THE JOURNAL OF PHYSICAL CHEMISTRY A
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Microwave Spectrum and Novel Molecular Structure of (*Z*)-1-Chloro-3,3,3-trifluoropropene−Acetylene

Published as part of The Journal of Physical Chemistry virtual special issue "Marsha I. Lester Festschrift".

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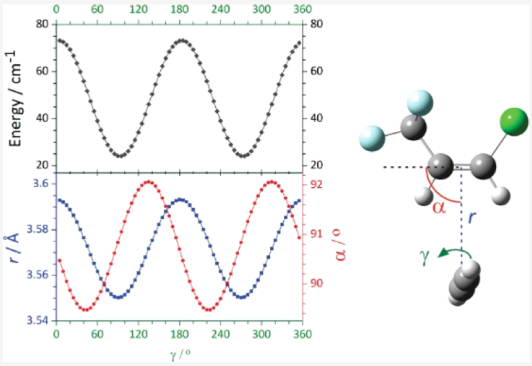
Cite This: https://doi.org/10.1021/acs.jpca.3c03517 Read Online

ABSTRACT: The gas-phase heterodimer formed between (*Z*)-1-chloro-3,3,3-trifluoropropene and acetylene is investigated using quantum chemistry calculations and observed via chirped-pulse Fourier transform microwave (FTMW) spectroscopy. Subsequent analysis of higher resolution spectra, including those using a sample enriched in $H^{13}C^{13}CH$, obtained with a Balle-Flygare FTMW spectrometer reveals a novel structure, as predicted by theory, for the complex, in which the acetylene functions as the gas-phase (Lewis) base and the halopropene as the acid. In the equilibrium structure, the acetylene molecule is located perpendicular to the symmetry plane of (*Z*)-1-chloro-3,3,3-trifluoropropene with the triple bond interacting with the two olefinic hydrogens. Mapped electrostatic potential surfaces suggest that this structure results from a reduction in the nucleophilicity of the halogen atoms as compared to previously studied acetylene halo-olefin complexes and a concomitant increase in the electrophilicity of the hydrogen atoms.



1. INTRODUCTION

The interplay between electrostatics and steric factors in the interactions between halosubstituted ethylenes and simple protic acids has been examined through the structures of a number of their van der Waals complexes revealed by their rotational spectra.[1] Here, we briefly summarize our findings on the interactions between ethylenes containing two halogen atoms (F, Cl) and the weak acid acetylene. When two F atoms are geminal, as in 1,1-difluoroethylene, the H atom and the triple bond in HCCH interact, respectively, with the F, H pair across the double bond of the ethylene (Figure 1a).[2] The motif remains unchanged when one of the F atoms is replaced by a Cl atom: in 1-chloro-1-fluoroethylene, HCCH prefers to bind to the F, H pair instead of the Cl, H pair across the double bond (Figure 1b).[3] This binding mode is in accord with chemical intuition: F is more nucleophilic than Cl and, therefore, should form a more favorable interaction with an electropositive H atom in HCCH. However, when the two halogen atoms in the ethylene subunit are located *cis* to each other, the binding mode of HCCH to the ethylenes does not remain the same. Specifically, in *cis*-1,2-difluoroethylene, HCCH binds to one of the two equivalent geminal F, H pairs (Figure 1c),[4] but in (*Z*)-1-chloro-2-fluoroethylene, HCCH prefers the geminal Cl, H pair, not the F, H pair (Figure 1d).[5] This finding for this mixed halogen complex is supported by theory. Indeed, both isomers, F bound and Cl bound, for (*Z*)-1-chloro-2-fluoroethylene−HCCH are predicted at the MP2/6-311++G(2d,2p) level, with the F bound

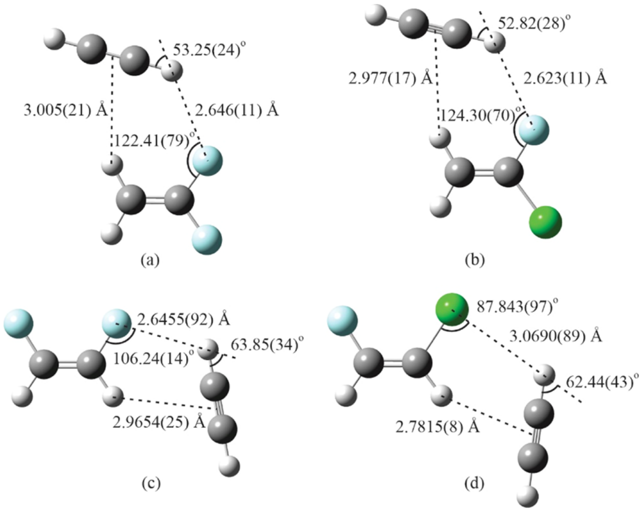


Figure 1. Experimental average structures of the HCCH complexes of (a) 1,1-difluoroethylene,[2] (b) 1-chloro-1-fluoroethylene,[3] (c) *cis*-1,2-difluoroethylene,[4] and (d) (*Z*)-1-chloro-2-fluoroethylene.[5] Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

