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The microwave spectra and molecular structures of the chiral and achiral rotamers of 2,3,3-trifluoropropene and their gas-phase heterodimers with the argon atom

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ABSTRACT

The microwave spectra of two rotamers, connected by rotation of the $-CHF_2$ group, of 2,3,3-trifluoropropene and all three of the singly substituted ^{13}C isotopologues of each are obtained in the 5.6 – 18.1 GHz region using broadband chirped pulse Fourier transform microwave spectroscopy. The lower energy rotamer, stabilized by a weak intermolecular hydrogen bond, is chiral, existing as a pair of enantiomers, while the higher energy isomer, lacking this interaction but having a plane of symmetry, is achiral. Heterodimers of both rotamers with the argon carrier gas are also observed in the broadband spectrum and further analyzed using spectra obtained from 5.0 to 20.6 GHz with a Balle-Flygare cavity Fourier transform microwave spectrometer. Although all singly substituted ^{13}C isotopologues are observed, in addition to the normal species, for the argon complex with the lower energy rotamer, only a single isotopologue of the argon complex, the parent, is observed with the higher energy rotamer. Despite differing slightly in detail, the argon atom occupies a similar position in the heterodimer with each rotamer, one that is also similar to the location of the argon atom in argon-2,3,3,3-tetrafluoropropene.

1. Introduction

Our investigations of the delicate balance of the attractive and repulsive forces operative in the intermolecular interactions between haloethylenes and protic acids show both predictable outcomes in accord with "chemical intuition" and unexpected, surprising motifs in the resulting van der Waals molecules [1]. To further our understanding of the different factors at play, we have begun consideration of systems in which one of the substituents of a haloethylene is formally replaced by a fluoromethyl (CH_nF_{3-n}) group. This choice extends the ethylene to a propene, and the fluoromethyl group is expected to be heavy enough to prevent observable effects of internal rotation that would complicate the rotational spectrum, while supplying additional nucleophilic atoms potentially to interact with the protic acid. Before commencing work on the propene-protic acid complexes, it is important to examine the structure of the propene in question. Furthermore, because our experiments use argon as a carrier gas, it is also helpful to identify the spectrum of the argon-propene complex to allow for easier identification of transitions originating from the propene-acid complex. The study of the argon complex also serves another important purpose: it allows us to determine how the propene interacts via dispersion forces with a large, structureless atom.

We have previously determined the structures of two propenes, 2,3,3,3-tetrafluoropropene [2,3] and (*E*)-1,3,3,3-tetrafluoropropene [4], and their argon complexes. Both monomers have the same groups attached to the ethylenic carbons, but the relative locations of the F atom and the $-CF_3$ substituent are different. As such, they greatly affect the electron density distribution of each other. Specifically, when these groups are geminal, as in 2,3,3,3-tetrafluoropropene, the F atom substituent is more nucleophilic than when the two groups are located *trans* to each other as in (*E*)-1,3,3,3-tetrafluoropropene. The opposite is true for the F atoms in the $-CF_3$ groups: they are less nucleophilic in 2,3,3,3-tetrafluoropropene than in (*E*)-1,3,3,3-tetrafluoropropene. This is likely a result of hyperconjugation, which allows the $-CF_3$ group to move electron density away from the F substituent through the C=C bond when they are *trans* to each other. *Ab initio* calculations using the MP2/6–311++G(2d,2p) model chemistry reveals two possible isomers of Ar-2,3,3,3-tetrafluoropropene and three possible isomers of Ar-(*E*)-1,3,3,3-

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tetrafluoropropene. Experimentally, we observe the isomer with Ar located away from the symmetry plane of each propene and interacting with several heavy atoms simultaneously.

We are particularly interested in using substituents to tune the electron density of a molecule and then studying how its ability to form intermolecular interactions is affected. Here, we seek to examine how 2,3,3-trifluoropropene, with one fewer F in the "–CF_3" group, behaves differently than 2,3,3,3-tetrafluoropropene in its intermolecular interaction with Ar.

2. *Ab initio* calculations

To ascertain the ease of –CHF_2 internal rotation in 2,3,3-trifluoropropene and by extension, the structures of the possible rotamers of the molecule, we carry out *ab initio* calculations at the MP2/6–311++G (2d,2p) level with GAUSSIAN 16 [5] where we optimize all other structural parameters while scanning the F8-C3-C2-C1dihedral angle (Fig. 1) from 0° to 360° in steps of 10°. The resulting potential energy curve is shown in Fig. 1. Three minima are located, and after a full optimization, they are found to occur at the dihedral angles of 1.7°, 116.8°, and 238.9°. The structures at 1.7° [labeled Rotamer (i)] and 116.8° are chiral, and are enantiomers of each other. As such, they have identical rotational spectra. The structure at 238.9°, labeled Rotamer (ii), is 90 cm^{-1} higher in energy, and has a plane of symmetry. [When harmonic zero point energy correction is considered, Rotamer (ii) is 96 cm^{-1} higher in energy than Rotamer (i).] The barrier between Rotamer (i) and its mirror image is ~ 760 cm^{-1}, while the barrier between each of these species and Rotamer (ii) is ~ 1240 cm^{-1}. Thus, the –CHF_2 group does not freely rotate, and we should be able to observe both Rotamers (i) (and its indistinguishable mirror image) and (ii) if both remain populated in the supersonic expansion in our spectrometers. (The atomic positions in the principal axis systems of these two rotamers are available as Supporting Information.) For convenience, we will label these two species as 233TFP(i) and 233TFP(ii), respectively. The rotational constants and dipole moment components of these two rotamers are listed in Table 1. 233TFP(i) and 233TFP(ii) should both have strong *b*-type transitions. Additionally, for the former species, *c* and *a*-type transitions should also be observable while for the latter, only *a*-type transitions are additionally possible. The structural parameters for the two rotamers of 2,3,3-trifluoropropene are listed in Table 2.

In 233TFP(i), except for F9, all heavy atoms are nearly planar while in 233TFP(ii), all atoms but F8 and F9 are planar. Otherwise, the structures of these two rotamers are practically the same, apart from the obvious difference of the orientation of the –CHF_2 group. Specifically, the bond distances between a C atom and another heavy atom (C or F) in one rotamer differ from the corresponding one in the other rotamer by

