BSSE correction is taken into account.

Table 3

Rotational constants, dipole moment components, and relative equilibrium and zero-point corrected energies for five isomers of the complex between argon and (*Z*)-1-chloro-3,3,3-trifluoropropene 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
	Isomer (a)		Isomer (b)		Isomer (c)	
A/MHz	1440	1454	1412	1416	1407	1406
B/MHz	826	775	859	797	561	538
C/MHz	615	588	589	560	432	418
$\|\mu_a\|$ / D	0.959	0.981	2.116	2.098	2.794	2.781
$\|\mu_b\|$ / D	0.759	0.749	1.800	1.810	0.605	0.618
$\|\mu_c\|$ / D	2.407	2.408	0.000	0.000	0.000	0.000
E_{equil}[a,b] / cm^{-1}	0.0	0.0	79.2	59.2	106.1	59.3
E_{zpe}[a,c]/ cm^{-1}	0.0	0.0	81.4	61.9	110.2	57.3
	Isomer (d)[d]		Isomer (e)			
A/MHz	3112	–	2509	2420		
B/MHz	411	–	555	523		
C/MHz	388	–	494	466		
$\|\mu_a\|$ / D	2.135	–	2.324	2.371		
$\|\mu_b\|$ / D	1.786	–	1.533	1.448		
$\|\mu_c\|$ / D	0.000	–	0.000	0.000		
E_{equil}[a,b] / cm^{-1}	114.8	–	132.7	105.2		
E_{zpe}[a,c] / cm^{-1}	117.0	–	135.6	115.2		

[a] The energies for each calculation method are given relative to the values obtained using the same calculation method for the most stable isomer. These are –1400.951139 Hartree, –1400.950378 Hartree, –1400.902383 Hartree, and –1400.901566 Hartree for E_{equil}, E_{equil} + BSSE, E_{zpe}, and E_{zpe} + BSSE, respectively.

[b] The equilibrium energy is determined by using the equilibrium structure of (*Z*)-1-chloro-3,3,3-trifluoropropene and optimizing the intermolecular degrees of freedom with argon, without and with BSSE correction, respectively.

[c] The equilibrium structure and energy of the complex are calculated while allowing a full relaxation of the complex geometry, including the structural parameters of (*Z*)-1-chloro-3,3,3-trifluoropropene. (These differs slightly from those found when (*Z*)-1-chloro-3,3,3-trifluoropropene is fixed to its equilibrium structure, as in the preceding line.) A harmonic zero-point correction to the energy is calculated for this structure, which is included in both columns for each isomer, as is a counterpoise correction for BSSE, which is included in the second column for each.

[d] The structure corresponding to isomer (d) is not at a potential minimum when BSSE correction is taken into account.

Fourier transform microwave spectrometer operating from 5.6 to 18.1 GHz [25–27]. A gas sample of 1% (*Z*)-1-chloro-3,3,3-trifluoropropene diluted in argon is introduced into the spectrometer via a pulsed-valve expansion using two valves, each equipped with a 0.8-mm orifice and a backing pressure of 1 atm. The spectrum is obtained in four segments (5.6 – 7.6, 7.6 – 10.1, 10.1 – 14.1, and 14.1 – 18.1 GHz), the frequencies obtained in each case by mixing a chirped microwave pulse of 4 µs duration and the appropriate frequency range with the output of phase-locked dielectric resonator oscillators at 10.6, 12.6, 14.6, and 18.6 GHz, respectively, and isolating the lower sideband, which is amplified to 20 – 25 W of power with a solid state amplifier to polarize the sample. The resulting free-induction decay (FID) is digitized at 50 Gs s^{-1} starting 0.5 µs after the end of the excitation pulse and continuing for 10 µs. Ten polarization-digitization cycles are performed for each 800 µs opening of the pulsed valves which operate at 4 Hz, and approximately 310,000 to 740,000 FIDs are averaged for each segment. The averaged FID is apodized, zero-filled and Fourier transformed, as described previously [26], to give a frequency domain spectrum with a resolution element of 23.84 kHz and typical line widths of 250 kHz. Using the guidance from theory, we are able to observe 5 isotopologues of the propene (the most abundant species, and 4 species singly substituted with ^{37}Cl and ^{13}C in natural abundance) and 2 isotopologues of the argon complex (the most abundant species and its ^{37}Cl isotopolgue). Fig. 4 shows a small portion of the spectrum, illustrating transitions from various species. Because chlorine quadrupole hyperfine components are often blended together, we turn to the narrowband, Balle-Flygare Fourier transform microwave spectrometer to better resolve these components.