Received: May 24, 2023
Revised: June 30, 2023

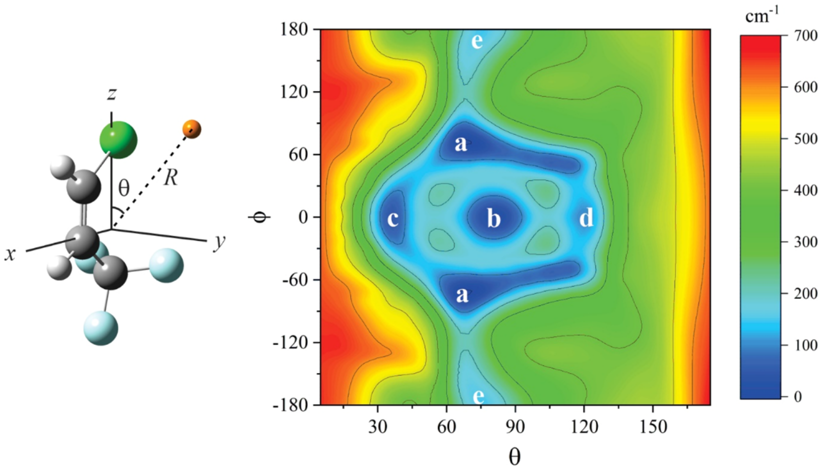
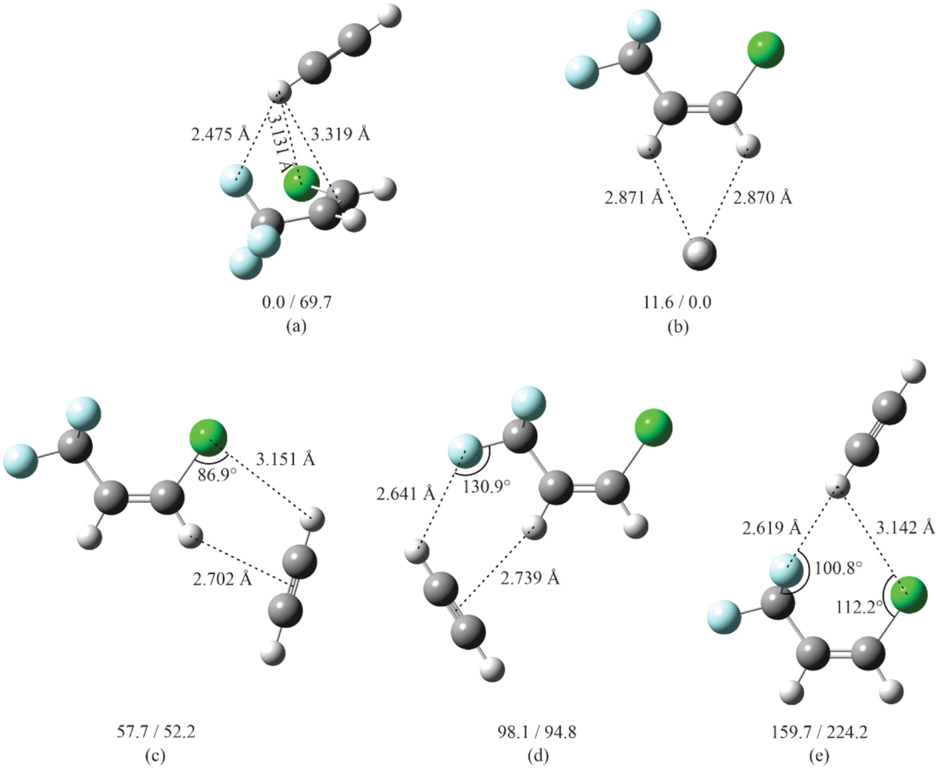


Figure 2. Interaction potential energy contour between (Z)-1-chloro-3,3,3-trifluoropropene and HCCH. The origin of the axis system is the center of mass of the propene, and the x, y, z axes are, respectively, the b, c, a inertial axes of the propene. The distance between the center of mass of HCCH (orange sphere) and the center of mass of the propene is R, which forms a polar angle (θ) with the z axis, and the projection of R onto the $x-y$ plane forms an azimuthal angle (ϕ, not indicated) with the x axis. The center of mass of HCCH is placed at various values of θ and ϕ while the value of R and the orientation of HCCH are optimized. Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.



0.0 / 69.7
(a)

11.6 / 0.0
(b)

57.7 / 52.2
(c)

98.1 / 94.8
(d)

159.7 / 224.2
(e)

Figure 3. Optimized structures of five isomers of (Z)-1-chloro-3,3,3-trifluoropropene−HCCH corresponding to the minima in the potential energy contour plot in Figure 2. The interaction lengths are appropriate to the structures without BSSE correction. The equilibrium energy, in cm^{-1}, without (first number) and with (second number) BSSE correction are listed. Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

isomer 115 cm^{-1} higher in energy than the Cl bound isomer without correcting for basis set superposition error (BSSE), and 80 cm^{-1} higher in energy with the BSSE correction. The energy difference can be rationalized as a balance between electrostatics and steric factors. The theoretical intermolecular distances between H of HCCH and each of the halogen atoms in (Z)-1-chloro-2-fluoroethylene reveal that the F···H bond length is 0.50 Å shorter than the Cl···H bond length (all structural parameters used here are those without BSSE correction), which is more than the difference between the van der Waals radii of F and Cl of 0.27 Å.[6] Thus, judging solely on intermolecular distances, the F···H bond is stronger than the Cl···H bond in the theoretical structures. These halogen atoms, however, have different electron density distributions when bonded to C, as illustrated previously in the mapped electrostatic potential surfaces of vinyl fluoride and vinyl chloride.[7] While the most negative potential of F is along the C−F bond and pointing away from it, the most negative potential of Cl is on a band about the atom, approximately perpendicular to the C−Cl bond. Consequently, when HCCH

Table 1. Rotational Constants, Dipole Moment Components, and Relative Equilibrium and Zero-Point Corrected Energies for Five Isomers of (Z)-1-Chloro-3,3,3-trifluoropropene−HCCH Obtained from Ab Initio Calculations at the MP2/6-311++G(2d,2p) Level without and with BSSE Correction

	Isomer (a)		Isomer (b)		Isomer (c)		Isomer (d)		Isomer (e)	
	no BSSE correction	BSSE correction	no BSSE correction	BSSE correction	no BSSE correction	BSSE correction	no BSSE correction	BSSE correction	no BSSE correction	BSSE correction
A/MHz	1594	1546	1375	1376	2598	2586	1746	1747	1531	1602
B/MHz	879	863	799	772	556	543	705	683	857	809
C/MHz	675	658	572	559	498	487	551	537	608	595
$\|\mu_a\|$/D	1.472	1.466	3.083	3.068	2.450	2.446	1.118	1.109	1.663	1.341
$\|\mu_b\|$/D	0.303	0.365	0.319	0.338	1.693	1.678	2.590	2.588	2.446	2.533
$\|\mu_c\|$/D	2.324	2.326	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.408
$E_{\mathrm{equil}}{}^{a,b}$/cm^{-1}	0.0	69.7	11.6	0.0	57.7	52.2	98.1	94.8	159.7	224.2
$E_{\mathrm{zpe}}{}^{a,c}$/cm^{-1}	0.0	64.0	25.2	0.0	62.8	42.1	102.1	85.2	172.5	244.7

[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 −951.107814, −951.106616, −951.032610, and −951.031277 hartree for E_{equil}, E_{equil} + BSSE, E_{zpe}, and E_{zpe} + BSSE, respectively. [b] The equilibrium energy is determined by using the average structures of the subunits and optimizing the intermolecular degrees of freedom, 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 and HCCH. 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.

binds to Cl, it can assume a smaller Cl···H−C angle. Additionally, the weak HCCH acid allows the weaker Cl···H bond (as opposed to the stronger F···H bond) to bend to a greater extent without a large energetic cost, allowing the acetylenic bond to interact closely with the electropositive H atom geminal to Cl. Ultimately, then, even though the Cl···H bond appears to be weaker than the F···H bond, the relaxed angular requirements of the interaction make possible less steric strain in the CCl···H angle (than the CF···H angle in the F bound isomer), and enhances the electrostatic interaction between the triple bond of HCCH and the geminal H in the ethylene.