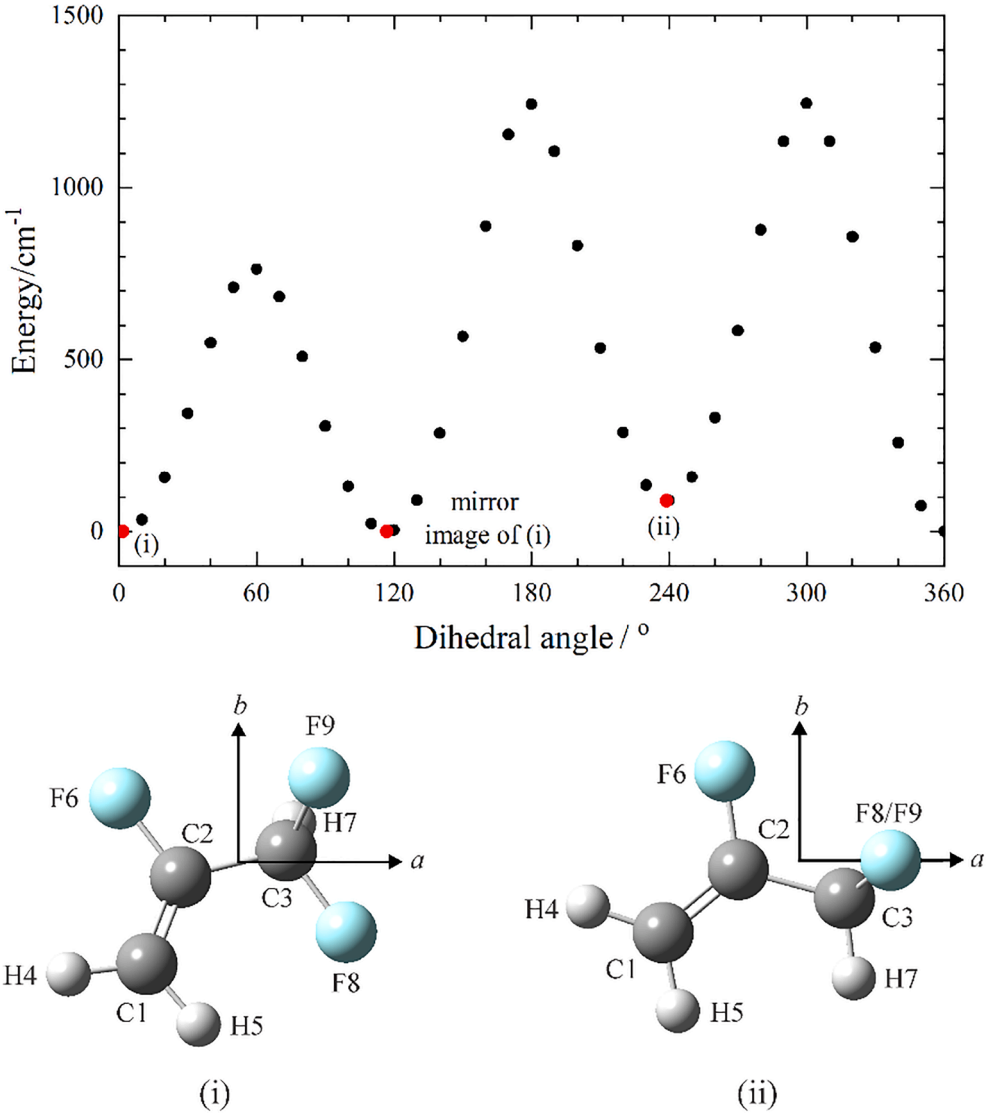

Fig. 1. A relaxed scan of the dihedral angle formed by F8, C3, C2, and C1 in 2,3,3-trifluoropropene. The angle is scanned from 0° to 360° in steps of 10°. Three minima are optimized and are displayed in red. Two of the corresponding structures, Rotamers (i) and (ii), together with their *a* and *b* principal axes are shown. [In Rotamer (ii), F8 and F9 are, respectively, above and below the symmetry plane of the molecule.] The third structure is a mirror image of Rotamer (i) and is not shown. Atom colors: C, dark gray; H, light gray; F, light blue.

Table 1
Rotational constants, dipole moment components, and relative energies (equilibrium and zero-point corrected)[a] for two rotamers of 2,3,3-trifluoropropene obtained from *ab initio* calculations at the MP2/6–311++G(2d,2p) level.

	233TFP(i)	233TFP(ii)
A / MHz	5177	5307
B / MHz	3191	2683
C / MHz	2187	2631
$\lvert\mu_a\rvert$ / D	0.79	1.66
$\lvert\mu_b\rvert$ / D	1.23	2.68
$\lvert\mu_c\rvert$ / D	0.92	0.00
E_{equil} / cm^{-1}	0.0	90.3
E_{zpe} / cm^{-1}	0.0	96.1

[a] The energies are given relative to the values for the more stable isomer, –414.882253 Hartree for E_{equil} and –414.824099 Hartree for E_{zpe}.

Table 2
Structural parameters for the each of the two diastereomic rotamers of 2,3,3-trifluoropropene obtained using *ab initio* calculations and from a structure fit to the moments of inertia of four isotopologues of the molecule.

	233TFP(i)[a]		233TFP(ii)[b]	
	Theory	Experiment[c]	Theory	Experiment[c]
C1 – C2 / Å	1.3241	1.3342(51)	1.3267	1.3330(14)
C2 – C3 / Å	1.4961	1.4809(42)	1.4913	1.4798(29)
C1 – H4 / Å	1.0767	[1.0767]	1.0766	[1.0766]
C1 – H5 / Å	1.0751	[1.0751]	1.0763	[1.0763]
C2 – F6 / Å	1.3493	[1.3493]	1.3424	[1.3424]
C3 – H7 / Å	1.0861	[1.0861]	1.0854	[1.0854]
C3 – F8 / Å	1.3593	[1.3593]	1.3638	1.36241(89)[d]
C3 – F9 / Å	1.3655	[1.3655]	1.3638	1.36241(89)[d]
∠H4C1C2 / °	120.44	[120.44]	121.00	[121.00]
∠H5C1C2 / °	119.02	[119.02]	119.20	[119.20]
∠F6C2C1 / °	122.17	121.21(21)	122.09	121.28(12)
∠C3C2C1 / °	127.28	127.67(18)	124.92	125.337(28)
∠H7C3C2 / °	112.62	[112.62]	111.81	[111.81]
∠F8C3C2 / °	110.04	110.17(40)	110.08	110.56(10)[d]
∠F9C3C2 / °	109.44	110.47(45)	110.08	110.56(10)[d]
∠H7C3C2C1 / °	123.37	[123.37]	0.00	[0.00]
∠F8C3C2C1 / °	1.71	3.42(26)	−121.09	[−121.09]
∠F9C3C2C1 / °	−116.85	−114.77(44)	121.09	[121.09]

[a] The C atoms, H4, H5, and F6 are essentially coplanar in the theoretical equilibrium structure: the dihedral angle formed by H4(or H5), C1, C2, and C3 and by H4, C1, C2, F6 differ from planarity by less than 1°. These six atoms are fixed to coplanarity in finding the experimental average structure.

[b] The C atoms, H4, H5, and F6 are coplanar in the theoretical equilibrium structure and are fixed as such for the experimental average structure.

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

[d] Because of symmetry, the bond lengths C3-F8 and C3-F9 are fixed to be the same, and the angles F8C3C2 and F9C3C2 are also fixed to be the same.

no more than 0.1% – 0.5%, and the bond angles formed by F8 (or F9) with C3 and C2 in the two rotamers differ by only 0.04 – 0.6%. The major (yet still small) difference is the C1-C2-C3 angle, which is 2.4° (1.9%) greater in 233TFP(i), and arises most likely so to allow a favorable interaction between H5 and F8 while avoiding steric crowding. This intramolecular hydrogen bond in 233TFP(i) is rather short (2.4536 Å); thus, it is stronger than that potentially formed by F6 and H7 (2.6202 Å). At first glance then, the stability of 233TFP(i) relative to 233TFP(ii) appears to come from these two intramolecular hydrogen bonds which are not possible in the latter. The energy difference of 90 cm^{-1} (1.1 kJ mol^{-1}), however, is too small if hydrogen bonds are the only contributing factor to the relative stability. Therefore, other factors must be at play. For example, in 233TFP(i), F8 is 2.7732 Å and 2.3410 Å from C1 and C2, respectively, shorter than the 3.17 Å van der Waals contact between C and F [6]. These steric repulsive interactions are absent in 233TFP(ii) where H7 takes the place of F8. A noncovalent interaction (NCI) analysis [7] performed using Multiwfn [8] and visualized with Chimera [9] (Figures S1 and S2 in the Supporting Information) on the two rotamers supports these ideas, showing for 233TFP(i) a weak hydrogen bonding interaction (regions of low reduced density gradient with moderately large electron density, ρ, and negative value for the second largest eigenvalue of the Hessian matrix of electron density) between F8 and H5 and some weak steric repulsion (regions of low reduced density gradient with moderately large electron density, ρ, and positive value for the second largest eigenvalue of the Hessian matrix of electron density) between F8 and the center of the C1=C2 double bond. For 233TFP(ii) no regions of intramolecular noncovalent interaction, neither attractive nor repulsive, are apparent.