The narrowband spectrometer operates from 5 to 21 GHz, and utilizes one pulsed-valve with a 0.8-mm orifice mounted behind one of the mirrors that forms the resonant cavity [26,28]. The sample mixture composition is similar to that used in the chirped pulse instrument, but a backing pressure 2 – 3 atm is employed. The background-corrected time domain signals are digitized for 1024 data points and zero-filled to a 2048-point record length before Fourier transformation to give frequency domain signals with a resolution element of 4.8 kHz. The higher resolution of this instrument can be observed in the inset of Fig. 4, where one of the transitions of 6_{42}–5_{32} for Ar-CH^{35}ClCHCF$_3$ observed with the chirped pulse instrument is resolved into two Doppler doublets by the narrowband instrument. In the end, we collect, with the narrowband instrument, the spectra of all species observed earlier in the chirped pulse spectrometer, and all analyses are done with the higher resolution data.

4. Results

4.1. Spectral analysis

4.1.1. (Z)-1-chloro-3,3,3-trifluoropropene

For the most abundant isotopologue of (*Z*)-1-chloro-3,3,3-trifluoropropene, 925 hyperfine components from 154 rotational transitions, representing a *J* range of 0 – 16 and a K_a range of 0 – 5, have been observed and analyzed. There are fewer rotational transitions, namely, 134, for the ^{37}Cl isotopologue, and about half of that for each ^{13}C isotopologue. The transitions are *a*- and *b*- types, and in general, *b*-type transitions are much stronger than *a*-type, as predicted by theory. The absence of *c*-type transitions is consistent with the existence of a symmetry plane in the molecule.

The spectrum for each species is analyzed using the Watson *S*-reduced Hamiltonian [29,30] in the I^r representation with the inclusion of chlorine nuclear quadrupole coupling interaction and Pickett's nonlinear least squares SPFIT program [31]. We determine 3 rotational constants, 5 quartic centrifugal distortion constants, and all non-zero chlorine nuclear quadrupole coupling constants (the symmetry of the molecule requires the values of χ_{ac} and χ_{bc} to be 0) with an rms deviation of 2 kHz or less. The spectroscopic constants are reported in Table 4 and tables of observed and calculated transition frequencies are available as Supporting Information.

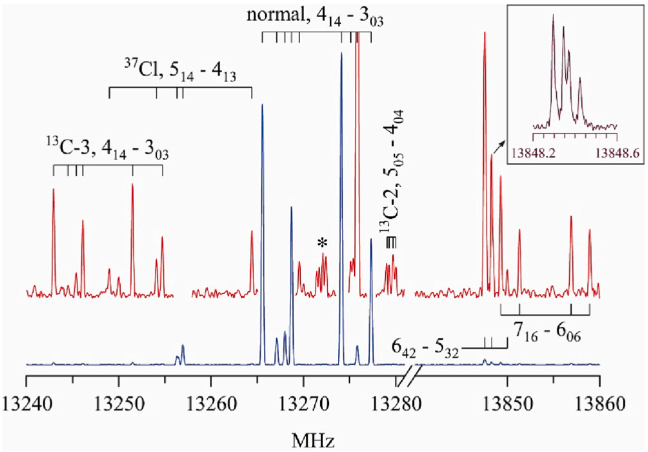


Fig. 4. Blue: a portion of the chirped pulse spectrum showing transitions mainly from the most abundant isotopologue of (*Z*)-1-chloro-3,3,3-trifluoropropene. Red: upon 50-fold magnification, transitions from the lesser abundant isotopologues and the argon complex are apparent. The combs above the transitions show the monomeric species and the rotational assignments. The 5_{24} – 4_{23} and 5_{05} – 4_{04} transitions (starred) due to the ^{13}C-1 and ^{13}C-3 isotopologues are barely resolvable. The combs below the transitions label those from Ar-(*Z*)-CH^{35}ClCHCF$_3$. One of these lines, when observed using the narrowband instrument, resolve into two Doppler doublets (inset). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.1.2. Ar-(Z)-1-chloro-3,3,3-trifluoropropene