To gain further insights into the balance of forces in systems with multiple functional groups, we replace the F atom in (Z)-1-chloro-2-fluoroethylene with a CF_3 group to introduce F atoms that provide different spatial environments for potential interactions with HCCH. We also expect that the CF_3 group in (Z)-1-chloro-3,3,3-trifluoropropene will affect the electron distribution of the molecule differently than the F atom that it replaces, and as such, it will affect the interaction of the Cl atom with HCCH. In fact, our experimental finding for the structure of (Z)-1-chloro-3,3,3-trifluoropropene−HCCH reveals a new mode of binding, one that does not involve any of the nucleophilic atoms in the propene directly.

2. AB INITIO CALCULATIONS

We use theory to explore the interaction potential energy surface between (Z)-1-chloro-3,3,3-trifluoropropene and HCCH, both subunits are fixed at their average ground-state structures.[8,9] (Z)-1-chloro-3,3,3-trifluoropropene has a plane of symmetry formed by its principal a and b inertial axes, in which lie all atoms with the exception of two of the F atoms of the trifluoromethyl group. Taking the center of mass of the propene as the origin and these two inertial axes as the z and x axes, the center of mass of HCCH can be specified with a distance, a polar angle (θ), and an azimuthal angle (ϕ) with respect to the propene (Figure 2). Employing GAUSSIAN 16 at the MP2/6-311++G(2d,2p) level,[10] we scan the value of θ between 5 and 175° and the value of ϕ between −180 and 180°, each in 10° increments, while optimizing the distance between the center of mass of HCCH and the origin of the axis system (that is, the center of mass of the propene), R, and the relative orientation of HCCH. The potential energy contour (Figure 2) clearly illustrates the symmetry of the complex about the $x-z$ plane ($\phi = 0°$). Five unique isomers are identified and optimized; their structures are shown in Figure 3 with important intermolecular interactions indicated. The energies of these isomers [labeled (a)−(e) in order of increasing energy], together with their rotational constants and dipole moment components, are tabulated in Table 1. (The atomic positions of each isomer in its principal axis system is available as Supporting Information).

The $-CF_3$ group furnishes three new binding motifs that are not possible for substituted ethylenes. Two of these motifs involve only one of the H atoms of HCCH: in Isomer (e), it interacts with the Cl atom and an out-of-plane F atom, whereas in Isomer (a), in addition to these two interactions, the H atom also forges a third one with the ethylenic bond. It is interesting to note that the H···Cl distances are very similar (3.131−3.142 Å) in both isomers. The H···F distance in Isomer (e), however, is 6% longer than that in Isomer (a), which together with the absence of a H···ethylenic bond, makes Isomer (e) higher in energy. The third new motif furnished by the CF_3 group, exhibited in Isomer (d), involves both an H atom of HCCH and the acetylenic bond, and they, respectively, interact with the planar F atom and the H atom of C-2. The H···F distance for this isomer (2.641 Å) is slightly longer than that in Isomer (e) (2.619 Å); thus, the fact that Isomer (d) is lower in energy than Isomer (e) indicates that the H···acetylenic bond for Isomer (d) is more stabilizing than the H···Cl bond for Isomer (e).

There are two other binding motifs for (*Z*)-1-chloro-3,3,3-trifluoropropene–HCCH, both of which we have encountered previously in our studies of haloethylene complexes. The binding mode in Isomer (c) is remarkably similar to that observed in the experimental, average structure of (*Z*)-1-chloro-2-fluoroethylene–HCCH (Figure 1d): the geminal Cl, H pair of the propene interacts with an H atom and the acetylenic bond in HCCH, with respective equilibrium interaction lengths of 3.151 and 2.702 Å, and an CCl···H angle of 86.9°. These differ by no more than 3% from the average parameters in the (*Z*)-1-chloro-2-fluoroethylene–HCCH complex; thus, it appears that the replacement of the F atom in (*Z*)-1-chloro-2-fluoroethylene with a CF_3 group has little effect on the binding motif of this isomer. Finally, Isomer (b), with HCCH located normal to the symmetry plane of the propene and its triple bond interacting with the two H atoms across the double bond, is a motif that has been predicted theoretically [also at the MP2/6-311++G(2d,2p) level], although not observed experimentally, as an isomer of (*Z*)-1-chloro-2-fluoroethylene–HCCH and of *cis*-1,2-difluoroethylene–HCCH (Figure 4). This isomer for (*Z*)-1-chloro-2-fluoroethylene–HCCH is higher in energy by 107 cm^{-1} than the global minimum structure, where HCCH binds to the geminal Cl, H pair as described earlier (the experimental structure is shown in Figure 1d).[5] On the contrary, at least at the MP2/6-311++G(2d,2p) level, this motif is the global minimum for *cis*-1,2-difluoroethylene–HCCH[4] even though it has not been observed experimentally. Instead, for *cis*-1,2-difluoroethylene–HCCH, we observe the structure 15.7 cm^{-1} higher in equilibrium energy where HCCH binds to the geminal F, H pair (Figure 1c). The energy ordering of these two *cis*-1,2-difluoroethylene–HCCH isomers does not change upon correcting for BSSE and zero-point energy, but switches when higher levels of theory are used: the equilibrium energy corresponding to the observed *cis*-1,2-difluoroethylene–HCCH is lower in energy by 40, 29, and 22 cm^{-1}, respectively, when MP4, coupled-cluster single double (CCSD), and coupled cluster singles-doubles with perturbative triples [CCSD(T)] are used. Our experience with this and other complexes suggest that theory is an important guide to our experimental search for the rotational spectra of molecular complexes, but with small energy differences among isomers (in our experience, less than 200 cm^{-1} or 2.4 kJ mol^{-1}), we have to take great care not to overestimate the accuracy of theory in predicting the inherently subtle and intricate nature of intermolecular interactions. Returning back to the complex of interest, Isomer (b) of (*Z*)-1-chloro-3,3,3-trifluoropropene is slightly higher in energy (by 11.6 cm^{-1}) than the global minimum structure, Isomer (a).

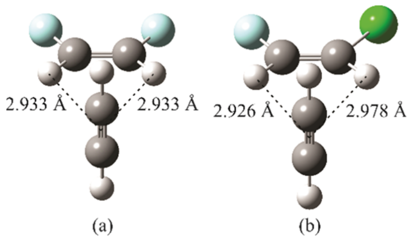


Figure 4. Theoretical structures of the HCCH complexes of (a) *cis*-1,2-difluoroethylene[4] and (b) (*Z*)-1-chloro-2-fluoroethylene[5] showing interactions that involve the acetylenic bond. Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

We also examine if applying a correction for BSSE and/or zero-point energy affects the theoretical energy ordering of the isomers of (*Z*)-1-chloro-3,3,3-trifluoropropene–HCCH. To calculate the zero-point energy for each species, we relax all geometric parameters in the complex, including those for the monomers. The zero-point energies are listed in Table 1, and the order of stability of the isomers does not change; that is, Isomer (a) remains the lowest in energy and Isomer (e) the highest. The energy gap between Isomers (a) and (b), however, increases from 11.6 cm^{-1} without zero-point correction to 25.2 cm^{-1} with the correction.