The interaction potential between argon and each of the 2,3,3-trifluoropropene rotamers is explored, once again, with *ab initio* calculations at the MP2/6–311++G(2d,2p) level, by placing argon at various polar and azimuthal angles with respect to the *c* inertial axis and the *a*-*b* plane of the propene and optimizing the distance of argon from the origin, that is, the center of mass of the propene. The structure of the propene subunit for any experimentally observed argon complex should be nearly identical to the vibrationally averaged structure of the propene, but for this initial theoretical search for possible isomers, we fix the propene to its equilibrium structure. The resulting potential energy contour plot (Fig. 2) for Ar and 233TFP(i) shows three minima while that for Ar and 233TFP(ii) shows six minima, of which only four are distinct diastereomers. The isomers are labeled, in order of increasing energy, for Ar-233TFP(i), from (a) to (c), and for Ar-233TFP(ii), from (d) to (g). As a result of the symmetry plane in 233TFP(ii), each of Isomers (d) and (e) has a corresponding, spectroscopically indistinguishable enantiomer.

The structures of these seven distinct isomers of argon complexes are then optimized and shown in Fig. 3. Table 3 lists the distances between Ar and the heavy atoms in the respective propenes and Tables 4 and 5 list the energies, rotational constants, and dipole moment components of these complexes. Because we have found that in some instances, basis set superposition error (BSSE) can be important in assessing the relative stability of van der Waals molecules, we carry out the correction for the isomers [10], and provide the results of these calculations in Tables 3 – 5 as well. As we have observed previously in other argon complexes, the argon-heavy atom distances are generally longer when BSSE correction is made. In particular, for Isomers (a) – (g), the distances are 0.12 – 0.24 Å longer with the correction, leading to, in general, smaller rotational constants. Regardless whether the BSSE correction is applied or not, the energy ordering of the isomers remains the same; namely, for Ar-233TFP (i), Isomer (a) is at the global minimum, whereas for Ar-233TFP(ii), Isomer (d) is the most stable. Furthermore, upon a harmonic correction to the zero-point energy, with or without BSSE correction, the energy ordering of Isomers (a) – (c) for Ar-233TFP(i) does not change (Table 4). The same is true for Isomers (d) and (e) for Ar-233TFP(ii). Isomers (f) and (g) remain higher in energy than (d) and (e), but the ordering of the former two is switched when zero-point energy correction is taken (Table 5). We are, of course, mindful that the energy differences among all isomers are too small for the energy ordering to be definitively determined using theory, but because these isomers have vastly different rotational constants and dipole moment components, we should be able to identify the structures of the ones we can observe.

3. Experiment

Both the 2,3,3-trifluoropropene monomer and its argon complex are studied using a mixture of 2/3% of the propene in argon. Two Fourier transform microwave spectrometers are used in this work: a broadband, chirped-pulse instrument operating from 5.6 to 18.1 GHz [2,11,12] and a narrow band, Balle-Flygare instrument operating from 5.0 to 20.6 GHz [11,13]. In each case the gas sample of 2,3,3-trifluoropropene in argon is introduced into the spectrometer via a pulsed-valve expansion through a 0.8-mm orifice utilizing a backing pressure of 2 – 3 atm. The broadband instrument uses two pulsed values while the narrow band instrument

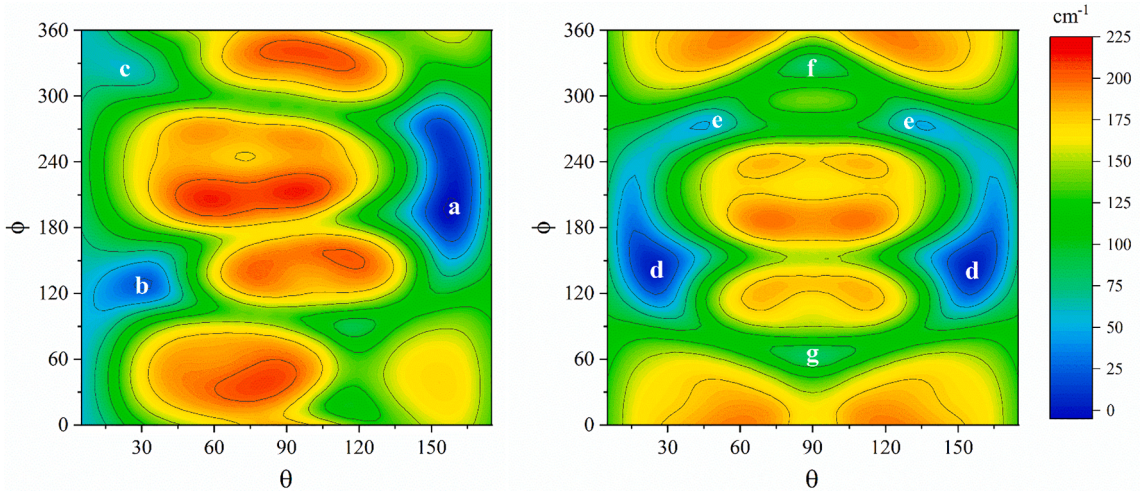

Fig. 2. Contour plots of the potential energy describing the interaction between argon and each of the two rotamers of 2,3,3-trifluoropropene. The distance between argon and the center of mass of the inertial system of each rotamer (shown in Fig. 1), *R*, forms a polar angle (θ) with the *c* axis and its projection in the *a*-*b* plane of the propene forms an azimuthal angle (ϕ) with respect to the *a* axis. The value of θ is scanned from 5° to 175° and that of ϕ from 0° to 360°, both in 10° increments, while allowing *R* to optimize. Three and four significant minima are observed, respectively, with Rotamer (i), or 233TFP(i) (left) and Rotamer (ii), or 233TFP(ii) (right).