For the most abundant isotopologue of the argon complex of (*Z*)-1-chloro-3,3,3-trifluoropropene, 491 hyperfine components in 126 rotational transitions (strong *c*-type, weaker *a*- and *b*-types) are observed and analyzed, whereas the number of rotational transitions, all *c*-type transitions, is only ~ 1/3 as many for the ^{37}Cl isotopologue. The transitions for the most abundant species sample a *J* range of 2 – 10 and a K_a range of 0 – 7. Using once again the Watson *S*-reduced Hamiltonian [29,30] in the I^r representation with the inclusion of chlorine nuclear quadrupole coupling interaction and Pickett's nonlinear SPFIT program [31], we fit 3 rotational constants, 5 quartic centrifugal distortion constant, the diagonal and two off-diagonal nuclear quadrupole coupling constants for each isotopologue. For the most abundant species, two sextic centrifugal distortion constants are also determined. The rms deviation for each fit is 1.3 kHz. The spectroscopic constants are reported in Table 5 and tables of observed and calculated transition frequencies are available as Supporting Information.

4.2. Structure determination

4.2.1. (Z)-1-chloro-3,3,3-trifluoropropene

The values of the planar moment, $P_{cc}\left(=\Sigma m_i c_i^2\right)$ for the five isotopologues of (Z)-1-chloro-3,3,3-trifluoropropene range from 44.3456 to 44.3504 u Å^2. This small range indicates that the *c* coordinates of all the atoms in the molecule remain practically unchanged upon a single isotopic substitution in Cl or in any C atom. This is consistent with the fact that these atoms lie in the *a*-*b* plane, as suggested by theory. The lack of *c*-type transitions lends further support to the existence of this plane of symmetry. Additional confirmation of the symmetry plane is provided by treating the most abundant species as the parent, and determining the Kraitchman substitution coordinates [32] for the Cl and C atoms in its principal axis system (Table 6). In each case, the *c* coordinate of the atom is nonphysical, indicating that the atom lies in or is very close to the *a*-*b* plane. The imaginary value arises because the minor isotopologue and the most abundant species exhibit slightly different zero-point motions, which causes the assumptions inherent in the Kraitchman analysis to fail when the coordinate in question has a value close to zero. The *a* coordinate of C-2 and *b* coordinate of C-3 are also nonphysical, suggesting that they, too, are nearly zero, and that these atoms lie on or close to the *b* axis and the *a* axis, respectively.

Restricting all but two F atoms to be co-planar, we fit 6 structural parameters: the C-1–C-2, C-2–C-3, C-1–Cl bond lengths and the ClC-1C-2, C-3C-2C-1, and F-1C-3C-2 angles to the 15 moments of inertia of the 5 isotopologues using Kisiel's STRFIT program [33]. The F-1C-3C-2 angle is restricted to be 2.7466° greater than the other two FC-3C-2 angles, as suggested by theory. The rms deviation is 0.0073 u Å^2 and the experimental structural parameters are listed in Table 1. The fitted values are very similar to those given by theory. The average coordinates of the Cl and C atoms are listed in Table 6 and they agree excellently with the Kraitchman coordinates, and indeed, the magnitudes of the average *a* coordinate of C-2 and *b* coordinate of C-3 are small, consistent with the Kraitchman analysis. The coordinates for all atoms are available as Supporting Information.

4.2.2. Ar-(Z)-1-chloro-3,3,3-trifluoropropene

The experimental rotational constants of Ar-CH^{35}ClCHCF$_3$ agree

Table 4

Spectroscopic constants (in MHz, unless otherwise noted) for five isotopologues of (*Z*)-1-chloro-3,3,3-trifluoropropene.[a]