Fixing the subunits at their average structures, all isomers are then reoptimized with BSSE correction.[11] Their energies, together with their respective rotational constants and dipole moment components are compiled in Table 1. Upon BSSE correction, the energy ordering of the three lowest energy isomers does change: now, Isomer (b) is the most stable, followed by Isomers (c) and (a). Isomers (d) and (e) remain the two highest in energy. To correct for both BSSE and zero-point energy, BSSE correction is applied to the fully relaxed structure of each isomer. The energy ordering remains the same as that when only BSSE correction is applied. That is, Isomer (b) has the lowest energy.

The structure of each isomer changes only slightly when it is optimized using BSSE correction or when all structural parameters are relaxed. Isomer (a) contains no symmetry plane, and therefore, it possesses dipole moment components along all three inertial axes. Isomers (b)–(d) each has a plane of symmetry, with or without any corrections made; as such, these isomers have a vanishing *c* dipole moment component. For Isomer (e), HCCH lies in the symmetry plane of the propene when the structure is optimized with MP2 calculation (giving no *c* dipole moment component), but when either BSSE or zero-point correction is applied, HCCH bends slightly away from the plane to allow a closer interaction with one of the two out-of-plane F atoms, resulting in a small, non-zero *c* dipole moment component. The rotational constants of all isomers differ significantly from each other; we should have no difficulty identifying the species present in the rotational spectrum once it is assigned.

3. EXPERIMENT

The spectrum of (*Z*)-1-chloro-3,3,3-trifluoropropene–HCCH was initially observed using a broadband, chirped-pulse Fourier transform microwave (FTMW) spectrometer operating from 5.6 to 18.1 GHz.[12−14] The complex is produced using a pulsed valve expansion through two valves, each equipped with a 0.8 mm orifice and a backing pressure of 2 atm of a mixture of 3/4% (*Z*)-1-chloro-3,3,3-trifluoropropene and 3/4% acetylene diluted in argon. The spectrum is obtained in three segments (5.6−10.1, 10.1−14.1, and 14.1−18.1 GHz), the frequencies are 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, 14.6, and 18.6 GHz, respectively. After isolation of the lower sideband, the pulse is amplified to 20−25 W of power with a solid-state amplifier and polarizes the sample. The subsequent 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 20 μs. Ten polarization−digitization cycles are performed for each 800 μs opening of the pulsed valves that operate at 4 Hz, and approximately 1,580,000 to 1,970,000 FIDs are averaged for each segment. The averaged FID is apodized, zero-filled, and Fourier transformed, as described previously,[13] to give a frequency domain spectrum with a resolution element of 11.92 kHz and typical line widths of 125 kHz.

The only isomer of the ^{35}Cl- and ^{37}Cl- containing isotopologues of the complex we are able to identify in the chirped pulse spectrum is Isomer (b). In addition to a small value predicted for the *b* dipole moment component (~0.27 D), the presence of the quadrupolar Cl nucleus splits each rotational transition into several hyperfine components. As a result, we are not able to observe any *b*-type transitions. On the other hand, we can readily assign transitions due to the *a* dipole moment component (predicted to be ~3.1 D). A portion (20 MHz) of the spectrum is shown in Figure 5, illustrating the relative intensities of several transitions due to the (*Z*)-$CH^{35}ClCHCF_3$ and its Ar and HCCH complexes as well as (*Z*)-$CH^{37}ClCHCF_3$−HCCH.

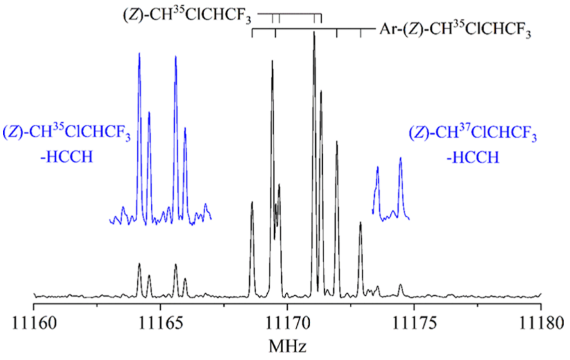


Figure 5. Portion of the chirped pulse spectrum showing transitions due to four (*Z*)-1-chloro-3,3,3-trifluoropropene species. The blue trace has been magnified five folds to more clearly illustrate transitions due to two (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH isotopologues. The resolved hyperfine components of 8_{26}−7_{25} for (*Z*)-$CH^{35}ClCHCF_3$−HCCH are at lower frequency and the unresolved hyperfine components of 9_{18}−8_{17} for (*Z*)-$CH^{37}ClCHCF_3$−HCCH are at higher frequency.

Because we are not able to resolve the hyperfine components for many transitions in the chirped pulse spectrum, we turn to the narrowband Balle-Flygare spectrometer[13,15] to fully collect the spectra of the ^{35}Cl and ^{37}Cl isotopologues of the complex. Figure 6 shows an example of a congested region, where 8 sets of Doppler doublets (due to the $12_{1\,12}$−$11_{1\,11}$ and $12_{0\,12}$−$11_{0\,11}$ transitions) are observed for $CH^{35}ClCHCF_3$−HCCH within 1 MHz. In addition to these two isotopologues, we also use $H^{13}C^{13}CH$ in the sample mixture to obtain the spectra of its complexes with the ^{35}Cl and ^{37}Cl isotopologues of the propene. Transitions are measured in the 5.2−18.5 GHz region. The time domain signal is background-corrected and digitized for 1024 data points and zero-filled to a 2048-point record length before Fourier transformation, resulting in a frequency domain spectrum with a 4.8 kHz resolution.

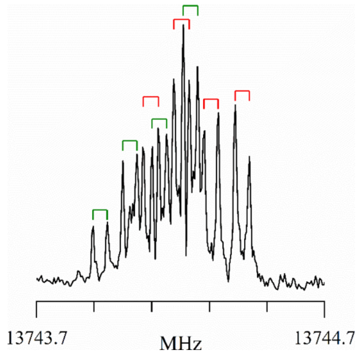


Figure 6. Two rotational transitions with resolved ^{35}Cl nuclear quadrupole hyperfine component for the most abundant isotopologue, (*Z*)-$CH^{35}ClCHCF_3$−HCCH, observed using a Balle-Flygare FTMW spectrometer. The four Doppler doublets corresponding to $12_{1\,12}$−$11_{1\,11}$ and $12_{0\,12}$−$11_{0\,11}$ are marked by green and red tie lines, respectively.