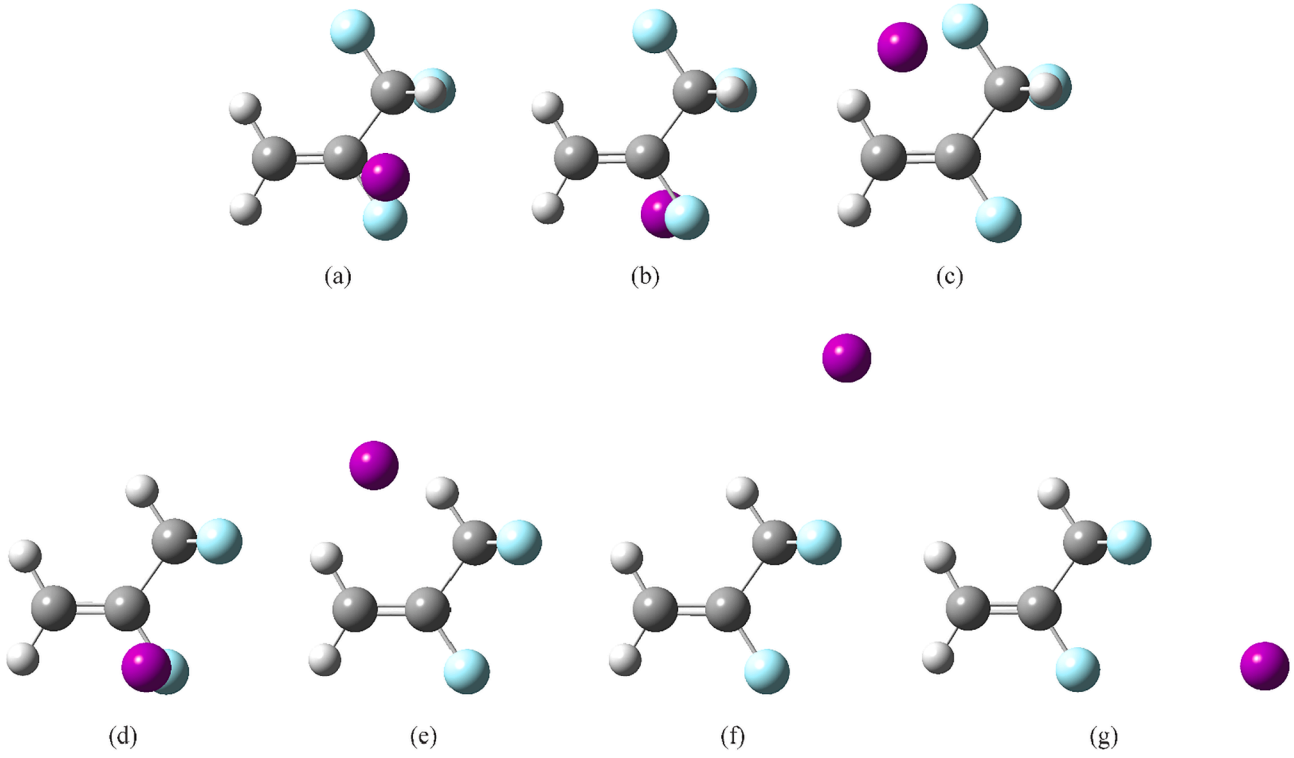

Fig. 3. The optimized structures (without BSSE correction) corresponding to the minima found in the potential scans displayed in Fig. 2. Isomers (a) – (c) and (d) – (g) correspond to the isomers of the argon complexes of 233TFP(i) and 233TFP(ii), respectively. Argon is away from the plane formed by the three C atoms in Structure (a) – (e), but share the same plane as these atoms in Isomers (f) and (g). Atom colors: C, dark gray; H, light gray; F, light blue; Ar, purple.

has only one, mounted behind one of the two mirrors forming the resonator cavity.

Initially, a broadband spectrum is obtained as three 4.0 or 4.5 GHz segments that are appended to each other. The sample is polarized using a chirped microwave pulse of 4 μs duration and 20 – 25 W of power. Digitization at 50 Gs s^{-1} of the resulting free induction decay (FID) is started 0.5 μs after the end of the excitation pulse and continues for 20 μs. Ten polarization-digitization cycles are performed for each 800 μs opening of the pulsed valves which operate at 4 Hz. Approximately 1,700,000 to 1,800,000 FIDs are averaged for each segment, and as described previously [11] the average is apodized, zero-filled, and Fourier transformed to give a frequency domain spectrum with a resolution element of 11.92 kHz and typical line widths (FWHM) of 125 kHz. Using this procedure, we estimate the uncertainty in frequency measurement to be 5 – 10 kHz.

In the broadband spectrum, we are able to observe both rotamers of the propene, 233TFP(i) and 233TFP(ii) and their ^{13}C isotopologues, as well as one argon complex each for the most abundant isotopologue of the two rotamers. An example of the quality of the spectrum can be found in Fig. 4. The transition frequencies obtained from the broadband

Table 3
Interaction lengths in Ångstroms between Ar and heavy atoms in three isomers of Ar-233TFP(i) [Isomers (a) – (c)] and in four isomers of Ar-233TFP(ii) [Isomers (d) – (g)] obtained from *ab initio* calculations. The experimental results come from a fit to the moments of inertia of four isotopologues of Ar-233TFP(i) and from the position of Ar that best reproduces the rotational constants of the most abundant isotopologue of Ar-233TFP(ii).

	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction			
	Isomer (a)		Isomer (b)		Isomer (c)		Experiment		
Ar − C1	4.062	4.204	3.974	4.108	3.901	4.022	4.0456(18)		
Ar − C2	3.582	3.731	3.634	3.797	4.002	4.188	3.60247(43)		
Ar − C3	3.814	3.947	4.190	4.374	3.931	4.141	3.84539(40)		
Ar − F6	3.562	3.703	3.490	3.633	4.875	5.078	3.6412(13)		
Ar − F8	4.398	4.518	4.909	5.087	3.628	3.790	4.3644(13)		
Ar − F9	4.974	5.104	3.526	3.710	3.507	3.749	5.0452(12)		
	Isomer (d)		Isomer (e)		Isomer (f)		Isomer (g)		Experiment
Ar − C1	3.985	4.108	3.953	4.098	5.774	5.916	5.607	5.799	4.2431
Ar − C2	3.630	3.784	4.058	4.255	5.081	5.249	4.311	4.508	3.6915
Ar − C3	4.170	4.339	3.731	3.910	3.619	3.795	4.034	4.237	4.2942
Ar − F6	3.471	3.617	5.066	5.299	5.914	6.100	3.466	3.642	3.1609
Ar − F8	3.536	3.704	3.511	3.738	3.576	3.759	3.574	3.764	3.6631
Ar − F9	5.259	5.431	5.016	5.177	3.576	3.759	3.574	3.764	5.0201

Table 4
Rotational constants, dipole moment components, and relative equilibrium and zero-point corrected energies for three isomers of the complex between argon and 233TFP(i) 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	2444	2424	2532	2534	2436	2428
B / MHz	945	894	1021	947	1009	932
C / MHz	879	833	904	848	920	851
$\lvert\mu_a\rvert$ / D	1.407	1.388	0.963	0.945	0.856	0.783
$\lvert\mu_b\rvert$ / D	0.091	0.131	1.375	1.380	0.611	0.670
$\lvert\mu_c\rvert$ / D	1.104	1.106	0.378	0.392	1.337	1.349
E_{equil} [a,b] / cm^{-1}	0.0	0.0	24.4	17.1	61.9	35.8
E_{zpe} [a,c] / cm^{-1}	0.0	0.0	24.6	20.5	50.3	29.1

[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 –941.860868 Hartree, –941.8600724 Hartree, –941.802517 Hartree, and –941.801668 Hartree for E_{equil}, E_{equil} + BSSE, E_{zpe}, and E_{zpe} + BSSE, respectively.
[b] This equilibrium energy is determined by using the equilibrium structure of 233TFP(i) 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 233TFP(i). (These differ slightly from those found when 233TFP(i) 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.

Table 5
Rotational constants, dipole moment components, and relative equilibrium and zero-point corrected energies for four isomers of the complex between argon and 233TFP(ii) 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	No BSSE Correction	BSSE Correction
	Isomer (d)		Isomer (e)		Isomer (f)		Isomer (g)	
A / MHz	2824	2832	2657	2660	4334	4270	3053	3036
B / MHz	989	922	913	841	706	666	968	894
C / MHz	854	805	780	726	682	643	848	789
$\lvert\mu_a\rvert$ / D	0.017	0.036	1.840	1.928	0.237	0.167	3.222	3.202
$\lvert\mu_b\rvert$ / D	1.785	1.781	1.713	1.719	3.073	3.080	0.067	0.006
$\lvert\mu_c\rvert$ / D	2.548	2.546	1.862	1.773	0.000	0.000	0.000	0.000
E_{equil} [a,b] / cm^{-1}	0.0	0.0	44.7	12.7	74.3	43.0	76.5	43.4
E_{zpe} [a,c] / cm^{-1}	0.0	0.0	39.1	9.2	72.9	41.7	68.7	38.2

[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 –941.860381 Hartree, –941.859599 Hartree, –941.802001 Hartree, and –941.801160 Hartree for E_{equil}, E_{equil} + BSSE, E_{zpe}, and E_{zpe} + BSSE, respectively.
[b] This equilibrium energy is determined by using the equilibrium structure of 233TFP(ii) 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 233TFP(ii). (These differ slightly from those found when 233TFP(ii) 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.