	$CH^{35}ClCHCF_3$	$CH^{37}ClCHCF_3$	$^{13}CH^{35}ClCHCF_3$	$CH^{35}Cl^{13}CHCF_3$	$CH^{35}ClCH^{13}CF_3$
A	4387.269400(64)	4379.777969(63)	4339.24272(13)	4333.51074(14)	4387.69088(14)
B	1381.699344(15)	1348.992528(16)	1376.148357(47)	1381.722996(52)	1377.794739(48)
C	1288.385357(14)	1259.279256(17)	1279.400625(42)	1283.715455(46)	1284.994091(47)
D_J / 10^{-3}	0.313221(75)	0.30435(11)	0.30947(40)	0.31289(43)	0.31376(42)
D_{JK} / 10^{-3}	4.24534(56)	4.13091(76)	4.0307(39)	4.0760(36)	4.2264(33)
D_K / 10^{-3}	−3.6541(41)	−3.5225(44)	−3.439(14)	−3.475(15)	−3.701(16)
d_1 / 10^{-3}	−0.026932(17)	−0.025788(31)	−0.02664(28)	−0.02768(33)	−0.02605(33)
d_2 / 10^{-3}	0.0132019(70)	0.012162(11)	0.01338(26)	0.01402(26)	0.01339(26)
χ_{aa} [b]	8.77847(68)	6.49389(65)	9.3560(12)	8.7222(14)	8.7718(13)
χ_{bb} [b]	−39.18025(77)	−30.46004(74)	−39.7677(12)	−39.1301(14)	−39.1779(12)
χ_{cc} [b]	30.40179(75)	23.96616(73)	30.4117(13)	30.4080(14)	30.4061(14)
$\lvert\chi_{ab}\rvert$	51.9948(85)	41.093(32)	51.573(71)	51.979(71)	51.966(65)
No. of rotational transitions	154	134	64	65	65
No. of *a* type	43	47	30	31	31
No. of *b* type	111	87	34	34	34
No. of hyperfine components	925	789	254	265	260
J range	0 – 16	0 – 13	0 – 8	0 – 8	0 – 8
K_a range	0 – 5	0 – 5	0 – 3	0 – 3	0 – 3
rms/kHz	2.18	1.89	1.64	1.85	1.69

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

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

Table 5

Spectroscopic constants (in MHz, unless otherwise noted) for the complex formed by argon and (*Z*)-1-chloro-3,3,3-trifluoropropene.[a,b]

	$Ar\text{-}CH^{35}ClCHCF_3$	$Ar\text{-}CH^{37}ClCHCF_3$
A	1475.617913(70)	1440.725810(89)
B	812.245669(23)	811.728880(56)
C	611.925891(22)	605.78134(17)
D_J / 10^{-3}	1.48694(14)	1.4729(16)
D_{JK} / 10^{-3}	−2.1408(16)	−2.2186(50)
D_K / 10^{-3}	8.1103(29)	8.0667(49)
d_1 / 10^{-3}	−0.533534(80)	−0.54147(94)
d_2 / 10^{-3}	−0.049419(31)	−0.04981(16)
H_{KJ} / 10^{-6}	−0.970(45)	[−0.970]
H_K / 10^{-6}	0.982(47)	[0.982]
χ_{aa} [c]	28.0334(23)	22.0237(35)
χ_{bb} [c]	9.5902(16)	7.1919(25)
χ_{cc} [c]	−37.6236(14)	−29.2156(17)
$\lvert\chi_{ac}\rvert$	22.74(12)	17.82(53)
$\lvert\chi_{bc}\rvert$	46.9903(91)	37.19(11)
No. of rotational transitions	126	47
No. of *a* type	41	0
No. of *b* type	18	0
No. of *c* type	67	47
No. of hyperfine components	491	179
J range	2 – 10	2 – 9
K_a range	0 – 7	0 – 5
rms/kHz	1.34	1.29

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

[b] Constants that cannot be fitted are fixed to those appropriate to the most abundant isotopologue and enclosed by square brackets.

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

Table 6

The coordinates of the carbon and chlorine atoms in (*Z*)-1-chloro-3,3,3-trifluoropropene determined from the structure fit[a] and from Kraitchman analysis.[b]

	a / Å	*b* / Å
From structure fit		
C-1	1.2206(16)	1.1335(27)
C-2	−0.1163(63)	1.1963(23)
C-3	−1.02506(19)	0.01440(28)
Cl	2.12428(51)	−0.31954(24)
Substitution coordinates[c,d]		
C-1	1.2151(12)	1.1359(13)
C-2	nonphysical	1.1989(13)
C-3	−1.0227(15)	nonphysical
Cl	2.12264(71)	−0.3226(47)

[a] In the equilibrium structure of the molecule, these atoms are in the symmetry plane of the propene, and are fixed to be so in the determination of the average structure. As such, the *c* coordinate of each is 0.