4. RESULTS

4.1. Spectral Analysis. Only *a*-type transitions are observed in the narrowband spectrometer for four isotopologues of the (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH complex. As is the case with the chirped pulse spectrometer, *b*-type transitions are not detectable. The ^{35}Cl isotopologue of the propene is more abundant naturally; over 107−123 rotational transitions (giving more than 400 hyperfine components) are measured for its HCCH and $H^{13}C^{13}CH$ complexes. The number of transitions decreases to 68−79 (giving more than 250 hyperfine components) for the ^{37}Cl isotopologue of the propene. The *J* and K_a ranges sampled are the greatest for (*Z*)-$CH^{35}ClCHCF_3$−HCCH and are, respectively, 3−15 and 0−7. They are either the same or slightly smaller for the other three isotopologues. These transitions are analyzed using the Watson *S*-reduced Hamiltonian in the I^r representation[16] with the inclusion of chlorine nuclear quadrupole coupling interaction, and Pickett's nonlinear least squares SPFIT program.[17] In addition to three rotational constants and five quartic centrifugal distortion constants, we have also determined four components of the nuclear quadrupole coupling tensors. The three diagonal components are determined via a fit to χ_{aa} and $\chi_{bb}-\chi_{cc}$, and then application of the Laplace condition, $\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$. Of the three non-diagonal components, the magnitude of χ_{ab} is obtained. The spectroscopic constants are listed in Table 2. (Tables of observed and calculated transition frequencies with assignments for the four isotopologues are in Supporting Information). The rms deviation of each fit is less than 2 kHz, less than half of the resolution element of the spectrum. The three rotational constants are well predicted by our level of theory, differing from the experimentally determined values by less than 5% for the calculation uncorrected for BSSE and less than 1% for the BSSE-corrected calculation. Similarly, a harmonic vibrational calculation predicts quartic centrifugal distortion constants in reasonable agreement with experiment (20−50%).

4.2. Structure Determination. The rotational constants, *A*, *B*, and *C*, determined experimentally for the most abundant isotopologue of (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH agree excellently with those for the theoretical equilibrium

Table 2. Spectroscopic Constants (in MHz, Unless Otherwise Noted) for Four Isotopologues of the (*Z*)-1-Chloro-3,3,3-trifluoropropene−HCCH Complex[a]

	(*Z*)-$CH^{35}ClCHCF_3$−HCCH	(*Z*)-$CH^{37}ClCHCF_3$−HCCH	(*Z*)-$CH^{35}ClCHCF_3$−$H^{13}C^{13}CH$	(*Z*)-$CH^{37}ClCHCF_3$−$H^{13}C^{13}CH$
A	1378.46253(41)	1342.46770(41)	1373.55759(38)	1337.83019(45)
B	767.436455(33)	766.929471(39)	731.221301(29)	730.583694(42)
C	555.287322(27)	549.076508(30)	536.137440(23)	530.253811(30)
$D_J/10^{-3}$	0.327466(98)	0.31062(14)	0.300095(79)	0.28464(13)
$D_{JK}/10^{-3}$	1.94331(60)	2.0439(11)	1.94136(55)	2.0356(23)
$D_K/10^{-3}$	−1.090(14)	−1.261(16)	−1.138(14)	−1.316(22)
$d_1/10^{-3}$	−0.135981(51)	−0.134532(83)	−0.118929(45)	−0.117574(78)
$d_2/10^{-3}$	−0.042906(43)	−0.046490(63)	−0.037681(37)	−0.040772(68)
χ_{aa}[b]	−4.2981(25)	−4.0221(24)	−5.8619(32)	−5.2903(51)
χ_{bb}[b]	−25.6028(49)	−19.5450(41)	−24.0295(43)	−18.2669(47)
χ_{cc}[b]	29.9009(58)	23.5672(48)	29.8914(52)	23.5572(59)
$\lvert\chi_{ab}\rvert$	55.672(98)	44.07(13)	55.965(52)	44.31(12)
no. of rotational transitions[c]	123	79	107	68
no. of hyperfine components	476	296	415	264
J range	3−15	3−12	4−14	4−13
K_a range	0−7	0−5	0−7	0−4
rms/kHz	1.65	1.25	1.30	1.31

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

structure of Isomer (b), with the respective theoretical values differing from the experimental values (experimental−theoretical) by 3.5, −31.6, −16.7 MHz (0.3, −4.1, −3.0%) when BSSE correction is not taken into account. When BSSE correction is applied, the differences become much smaller: 2.5, −4.6, and −3.7 MHz (0.2, −0.6, and −0.7%).

In the equilibrium structure of Isomer (b), both the (*Z*)-1-chloro-3,3,3-trifluoropropene subunit and its HCCH complex share the same plane of symmetry. In the average structure, because of zero-point motion, HCCH is expected to point away from the normal to this plane at an angle. This angle can be determined readily by comparing the mass distribution about the *a*−*b* inertial plane for the propene [$P_{cc} = \sum_i m_i c_i^2 = (I_a + I_b - I_c)/2$] with that for the complex. For the $CH^{35}ClCHCF_3$ monomer,[9] the value of P_{cc} is 44.3504 u Å^2. If $H^{12}C^{12}CH$ lies perpendicular to the symmetry plane of the propene subunit, it would contribute an additional 14.3257 u Å^2. Experimentally, the value of P_{cc} increases only by 13.1658 u Å^2, indicating that $H^{12}C^{12}CH$ makes an angle of 16.532° with the axis normal to the propene symmetry plane. A similar angle (16.635°) is obtained for the ^{37}Cl-containing isotopologue of the complex. When the acetylene subunit is $H^{13}C^{13}CH$, the values for this angle are smaller: 16.287 and 16.389°, respectively, for the ^{35}Cl- and ^{37}Cl-containing species. Thus, the angular position of the heavier $H^{13}C^{13}CH$ deviates slightly less from the equilibrium structure of the complex than $H^{12}C^{12}CH$.

Assuming the structures of the subunits remain unchanged upon complexation, four parameters are required to completely specify the structure of the complex (Figure 7). Two are used to locate the center of mass of the acetylene while two are necessary to specify how the acetylene tilts from the axis normal to the symmetry plane of the propene. Specifically, *r* is the distance between the center of the C≡C triple bond in acetylene and the center of the C═C double bond in the propene and *α* is the angle formed by *r* and the line joining the center of the C═C double bond and C-2 in the propene. Designating the center of mass of the acetylene as the origin of a new set of axes, with the axis colinear to *r* as the *x*′ axis and that normal to the propene symmetry plane as the *z*′ axis, the tilt of acetylene can be described by its polar (*β*) and azimuthal (*γ*) angles relative to these axes. We attempt to fit all four structural parameters to the three moments of inertia of each of the four isotopologues using Kisiel's strfit program,[18] but the parameters are correlated, and thus, unsurprisingly, ill determined.