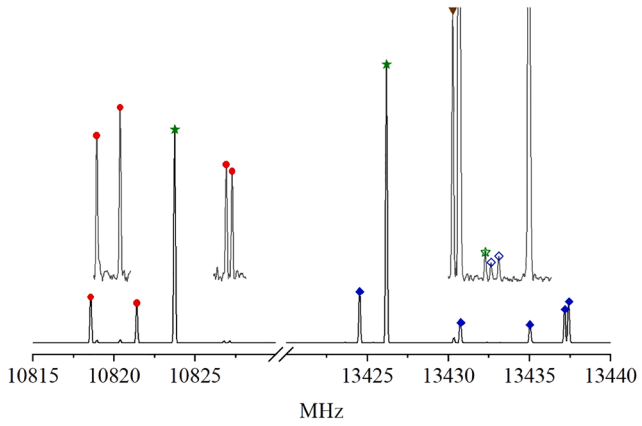

Fig. 4. A portion of the chirped pulse spectrum showing transitions arising from the most abundant and one of its ^{13}C isotopologues of 233TFP(i) (filled and hollow green stars), the most abundant and two of its ^{13}C isotopologues (filled blue and hollow blue diamonds) of 233TFP(ii), and the argon complexes of 233TFP(i) and 233TFP(ii) (red circles and brown triangle, respectively). The upper trace has been magnified 50 times.

spectra are used in the analyses for all the isotopologues of the monomeric species, but because the transitions of the argon complexes and their ^{13}C isotopologues are fewer and weaker in this spectrum, we turn to the more sensitive, higher resolution narrow band Balle-Flygare spectrometer for the analysis of their spectra.

The background-corrected time domain signals from the Balle-Flygare instrument 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. We are able to collect the spectra of the most abundant and ^{13}C isotopologues of Ar-233TFP(i), and of the most abundant isotopologue of Ar-233TFP(ii). Despite trying different combinations of argon and neon as a carrier gas, we were not able to observe the ^{13}C isotopologues of Ar-233TFP(ii).

4. Results

4.1. Spectral analysis

4.1.1. 2,3,3-Trifluoropropene

The transitions for both rotamers of 2,3,3-trifluoropropene sample large J and K_a ranges. For the most abundant species, the J ranges are 0 – 10 and 0 – 16, respectively, for 233TFP(i) and 233TFP(ii), while the K_a ranges are the same for both species, namely, 0 – 6. Because the ^{13}C-containing isotopologues are much less abundant, the J and K_a ranges covered are smaller (Tables 6 and 7). We observe 58 – 136 rotational transitions, all a, b, and c type for the four isotopologues of 233TFP(i). As predicted by theory, the b type transitions are the most intense, followed in turn by c and a type transitions. Fewer transitions are observed for the four isotopologues of 233TFP(ii): 36 – 93 a and b type transitions, with b type transitions being stronger. The absence of c type transitions is consistent with theory, supporting the presence of a symmetry plane in 233TFP(ii).

The value of the asymmetry parameter ultimately determined for each isotopologue of 233TFP(i) is between −0.35 and −0.33, while that for each of the 233TFP(ii) isotopologues is −0.96. Consequently, it was not surprising to find that the Watson A-reduced Hamiltonian [14,15] does not perform well for the analysis of 233TFP(ii). Thus, the Watson S-reduced Hamiltonian [14,16] is used with Pickett's nonlinear SPFIT program [17] for the analysis of the spectra for both rotamers. Nevertheless, for the sake of completeness, the results of analyses using the A-reduction are available as Supporting information.

For each isotopologue of 233TFP(i) the rotational constants and five quartic centrifugal distortion constants are determined and are listed in Table 6. The rms deviation of each fit is 4 kHz. The fits for each isotopologue of 233TFP(ii) determine the rotational constants and three quartic centrifugal distortion constants with an rms deviation of 3 – 5 kHz. The results of these fits appear in Table 7.

4.1.2. Ar-2,3,3-trifluoropropene

We observed 57 – 240 rotational transitions for the four isotopologues of the complex between argon and 233TFP(i) in the narrow band spectrometer, with the most abundant species sampling J and K_a ranges of 1 – 13 and 0 – 6, respectively, and smaller ranges for the ^{13}C-containing isotopologues (Table 8). Both a and c type transitions are observed for all isotopologues, but because b type transitions are very weak, they are observable only for the most abundant species. This is consistent with the theoretical prediction of the magnitudes of the dipole moment components of Isomer (a). The spectrum of each species is fitted, once again using the Watson S-reduced Hamiltonian [14,16] and Pickett's nonlinear SPFIT program [17]. We were initially surprised by the large number of centrifugal distortion constants required to fit the spectrum of the most abundant species: 5 quartic, 7 sextic, and 2 octic. To eliminate the possibility that transitions were incorrectly assigned, a closed-loop analysis of the transition frequencies is performed, but it provides no indication of inconsistencies. The large number of centrifugal distortion constants must therefore be an indication that argon exhibits large amplitude motion in the complex. Because many fewer transitions are observed for the ^{13}C-containing isotopologues, only 5 quartic and 2 sextic centrifugal constants are required to fit their spectra. The spectroscopic constants are given in Table 8. (Once again those obtained using the A-reduction are provided in the Supporting Information.) The rms deviation of each fit is 1 – 2 kHz.

Table 6
Spectroscopic constants (in MHz, unless otherwise noted) for four isotopologues of the 233TFP(i) rotamer.[a]

	CH_2CFCHF_2(i)	$^{13}CH_2CFCHF_2$(i)	$CH_2^{13}CFCHF_2$(i)	$CH_2CF^{13}CHF_2$(i)
A	5204.72103(27)	5102.85565(50)	5202.94083(43)	5196.47787(45)
B	3172.82369(15)	3139.20770(43)	3161.34764(29)	3162.03594(34)
C	2191.04473(11)	2159.86477(42)	2185.27714(25)	2186.99998(34)
D_J / 10^{-3}	1.0361(15)	1.013(20)	0.9965(70)	1.026(12)
D_{JK} / 10^{-3}	−0.5727(31)	−0.413(12)	−0.5450(82)	−0.5460(85)
D_K / 10^{-3}	1.0417(50)	0.681(35)	1.067(21)	1.055(23)
d_1 / 10^{-3}	−0.49292(35)	−0.4658(31)	−0.4868(18)	−0.4854(20)
d_2 / 10^{-3}	−0.17195(13)	−0.1697(11)	−0.17008(76)	−0.16876(69)
No. of rotational transitions	136	58	70	68
No. of a type	19	12	11	12
No. of b type	66	31	40	40
No. of c type	51	15	19	16
J range	0 – 10	0 – 9	0 – 9	0 – 9
K_a range	0 – 6	0 – 4	0 – 4	0 – 4
rms/kHz	3.75	3.85	3.96	4.06

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

Table 7
Spectroscopic constants (in MHz, unless otherwise noted) for four isotopologues of the 233TFP(ii) rotamer.[a]

	CH_2CFCHF_2(ii)[b]	$^{13}CH_2CFCHF_2$(ii)	$CH_2^{13}CFCHF_2$(ii)	$CH_2CF^{13}CHF_2$(ii)
A	5340.03378(28)	5290.14299(73)	5339.45560(57)	5326.09691(43)
B	2680.66377(19)	2633.21907(59)	2671.33281(36)	2675.39126(29)
C	2625.59785(19)	2568.29029(59)	2616.51995(38)	2617.04776(30)
D_J / 10^{-3}	1.1940(26)	1.111(28)	1.154(13)	1.173(11)
D_{JK} / 10^{-3}	0.6831(16)	0.771(14)	0.713(14)	0.7177(88)
d_2 / 10^{-3}	0.371658(24)	0.35121(66)	0.36613(66)	0.36978(39)
No. of rotational transitions	93	36	36	36
No. of *a* type	8	8	8	8
No. of *b* type	85	28	28	28
J range	0 – 16	0 – 8	0 – 8	0 – 9
K_a range	0 – 6	0 – 3	0 – 3	0 – 3
rms/kHz	4.09	4.75	3.99	3.23

[a] 1σ standard deviations in the parameters are given in parentheses.
[b] Because the *B* and *C* rotational constants are highly correlated, instead of fitting the three rotational constants separately, the combinations $A - (B + C)/2$, $(B + C)/2$, $(B - C)/4$ were fitted instead, and the rotational constants were derived from these linear combinations.