[b] The *c* substitution coordinates for these atoms are all nonphysical, indicating they lie in the *a-b* plane.

[c] Costain errors [42] in the parameters are given in parentheses.

[d] Although only the absolute values of the substitution coordinates can be determined from the Kraitchman analysis, the relative signs are assigned using physically reasonable atomic distances.

better with the theoretical rotational constants for Isomer (a) than with those for Isomer (b): the difference between corresponding experimental and theoretical constants is 0.5 – 2.4% for Isomer (a) and 3.7 – 5.8% for Isomer (b). Additionally, the observation of *c*-type transitions confirms that the spectrum is due to Isomer (a), where Ar is located out of the symmetry plane, instead of Isomer (b), where Ar is in the symmetry plane.

After establishing the general position of argon, we determine its location using Kisiel's STRFIT program [33]. We assume that the average structure of (*Z*)-1-chloro-3,3,3-trifluoropropene remains unchanged upon complexion, and fit the position of argon to 6 moments of inertia from two isotopologues of the complex. Ar is found to be located 3.6036 Å out of the symmetry plane of the propene, almost directly above C-1 (Fig. 5), and its distances from the heavy atoms in the propene are calculated using Kisiel's EVAL program [34,35] and listed in Table 2. The experimental distances are similar to those predicted theoretically. The atomic coordinates are available as Supporting Information. The rms deviation for the fit is 0.144 u Å^2.

4.3. Chlorine nuclear quadrupole coupling constants

Because all nonzero components of the nuclear quadrupole coupling tensor for (*Z*)-1-chloro-3,3,3-trifluoropropene are available experimentally, we are able to determine the values for the principal nuclear quadrupole coupling components, χ_{xx}, χ_{yy}, and χ_{zz}, and they are 30.4018, 42.0570, and –72.4588 MHz, respectively, for the most abundant species. Here, the *x* principal electric field gradient (efg) axis is perpendicular to the molecular symmetry plane, whereas the *z* principal

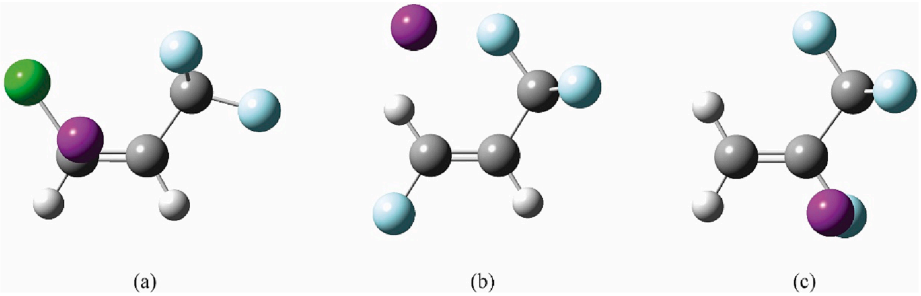


Fig. 5. The experimental structures of the argon complexes of (a) (*Z*)-1-chloro-3,3,3-trifluoropropene, (b) (*E*)-1,3,3,3-tetrafluoropropene [39], and (c) 2,3,3,3-tetrafluoropropene [40]. All atoms, except two F atoms and Ar lie in the plane of the page. Atom colors: C, dark gray; H, light gray; Cl, green; 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.)

efg axis forms an angle of 0.74° with the C-Cl bond. In other words, the z axis lies practically on the C-Cl bond.

Spectroscopically, we are not able to determine the sign of χ_{ab} for (*Z*)-1-chloro-3,3,3-trifluoropropene, as is the case for the signs of all off-diagonal components of the nuclear quadrupole coupling tensors for any molecule. The signs are only relevant when the quadrupole coupling tensors of two related species are compared. For example, in the absence of electric field gradient perturbation, the principal nuclear quadrupole coupling constants for the Cl atom will be the same for (*Z*)-$CH^{35}ClCHCF_3$ and its argon complex. Experimentally, these constants are determined as second-rank tensor projections onto the inertial axis system of the molecule under investigation. Thus, the quadrupole coupling tensor of the two species are related by a rotation. This rotation is represented by the same rotation matrix that transforms the inertial axis system of the monomer to that of the dimer and can be readily determined. Using the directions of the axis system indicated in Fig. 1 for the monomer and applying the rotation matrix to the quadrupole coupling tensor of the monomer, we have found that a positive value of χ_{ab} best reproduces the quadrupole coupling constants of the argon complex. A negative value for χ_{ab} of the monomer gives constants for the argon complex that do not resemble the experimental values. Additionally, the rotation shows that the signs for χ_{ac} and χ_{bc} in the complex are both negative.