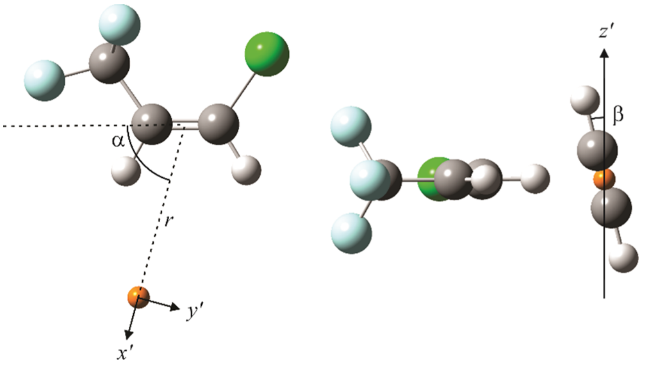


Figure 7. Geometric parameters describing the structure of the (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH complex. Left: the line connecting the center of mass of HCCH (orange sphere) and the center of the C═C bond has a length of *r* and lies on the *x*′ axis, and it forms an angle of *α* with the line connecting the center of the C═C bond and C-2. Right: with the center of mass of HCCH as the origin, the orientation of HCCH can be specified by the polar angle *β* it forms with the *z*′ axis, which is parallel to the normal of the propene plane of symmetry, and by the azimuthal angle formed with the *x*′ axis, *γ* (not indicated here). Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

To circumvent the correlation problem, we fit the values of three parameters, *r*, *α*, and *β* while fixing the azimuthal angle *γ* to a value between 5 and 355°. (*γ* = 0 or 360° is undefined). The value of this angle is sampled first in 10° increments to roughly locate where the rms error of the fit is minimized, and decreasing around those locations to 1° increments to arrive at

Table 3. Structure Fits Using the Moments of Inertia of Three Sets of Isotopologues[a]

	γ/°	r/Å	α/°	β/°	rms/u Å^2
all four isotopologues	93 or 273	3.65612(41)	91.750(34)	16.03(40)	0.132865
two H^{12}C^{12}CH isotopologues	152 or 332	3.658771(31)	91.4203(23)	16.272(33)	0.007532
two H^{13}C^{13}CH isotopologues	151 or 331	3.657406(31)	91.4217(25)	16.021(33)	0.007852

[a] The value of γ is fixed to obtain the lowest value of rms for each fit.

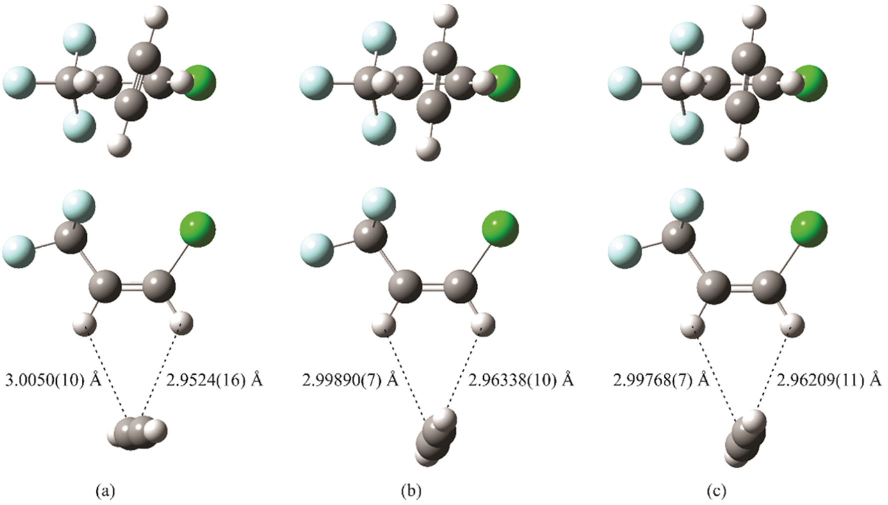


Figure 8. Structure of the (Z)-1-chloro-3,3,3-trifluoropropene−HCCH complex is shown in two views after a fit to the moments of inertia of (a) all four isotopologues, (b) two H^{12}C^{12}CH isotopologues, and (c) two H^{13}C^{13}CH isotopologues. The distances between the center of mass of HCCH and the two H atoms in the propene are calculated using Kisiel's EVAL program.[22,23] Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

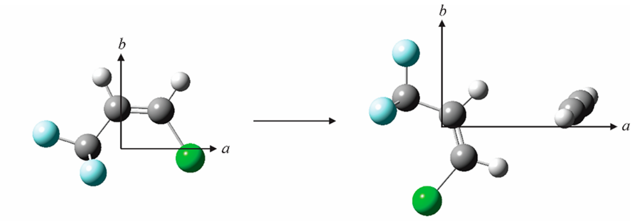
the smallest value of rms error. Interestingly, regardless of the value of γ, the resulting parameters are fairly constant: the values of r range from 3.656 to 3.660 Å, the values of α range from 91.1 to 91.8°, and the values of β range from 16.0 to 16.2°, with the rms error ranging from 0.133 to 0.156 u Å^2. Thus, HCCH does not appear to have a significant preference for γ. The best fit is at γ = 93°, and equivalently at 273° (these structures are mirror images of each other). The structural parameters corresponding to this fit are listed in Table 3, with the structure shown in Figure 8a.

Our analysis of P_{cc} values shows that the values of β for the H^{12}C^{12}CH-containing isotopologues are noticeably different from those for the H^{13}C^{13}CH-containing isotopologues; thus, we fit the two sets of isotopologues separately to observe if the structural parameters are greatly affected. Using the same procedure outlined above, we once again observe that the values of r, α, and β are not very sensitive to the value of γ. In the entire range of γ sampled (5−355°), the values of r and α have the same range as the fit using all four isotopologues, but the values of β range from 16.1−16.4° for the fit using H^{12}C^{12}CH isotopologues and 15.9−16.1° for the fit using H^{13}C^{13}CH isotopologues. The best fit occurs at γ = 152° (or equivalently, 332°) for the two H^{12}C^{12}CH containing isotopologues and at γ = 151° (or equivalently, 331°) for the two H^{13}C^{13}CH containing isotopologues. Except for the value of γ, the resulting structures (Table 3 and Figure 8b,c) differ slightly from the fit with all four isotopologues, but the rms errors decrease to 0.0075 and 0.0079 u Å^2, respectively, indicating that the zero-point motions of H^{12}C^{12}CH and H^{13}C^{13}CH in the complex are indeed different. Once again, we observe that the values of r, α, and β are not very sensitive to the value of γ. (The atomic positions for each fit are available in Supporting Information).