Table 8
Spectroscopic constants (in MHz, unless otherwise noted) for four isotopologues of the complex formed by argon and the 233TFP(i) rotamer.[a,b]

	Ar-CH_2CFCHF_2(i)	Ar-$^{13}CH_2CFCHF_2$(i)	Ar-$CH_2^{13}CFCHF_2$(i)	Ar-$CH_2CF^{13}CHF_2$(i)
A	2448.98689(26)	2405.02946(48)	2441.30421(37)	2444.52801(46)
B	936.664951(79)	931.948041(91)	935.677522(72)	934.500919(94)
C	865.938795(65)	862.91250(11)	864.329454(75)	863.667314(96)
D_J / 10^{-3}	3.23862(87)	3.19746(64)	3.19952(49)	3.24646(70)
D_{JK} / 10^{-3}	58.307(11)	56.324(24)	57.698(18)	57.831(22)
D_K / 10^{-3}	−33.683(17)	−33.140(45)	−33.133(34)	−33.107(45)
d_1 / 10^{-3}	−1.01767(42)	−0.95844(40)	−0.99909(30)	−1.02012(44)
d_2 / 10^{-3}	−0.21044(14)	−0.16341(29)	−0.20631(21)	−0.20725(29)
H_J / 10^{-6}	0.0369(37)	[0.0369]	[0.0369]	[0.0369]
H_{JK} / 10^{-6}	58.96(16)	55.70(15)	57.45(12)	59.11(15)
H_{KJ} / 10^{-6}	−267.26(41)	−246.5(19)	−258.1(14)	−262.9(19)
H_K / 10^{-6}	207.62(45)	[207.62]	[207.62]	[207.62]
h_1 / 10^{-6}	0.2498(20)	[0.2498]	[0.2498]	[0.2498]
h_2 / 10^{-6}	0.2434(11)	[0.2434]	[0.2434]	[0.2434]
h_3 / 10^{-6}	0.01045(30)	[0.01045]	[0.01045]	[0.01045]
L_{JJK} / 10^{-6}	−0.03812(73)	[−0.03812]	[−0.03812]	[−0.03812]
L_{JK} / 10^{-6}	−0.0977(33)	[−0.0977]	[−0.0977]	[−0.0977]
No. of rotational transitions	240	58	57	60
No. of *a* type	79	38	37	39
No. of *b* type	50	0	0	0
No. of *c* type	111	20	20	21
J range	1 – 13	1 – 9	1 – 9	1 – 9
K_a range	0 – 6	0 – 3	0 – 3	0 – 3
rms/kHz	2.09	1.63	1.20	1.56

[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.

For the most abundant species of Ar-233TFP(ii), 222 *b* and *c* type transitions are observed, with *c* type transitions stronger. The *J* range is 1 – 13 and K_a range is 0 – 5. No *a* type transitions were observable. This is consistent with Isomer (d) predicted theoretically. The transitions for the ^{13}C-containing isotopologues are too weak to be observed. The spectroscopic constants derived from the *S*-reduced Hamiltonian are listed in Table 9 and those from the *A*-reduced Hamiltonian are in Supporting Information. The rms deviation of the fit is 1 kHz. Once again, tables of observed and calculated transition frequencies using the *S*-reduced Hamiltonian with assignments for all isotopologues of both Ar-233TFP(i) and for Ar-233TFP(ii) studied are also provided as Supporting Information.

4.2. Structure determination

4.2.1. 2,3,3-Trifluoropropene

According to theory, the atoms connected to the ethylenic carbons are nearly planar in 233TFP(i). In determining an experimental structure for this molecule, we restrict these atoms to lie in a plane, and fit 2 bond lengths (C1-C2 and C2-C3), 4 bond angles (F6C2C1, C3C2C1, F8C3C2, and F9C3C2), and 2 dihedral angles (F8C3C2C1 and F9C3C2C1) to the 12 rotational constants of the 4 isotopologues using Kisiel's STRFIT program (Table 2) [18]. The rms deviation of the fit is 0.0037 u Å^2, and the coordinates of each atom are available as Supporting Information. The two hydrogen bonds formed by the –CHF_2 group and the ethylenic substituents are similar in length to those in the equilibrium structure predicted by the quantum chemistry calculations; namely, 2.4640 Å for H5-F8 and 2.6244 Å for H7-F6 in the average structure.

For 233TFP(ii), the atoms connected to the ethylenic carbons are planar in the theoretical structure, and we treat them as such in determining the experimental structure. This time, we fit 3 bond lengths (C1-C2, C2-C3, and C3-F8 which is restricted to be the same as C3-F9), and 3 angles (F6C2C1, C3C2C1, and F8C3C2 which is restricted to be the same as F9C3C2) with Kisiel's STRFIT program (Table 2) [18]. The rms deviation of the fit is 0.0029 u Å^2, and the coordinates of each atom are available as Supporting Information.

We have also determined the Kraitchman substitution coordinates [19] for the C atoms in the principal axis system of each rotamer, listing them in Table 10. For 233TFP(ii), the Kraitchman *c* coordinate of C2 is

Table 9
Spectroscopic constants (in MHz, unless otherwise noted) for the complex formed by argon and the 233TFP(ii) rotamer.[a]

	Ar-CH_2CFCHF_2(ii)
A	2818.119156(76)
B	982.116190(44)
C	845.855540(46)
D_J / 10^{-3}	2.30975(48)
D_{JK} / 10^{-3}	12.6453(18)
D_K / 10^{-3}	−0.2999(32)
d_1 / 10^{-3}	−0.43848(23)
d_2 / 10^{-3}	−0.075590(16)
H_J / 10^{-6}	−0.0388(17)
H_{JK} / 10^{-6}	−0.7562(97)
H_{KJ} / 10^{-6}	2.153(39)
h_1 / 10^{-6}	−0.0213(11)
No. of rotational transitions	222
No. of *b* type	100
No. of *c* type	122
J range	1 – 13
K_a range	0 – 5
rms/kHz	1.32

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

Table 10
The coordinates of the carbon atoms in the two rotamers of 2,3,3-trifluoropropene and the argon complex of the lower energy rotamer of 2,3,3-trifluoropropene determined from structure fits and from Kraitchman analyses.[a]

	a / Å	*b* / Å	*c* / Å
2,3,3-trifluoropropene(i)			
From structure fit			
C1	1.2291(16)	−1.3550(14)	−0.4118(13)
C2	0.7617(20)	−0.1889(56)	0.03766(87)
C3	−0.6393(27)	0.1568(26)	0.3703(33)
Substitution coordinates[b]			
C1	1.2301(12)	−1.3544(11)	−0.4051(37)
C2	0.7620(20)	−0.1800(83)	0.037(41)[c]
C3	−0.6406(23)	0.137(11)	0.3699(41)
2,3,3-trifluoropropene(ii)			
From structure fit			
C1	−1.84125(85)	−0.96775(74)	0
C2	−0.8140(15)	−0.11821(25)	0
C3	0.6148(20)	−0.50299(66)	0
Substitution coordinates[b]			
C1	1.84150(81)	0.9669(16)	nonphysical[d]
C2	0.8140(18)	0.100(15)	±0.022(68)[e]
C3	0.6148(24)	0.5056(30)	nonphysical[d]
Ar-2,3,3-trifluoropropene(i)			
From structure fit			
C1	−0.6615(18)	1.1190(20)	−1.58278(99)
C2	−0.70129(38)	0.75515(38)	−0.29974(57)
C3	−1.13351(37)	−0.54644(32)	0.25884(57)
Substitution coordinates[b]			
C1	−0.7069(21)	1.2140(12)	−1.52259(99)
C2	−0.7102(21)	0.7653(20)	−0.2594(58)
C3	−1.0989(14)	−0.5772(26)	0.2148(70)