5. Discussion

The experimental rotational constants of the most abundant isotopologue of (*Z*)-1-chloro-3,3,3-trifluoropropene agree remarkably well with those predicted theoretically for the equilibrium structure. The values of the corresponding *A*, *B*, and *C* constants differ by 11, 5, and 5 MHz, or 0.26%, 0.36%, and 0.36%, respectively. Thus, the geometric parameters of the experimental average structure and the equilibrium structure predicted at our level of theory differ only slightly. The experimental structure shows that the intramolecular hydrogen bond between F-1 and H-2 has a favorable distance of 2.4463(67) Å, and each out-of-plane F atom is 3.2037(28) Å from the Cl atom. We do not observe any evidence of internal rotation of the CF_3 group.

Theory also provides excellent assistance for our search for the argon complex. In fact, the experimental rotational constants for this species and those for the equilibrium structure of Isomer (a) [in which (*Z*)-1-chloro-3,3,3-trifluoropropene is fixed to its equilibrium structure] computed without BSSE correction, agree to 36, 14, and 3 MHz, respectively, for the *A*, *B*, *C* constants. These translate to 2.4%, 1.7%, and 0.5% of the experimental values. The prediction with BSSE correction does not in general do quite as well, differing by 22, 37, and 24 MHz (or 1.5, 4.6, and 3.9 %) from the experimental values. In the experimental structure (Fig. 5 and Table 2), Ar interacts most strongly with C-1: at a distance of 3.6172(58) Å, it is only 0.04 Å longer than the van der Waals contact between the two atoms [23]. Other interactions are important as well, although perhaps less so. The Ar–C-2, Ar–Cl, and Ar–F-2 distances are only 7.2, 7.6, and 13.6% longer than the corresponding van der Waals contacts [23]. As discussed earlier for Isomer (a), experimentally, argon appears to be positioned to interact with the greatest number of heavy atoms, including the most polarizable atom, Cl, in (*Z*)-1-chloro-3,3,3-trifluoropropene. Its proximity to C-1 and C-2 suggests that it also interacts with the π electron density.

Indeed, argon has been observed typically to interact with the greatest number of heavy atoms in haloethylenes by positioning above the XC=CY or XCY (where X and Y are halogen atoms) cavity in 1,1-difluoroethylene and 1,1,2-trifluoroethylene [36], in *cis*-1,2-difluoroethylene [37], in (*Z*)-1-chloro-2-fluoroethylene [26], and in 2-chloro-1,1-difluoroethylene [27]. In the case of (*E*)-1-chloro-1,2-difluoroethylene, however, even though the FCCF cavity contains more heavy atoms, the binding is to the FCCl cavity, which contains the more polarizable Cl atom [38]. The same trends are followed in halopropenes with a trifluoromethyl group: the system reported here, (*E*)-1,3,3,3-tetrafluoropropene [39], and 2,3,3,3-tetrafluoropropene [40] (Fig. 5). Each of the two tetrafluoropropenes has a symmetry plane that contains the F atom closest to the H atom connected to C-1; this is unlike the case for (*Z*)-1-chloro-3,3,3-trifluoropropene, where the F atom in the symmetry plane is closest to the H atom connected to C-2. Argon is positioned to interact with two F atoms and all three C atoms in these tetrafluoropropenes, and the interaction lengths are approximately 15% or less than the corresponding van der Waals contact [23].