4.3. Nuclear Quadrupole Coupling Constants.

We are able to determine the chlorine nuclear quadrupole coupling constants for all four isotopologues of (Z)-1-chloro-3,3,3-trifluoropropene−HCCH, but only the magnitude of one of three non-diagonal components, χ_{ab}. The sign of a non-diagonal component is dependent on how the directions of the inertial axes are assigned and is only relevant when two related species, such as a molecule and its molecular complex, are compared. The complete chlorine nuclear quadrupole coupling tensors for the ^{35}Cl and ^{37}Cl isotopologues of (Z)-1-chloro-3,3,3-trifluoropropene have already been determined.[9] If we assume that intermolecular interactions do not affect the electric field gradient of the Cl atom to any significant extent and that the zero-point motions of (Z)-1-chloro-3,3,3-trifluoropropene in the complex and in the monomer are similar, then the chlorine nuclear quadrupole coupling tensor for the complex can be obtained by simply expressing the tensor for the propene monomer in the inertial system of the complex. In other words, all we have to do is to rotate the tensor appropriately for (Z)-1-chloro-3,3,3-trifluoropropene to determine the sign of χ_{ab} and the values of the other non-diagonal components in the complex.

The necessary rotational matrix is the same as the one that rotates the inertial axis system of (Z)-1-chloro-3,3,3-trifluoropropene into that of its HCCH complex and can be readily determined. We have done so using the structure of the propene[9] and that of the HCCH complex determined from the two H^{12}C^{12}CH isotopologues (the atomic coordinates of the complex are given in Supporting Information). However, to preserve the C_s symmetry of the vibrationally averaged structure of the complex, we perform the rotation only about the *c* inertial axis, bringing the monomer's *a* and *b* axes into coincidence with those of the complex. (This is equivalent to considering the acetylene molecule to be normal to the symmetry plane of the propene). Using the directions of the inertial axis system indicated for the propene and the experimental quadrupole coupling tensor of ^{35}Cl in the most abundant isotopologue of (*Z*)-$CH^{35}ClCHCF_3$, both shown in Figure 9, we obtain the tensor for the complex, expressed in the inertial axis system indicated. The diagonal components of the tensor obtained after the rotation agree excellently with the experimental values, differing in magnitudes by 0.256 MHz, 0.245 MHz, and 0.501 MHz (or 5.9, 0.96, 1.7%), respectively, for χ_{aa}, χ_{bb}, and χ_{cc}. Additionally, the rotation yields a negative value for χ_{ab} for the dimer (−56.2593 MHz), thus establishing the sign of the value that we are not able to determine experimentally. It is remarkable that the experimental value of χ_{ab}, −55.672(98) MHz, differs from the calculated value by only 1.1%; thus, the assumptions made earlier are sound: HCCH is located far enough away to not perturb the electric field gradient of Cl in the propene, and the zero-point motions of the propene in the monomer and dimer are similar. (A similar rotation for each isotopologue of the complex also establishes a negative value for χ_{ab} in each case). The vibrationally averaged values of the other two non-diagonal components, χ_{ac}, and χ_{bc}, remain zero due to the symmetry of the species.



$$\begin{pmatrix} 8.77847 & 51.9948 & 0 \\ 51.9948 & -39.18025 & 0 \\ 0 & 0 & 30.40179 \end{pmatrix} \qquad \begin{pmatrix} -4.5539 & -56.2593 & 0 \\ -56.2593 & -25.8479 & 0 \\ 0 & 0 & 30.40179 \end{pmatrix}$$

Figure 9. (*Z*)-$CH^{35}ClCHCF_3$ monomer and the experimental ^{35}Cl quadrupole coupling tensor (in MHz) in its inertial axis system are rotated, respectively, into the inertial axis system of the (*Z*)-$CH^{35}ClCHCF_3$−$H^{12}C^{12}CH$ complex. Atom colors: C, dark gray; H, light gray; Cl, green; F, light blue.

5. DISCUSSION

We have assigned the rotational spectra for four isotopologues of (*Z*)-1-chloro-3,3,3-trifluoropropene and have determined that the structure is consistent with Isomer (b). With argon as a buffer gas, the many-body collisions that occur during the molecular beam expansion are known to relax molecular complexes to their lowest energy arrangement.[19−21] Thus, the observed structure represents the lowest-energy structure of the (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH complex. Theory has served us extremely well: the MP2 energies of Isomers (a) and (b) are very similar, with Isomer (b) 12 and 25 cm^{-1} higher in energy without and with zero-point correction, respectively. When BSSE correction is applied, however, Isomer (b) becomes correspondingly 70 and 64 cm^{-1} lower in energy, and indeed, this is the structure we observe. It is impressive that theory has been such an excellent guide for predicting the ground-state structure here. We will continue to be mindful of small energy differences between isomers and keep track of how well experiment and theory complement each other.

In the equilibrium structure of the complex, HCCH is perpendicular to the (*Z*)-1-chloro-3,3,3-trifluoropropene symmetry plane (β = 0°), with a distance between its center of mass and the middle of the ethylenic bond, *r*, of 3.5369 Å, and *r* making an angle (α) of 90.7° with the line connecting the center of the C=C bond and C-2. In the vibrationally averaged structure, the three structural fits (Table 3) show that HCCH deviates by ∼16° from the normal to the propene symmetry plane, the value of α is somewhat greater (91.4−91.7°), and the center of mass of HCCH is further away from the center of the C=C bond (r = ∼3.66 Å). The slight difference in mass between $H^{12}C^{12}CH$ and $H^{13}C^{13}CH$ does affect the zero-point motion of the complex. The experimental value of β determined using two $H^{12}C^{12}CH$ isotopologues, 16.272(33)°, is 0.25° greater for the lighter $H^{12}C^{12}CH$ than that for $H^{13}C^{13}CH$ [16.021(33)°]. This is consistent with what we find by comparing the P_{cc} value of each isotopologue with that of its corresponding propene: 16.532 and 16.635° for the ^{35}Cl- and ^{37}Cl-isotopologues, respectively, containing $H^{12}C^{12}CH$. Each of these values is also 0.25° greater than its counterpart when $H^{13}C^{13}CH$ is used (16.287 and 16.389°). Because of this difference, it is better to specify the structures of the $H^{12}C^{12}CH$ and $H^{13}C^{13}CH$ isotopologues separately rather than using them together for a structure fit. In fact, the apparently large difference between the values of γ, 93° when all four isotopologues are used vs 152 or 151° when only isotopologues of $H^{12}C^{12}CH$ or $H^{13}C^{13}CH$ are used, is merely a