[a] Costain errors [20] 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 are assigned using physically reasonable atomic distances.
[c] The *c* coordinate of C2 is not well determined; its sign is set to be the same as that from the structure fit.
[d] The unphysical value arises because the C atom lies in or very close to the *a*-*b* plane. Thus, the differences in zero-point motion (contained within the rotational constants) between the ^{12}C parent and ^{13}C-substituted molecule at this atomic position result in an imaginary value for the Kraitchman coordinate.
[e] Within the Costain uncertainty, this value is zero, as expected given the plane of symmetry existing in this rotamer.

ill-determined, and furthermore, those of C1 and C3 are nonphysical, indicating that they all lie in the *a*-*b* inertial plane, which is the symmetry plane of the molecule, as expected. Those Kraitchman coordinates of 233TFP(i) and of 233TFP(ii) that can be determined agree excellently with coordinates derived from the structure fits. Any difference is within 2σ using the higher uncertainty of the two parameters under comparison, suggesting that each rotamer is rather rigid and does not exhibit large amplitude motion.

4.2.2. *Ar-2,3,3-trifluoropropene*

Fixing 233TFP(i) to its experimentally determined average structure, the location of argon is fitted to 12 rotational constants of the 4 isotopologues of Ar-233TFP(i) using Kisiel's STRFIT program [18]. Specifically, we fit the distance Ar-C3, the angle Ar-C3-C2, and the dihedral angle Ar-C3-C2-C1, which are determined to be 3.84538(30) Å, 69.427 (26)°, and 100.591(67)°, respectively. The rms deviation of the fit is 0.095 u $Å^2$. The structure of the complex is shown in Fig. 5, with the coordinates of each atom available as Supporting Information. With the availability of the ^{13}C isotopologues, we also determine the Kraitchman substitution coordinates of the C atoms and list them in Table 10, together with those derived from the structure fit. The two sets of coordinates differ by 0.009 – 0.95 Å, corresponding to 4 – 60 times the of the larger uncertainty, an indication that there is large amplitude motion in the dimer, as we suspected from the large number of centrifugal distortion constants required to fit the rotational spectrum of the most abundant isotopologue.

For Ar-233TFP(ii), because only the rotational spectrum of the most abundant isotopologue was observed, the position of Ar cannot be fitted, but is calculated using the three rotational constants: Ar is at a distance of 4.2941 Å from C3, and the ArC3C2 angle and ArC3C2C1 dihedral angle are respectively, 56.567° and 120.590°. This procedure is equivalent to the commonly employed adaptation of the Kraitchman equations to a substitution of a hypothetical atom of zero mass with an argon atom. The structure of the complex is shown in Fig. 5 and the coordinates of the atoms are available as Supporting Information.

5. Discussion

The theoretical, equilibrium values of the rotational constants for the two rotamers of 2,3,3-trifluoropropene differ from the experimental, average values by only 0.09 – 0.57% (or 2 – 33 MHz). Thus, we are well guided by theory. The intense transitions of the two rotamers also allow us to readily assign their spectra and consequently, to locate the transitions from the ^{13}C-containing isotopologues with little effort. According to theory, the magnitude of the *b* component of the dipole moment for each rotamer is the greatest, and that for 233TFP(ii), 2.68 D, is more than twice that for 233TFP(i), 1.23 D. Therefore, because the rotational constants of the two species are not drastically different, if the populations of these two rotamers are similar in the molecular beam, then roughly speaking, the *b* type transitions for 233TFP(ii) should be much more intense than those for 233TFP(i). Experimentally, for the same transition, the reverse is observed. It is not possible to ensure constant microwave power across the entire bandwidth of the chirped pulse, so quantitative comparisons of intensities and populations derived from them cannot be made. However, we can conclude with confidence that 233TFP(i) is more abundant in the molecular beam, and hence is the lower energy rotamer, consistent with theoretical prediction and the symmetry factor of two for this rotamer.

The rotational constants that give rise to the spectrum of the complex formed between argon and each rotamer agree with the lowest energy isomer predicted theoretically; namely, Isomers (a) for Ar-233TFP(i) and (d) for Ar-233TFP(ii). Despite using the equilibrium structure instead of the average structure for each rotamer in theoretical calculations, the predicted values of the rotational constants for the argon complexes observed differ from those of the experimental values by only 0.2 – 1.5% (5 – 13 MHz). (It is interesting to note that BSSE correction provides slightly worse predictions for the values of the rotational constants; they differ from the experimental values by 0.2 – 6.1%, or 5 – 60 MHz.) The theoretical *c* dipole moment component for Isomer (a) (1.1 D) is much smaller than that for

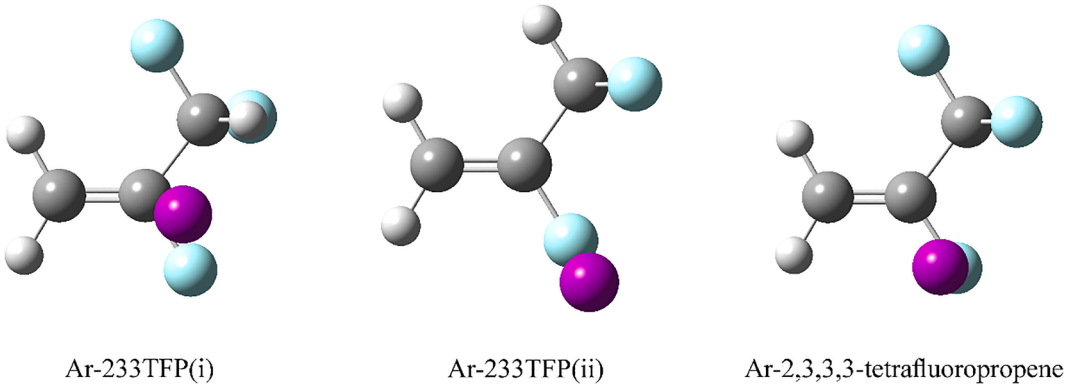

Fig. 5. The experimental structures of the argon complexes of the two rotamers of 2,3,3-trifluoropropene and of 2,3,3,3-tetrafluoropropene [3]. The ethylenic carbons and the 4 atoms directly attached to them for each propene lie in the plane of the page. Atom colors: C, dark gray; H, light gray; F, light blue; Ar, purple.

Isomer (d) (2.5 D), but we observed stronger *c* type transitions for Isomer (a), once again indicating that 233TFP(ii) is less abundant, forming fewer argon complexes.

Only one structure has so far been identified for the argon complex of each 2,3,3-trifluoropropene rotamer (Fig. 5). Our use of argon as a carrier gas allows effective relaxation of the complex to the lowest energy structure; thus, it is likely that the observed structure of each complex is indeed lower in energy than all other isomers predicted theoretically. It appears then the most favorable position for Ar to occupy in its complexes with both rotamers of 2,3,3-trifluoropropene is near the F substituent (F6) connected to C2. Using the sum of van der Waals radii as a guide [6], the van der Waals contact for Ar-C is 3.58 Å and for Ar-F is 3.35 Å. These values suggest that in 233TFP(i), Ar interacts most strongly with C2 (3.60 Å) and less so with C3 (3.85 Å) and F6 (3.64 Å) while in 233TFP(ii), Ar interacts very strongly with F6 (3.16 Å) and less strongly with C2 (3.69 Å) and F8 (3.66 Å) (Table 3). It is important to note that the structure of Ar-233TFP(ii) is determined using only the most abundant isotopologue. If more isotopologues were observed, the Ar-F6 distance will likely be closer to the van der Waals contact of 3.35 Å; the general location of Ar, however, will certainly be similar, as indicated by the excellent agreement of the rotational constants predicted theoretically and observed experimentally for the most abundant species. The placement of argon is not surprising: when the H atom in the $–CHF_2$ group is replaced by another F atom to become 2,3,3,3-tetrafluoropropene, argon occupies a similar position. It interacts closely with C2 (3.66 Å), the F substituent (F6 in the current numbering system) connected to it (3.46 Å), and with an out-of-plane F in the $–CF_3$ group (3.54 Å) [3].