To examine how the trifluoromethyl group affects the nucleophilicity of the fourth halogen atom in the three propenes, we map the electrostatic potential onto the total electron density of each molecule at the MP2/6–311++G(2d,2p) level (Fig. 6). The electron density appears to be similar for the four F atoms in 2,3,3,3-tetrafluoropropene; when the F atom connected to C-2 is placed on C-1, giving (*E*)-1,3,3,3-tetrafluoropropene, however, it becomes less nucleophilic while the F atoms in the CF_3 group become more nucleophilic. We have suggested that hyperconjugation is likely to be responsible in moving the electron density from the F atom connected to C-1 to the F atoms in the CF_3 group [41]. The F atoms in the CF_3 group are even more nucleophilic in (*Z*)-1-chloro-3,3,3-trifluoropropene, an indication that hyperconjugation, together with the fact that the fourth halogen atom, Cl, is quite polarizable, work cooperatively to render the F atoms very nucleophilic. The combination of electrostatic and steric requirements of this molecule should make the study of its intermolecular interactions with protic acids rather illuminating.

6. Conclusion

The microwave spectra for five isotopologues of (*Z*)-1-chloro-3,3,3-trifluoropropene and two isotopologues of its gas-phase heterodimer with the argon atom have been obtained and analyzed. Theoretical predictions of the equilibrium structures of both the monomeric halopropene and the argon complex at the MP2/6–311++G(2d,2p) level of theory provide rotational constants that are very close to the experimentally-determined constants for the ground-state,

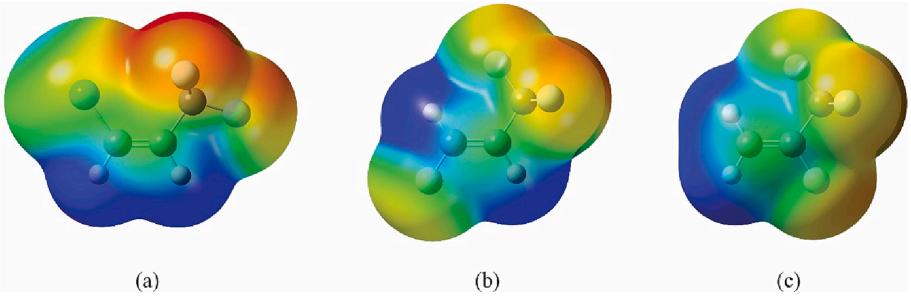


Fig. 6. The electrostatic potential surface mapped onto a total electron density isosurface for (a) (*Z*)-1-chloro-3,3,3-trifluoropropene, (b) (*E*)-1,3,3,3-tetrafluoropropene, and (c) 2,3,3,3-tetrafluoropropene. The same value of electron density is used for the isosurface in all three molecules and identical color scales are used. 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.)

vibrationally-averaged structure. This close agreement provides significant assistance in identifying and assigning the spectra. Applying the correction for basis set superposition error (BSSE) results in less favorable agreement between the two sets of constants, but does not change the predicted energy ordering of the various isomers of the argon complex, although one structure no longer corresponds to a local minimum in the BSSE-corrected interaction surface. The ordering of the second and third higher energy isomers do switch with the inclusion of zero-point energy effects.

The analyses of the spectra provide structural parameters for the halopropene and for the argon complex as well as the complete chlorine nuclear quadrupole coupling tensor for the monomer. (*Z*)-1-chloro-3,3,3-trifluoropropene possesses a plane of symmetry containing all but two of the fluorine atoms of the trifluoromethyl group, which “straddle” the chlorine atom. One of the principal axis for the nuclear quadrupole coupling tensor lies very nearly along the C–Cl bond, and a second is necessarily perpendicular to the molecular symmetry plane. Although only two of the three non-zero off-diagonal values of the quadrupole coupling tensor are able to be determined from the spectrum of the argon complex, the tensor of this species is found to be the result of a simple rotation of the inertial axis system between the monomer and complex.

The observed structure of Ar-(*Z*)-1-chloro-3,3,3-trifluoropropene is consistent with the expectation that the argon atom will interact with the greatest number of heavy atoms, and particularly the more polarizable chlorine atom, so to enhance the opportunity for favorable dispersion interactions. The presence of the chlorine atom in the propene molecule also renders the trifluoromethyl fluorine atoms more nucleophilic than they are in the two tetrafluoropropenes, (*E*)-1,3,3,3-tetrafluoropropene and 2,3,3,3-tetrafluoropropene.

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. **Seohyun Hong:** Formal analysis, Investigation. **Laboni Hoque:** 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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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