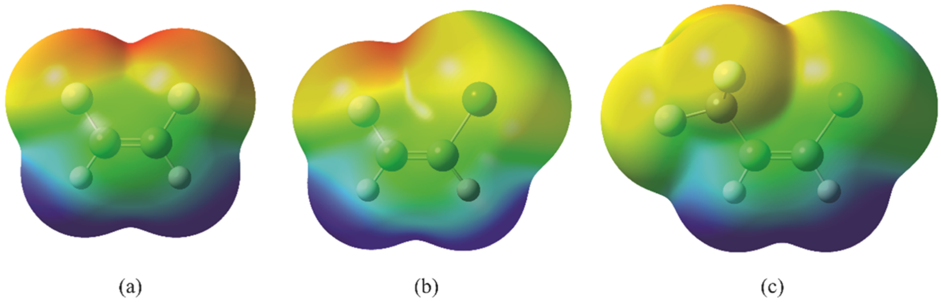


Figure 10. Electrostatic potential mapped onto the total electron density isosurface for (a) *cis*-1,2-difluoroethylene, (b) (*Z*)-1-chloro-2-fluoroethylene, and (c) (*Z*)-1-chloro-3,3,3-trifluoropropene. The same value of electron density and identical color scales are used for the surfaces. Blue represents positive electrostatic potential, and red represents negative electrostatic potential.

result of “averaging” the dissimilar values of β and distributing the disparity into other parameters. Of course, we have also established earlier that the structural parameters are not too sensitive to the value of γ.

The binding mode of (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH is novel. Although, as mentioned previously, this configuration has not been observed in any haloethylene−HCCH complexes, theory has revealed similar structures in the higher energy isomers of *cis*-1,2-difluoroethylene−HCCH and (*Z*)-1-chloro-2-fluoroethylene−HCCH (Figure 4). A comparison between the two H···acetylenic bond interaction distances for this motif shows that they are necessarily the same for *cis*-1,2-difluoroethylene−HCCH because of the symmetry of the complex, but for (*Z*)-1-chloro-2-fluoroethylene−HCCH, the interaction involving the H atom geminal to F is 2.926 Å, which is 0.052 Å shorter than that involving the H atom geminal to Cl (2.978 Å). The shorter, hence stronger interaction is not surprising: F is more nucleophilic than Cl; thus, it renders its geminal H more electropositive, and it interacts more with the π electrons of HCCH than the H geminal to Cl. In the present case, (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH, the two H···acetylenic bonds have almost identical lengths (2.87 Å) in the equilibrium structure (Figure 3), suggesting that the Cl atom and the CF_3 group have similar electron withdrawing ability from their respective H atoms. The interaction lengths in the average structure, however, reveal a bigger difference, with the one involving the H atom geminal to the Cl atom shorter by 0.036 Å. To attempt to explain these observations, we map the electrostatic potential of each of *cis*-1,2-difluoroethylene, (*Z*)-1-chloro-2-fluoroethylene, and (*Z*)-1-chloro-3,3,3-trifluoropropene onto its total electron density surface (Figure 10). The hydrogen atoms in each species are electropositive, and it appears that for (*Z*)-1-chloro-2-fluoroethylene, the positive potential extends over a greater region near the H atom geminal to the F atom, whereas for (*Z*)-1-chloro-3,3,3-trifluoropropene, the region with the more extended positive potential is near the H atom geminal to Cl. Because HCCH interacts via dispersion interaction, perhaps the π electron density of the acetylenic bond prefers to locate nearer to the more extended positive region in (*Z*)-1-chloro-2-fluoroethylene and in (*Z*)-1-chloro-3,3,3-trifluoropropene, resulting in the respective predicted and observed structures of the two species. Of course, it remains unclear then why theory predicts two such nearly equal interactions in the equilibrium structure of (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH.

The mapped electrostatic surfaces do provide a reason for the novel structure observed in the present case. In the propene, none of the F atoms is as nucleophilic as those in *cis*-1,2-difluoroethylene, and the Cl atom is also less nucleophilic than that in (*Z*)-1-chloro-2-fluoroethylene. As such, a hydrogen bond formed by HCCH with an F atom (as it does in *cis*-1,2-difluoroethylene) or with a Cl atom [as it does in (*Z*)-1-chloro-2-fluoroethylene] in the propene is likely not as strong as those formed in the respective ethylenes. With the presence of four halogen atoms, the H atoms in the propene are rendered sufficiently positive that they become a stronger gas-phase acid than HCCH, and they interact favorably with the acetylenic bond. It would be interesting to use acid partners such as HCl and HF to investigate how they compete with the H atoms in the propene to form a complex.

6. CONCLUSIONS

The microwave spectra for four isotopologues of the gas-phase heterodimer formed between (*Z*)-1-chloro-3,3,3-trifluoropropene and acetylene have been obtained and analyzed. Ab initio quantum chemistry calculations using the MP2/6-311++G(2d,2p) level of theory predict five isomers of the complex with equilibrium energies within 200 cm^{-1} of each other. Correction for BSSE moves the lowest energy (without the correction) isomer up two spots, whereas correcting for zero-point vibrational energy does not affect the relative ordering of the isomers. The spectroscopic constants obtained from the analysis of the spectra are consistent with the lowest-energy isomer predicted by the BSSE-corrected calculation.

The structure of the complex is novel, with none of the four halogens atoms in the propene directly involved in the intermolecular interactions. Instead, they exert their influence by modulating the electron density of the propene so that it functions as the electrophile, with the two hydrogen atoms interacting with the electron density of the acetylenic triple bond. The equilibrium position of the acetylene molecule is normal to the symmetry plane of the halopropene with zero-point vibrational motion resulting in an average deviation of 16° from normality, with $H^{12}C^{12}CH$ having a slightly greater average deviation (0.25°) than $H^{13}C^{13}CH$. Analysis of the chlorine nuclear quadrupole coupling constants provides additional support for the structure. Although an analogous bonding motif has been predicted for higher energy isomers of acetylene−haloethylene complexes, this is the first example of it being the global minimum, and experimentally observed, structure.

Mapped electrostatic potential surfaces reveal the nature of the electron density modulation resulting from the substitution of a $-CF_3$ for a fluorine atom in (*Z*)-1-chloro-2-fluoroethylene. The nucleophilicity of the halogen atoms are markedly reduced while the region of positive electrostatic potential in the vicinity of the hydrogen atoms is enhanced and extended.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.3c03517.

> Tables of observed and calculated transition frequencies for four isotopologues of the (*Z*)-1-chloro-3,3,3-trifluoropropene−HCCH complex, atomic coordinates for the theoretical structures, three different fits of the experimental structure, and complete citation for Gaussian 16 (ref 10) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under grant no. CHE-1856637. We thank Shantum Jha for preliminary quantum chemistry calculations performed on the (*Z*)-1-chloro-3,3,3-trifluoropropene−acetylene complex.

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