Mapping the electrostatic potential onto the total electron density of each of these propenes, again, at the MP2/6–311-G(2d,2p) level, shows that the F substituent connected to C2 is nucleophilic (Fig. 6). Ar, therefore, appears to locate where it can interact with the electron density of this F atom and with C2, and by extension, the π electron density associated with it. There are other nucleophilic F atoms in these propenes, but a close interaction with them would remove Ar further away from C2. The F substituent (connected to C2) in 233TFP(ii) is much more nucleophilic than the same atom in 233TFP(i) and in 2,3,3,3-tetrafluoropropene. It is therefore not surprising that Ar prefers to be close to this atom in 2333TFP(ii).

Lacking the plane of symmetry that exists in 233TFP(ii) and 2,3,3,3-tetrafluoropropene, Ar could potentially reside either on the same side of the ethylene plane as the H atom (H7), as observed experimentally, or as the F atom (F9) of the $–CHF_2$ group. If Ar resides on the same side as F9 while keeping the interactions with C2, C3, and F6 the same as the experimental structure, then it would be only 3.00 Å from F9, a very repulsive distance. Thus, even though F9 is nucleophilic, if Ar were to interact with it, it would likely have to be placed further away from the other atoms, making this configuration unfavorable, and the complex

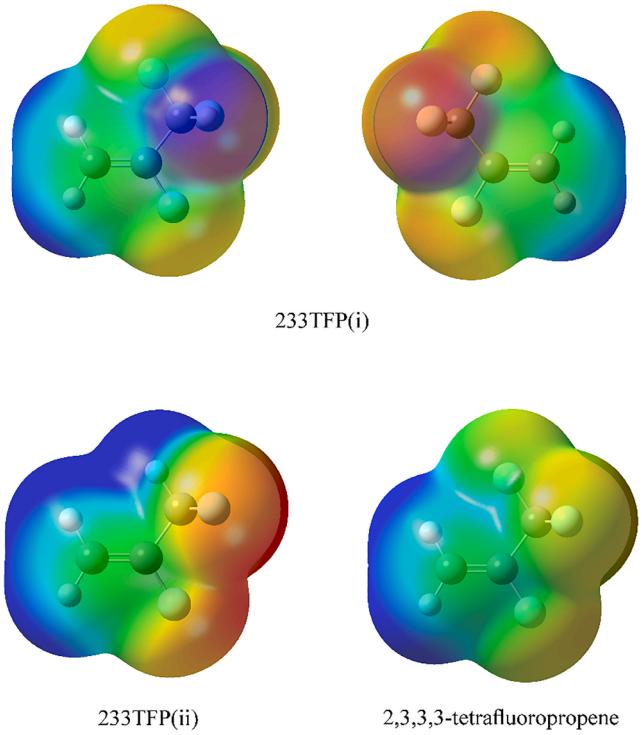

Fig. 6. The electrostatic potential surface mapped onto a total electron density isosurface for 233TFP(i) (two views), 233TFP(ii), and 2.3.3.3-tetrafluoropropene. The ethylenic carbons and the 4 atoms directly attached to them for each propene lie in the plane of the page. The same value of electron 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.

instead would adopt the theoretically-predicted structures of Isomers (b) or (c) (Fig. 3). In either Isomer (b) or (c), Ar is located further from C2 and C3 compared to that in the observed configuration, Isomer (a). This suggests that the electron density in the C2-C3 bond, perhaps due to delocalization of the ethylenic π electrons, makes the interaction with Ar in Isomer (a) more favorable. Given these three different electrostatic potential maps, it will interesting to explore whether, unlike the complexes with argon, heterodimers of the two 233TFP rotamers and 2,3,3,3-tetrafluoropropene with protic acids, such as HF, HCl, and HCCH, adopt different structural motifs in response to the varying electrostatic potentials.

6. Conclusion

Microwave spectra are observed and analyzed for four isotopologues each of two rotamers of 2,3,3-trifluoropropene, the lower energy chiral form and the achiral version of higher energy. Additionally, spectra for the gas-phase heterodimers formed between the argon carrier gas and each rotamer are obtained, although for the higher energy, achiral rotamer, only the most abundant isotopologue is seen. Structures are determined for all species.

Mapped electrostatic potential surfaces for 2,3,3-trifluoropropene reveal that the two rotamers have different electron density distributions, showing that regions of nucleophilicity and electrophilicity can be modulated not only by varying patterns of halogen substitution, but also by the spatial location of those substituents. Regardless of these differences, the structures of the argon complexes of the two rotamers are similar with the argon atom located close to carbon atoms 1 and 2, allowing interaction with the electron density in the π bond and also with the fluorine atom attached to carbon atom 2. The increased nucleophilicity of this fluorine atom in Rotamer (ii) may be responsible for a shorter interaction distance with the argon atom for this rotamer. It will be valuable to investigate how these subtle differences are reflected in interactions with other species, including the protic acids we have used in complexes with haloethylenes. Complexes formed between the chiral rotamer of 2,3,3-trifluoropropene and small chiral molecules will be useful in providing information regarding chiral recognition and potential use as a chiral tag.

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. **Taha Z. Ahmad:** Formal analysis, Investigation. **David W. Borden:** Formal analysis, Investigation. **Caitlin A. Hoffman:** Formal analysis, Investigation. **Navie A. Kim:** 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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jms.2022.111656.

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] 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.
[3] 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.
[4] M.D. Marshall, H.O. Leung, O. Febles, A. Gomez, The microwave spectra and molecular structures of (E)-1,3,3,3-tetrafluoropropene and its complex with the argon atom, J. Mol. Spectrosc. 374 (2020), 111379.
[5] 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*, Revision A.03; Wallingford, CT, 2016.
[6] A. Bondi, van der Waals volumes and radii, J. Phys. Chem. 68 (3) (1964) 441–451.
[7] E.R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A.J. Cohen, W. Yang, Revealing noncovalent interactions, J. Am. Chem. Soc. 132 (18) (2010) 6498–6506.
[8] T. Lu, F.W. Chen, Multiwfn: A multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580–592.
[9] E.F. Pettersen, T.D. Goddard, C.C. Huang, G.S. Couch, D.M. Greenblatt, E.C. Meng, T.E. Ferrin, UCSF Chimera–a visualization system for exploratory research and analysis, J. Comput. Chem. 25 (13) (2004) 1605–1612.
[10] 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.
[11] 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.
[12] 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.
[13] 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.
[14] 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.
[15] J.K.G. Watson, Determination of centrifugal distortion coefficients of asymmetric-top molecules, J. Chem. Phys. 46 (5) (1967) 1935–1949.
[16] B.P. van Eijck, Reformulation of quartic centrifugal distortion Hamiltonian, J. Mol. Spectrosc. 53 (2) (1974) 246–249.
[17] H.M. Pickett, The fitting and prediction of vibration-rotation spectra with spin interactions, J. Mol. Spectrosc. 148 (2) (1991) 371–377.
[18] Z. Kisiel, Least-squares mass-dependence molecular structures for selected weakly bound intermolecular clusters, J. Mol. Spectrosc. 218 (1) (2003) 58–67.
[19] J. Kraitchman, Determination of molecular structure from microwave spectroscopic data, Am. J. Phys. 21 (1) (1953) 17–24.
[20] C.C. Costain, Determination of Molecular Structures from Ground State Rotational Constants, J. Chem. Phys. 29 (4) (1958) 864–874.