

Straining to Put the Pieces Together: The Molecular Structure of (E)-1-Chloro-1,2-difluoroethylene–Acetylene from Microwave Spectroscopy

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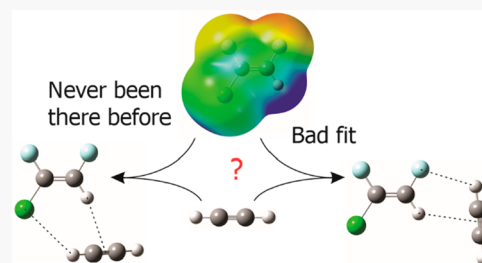


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ABSTRACT: The microwave, rotational spectrum between 5.6 and 19.7 GHz of the gas-phase heterodimer formed between acetylene and (E)-1-chloro-1,2-difluoroethylene is obtained using both broadband, chirped-pulse and narrow band, Balle–Flygare Fourier transform microwave spectrometers. The structure of the complex is determined from the rotational constants obtained via the analysis of the spectra for the normal isotopologue of the complex and three isotopically substituted species: the singly substituted ^{37}Cl isotopologue, obtained in natural abundance, and two isotopologues singly substituted with ^{13}C , obtained using an isotopically enriched HC^{13}CH sample. The acetylene forms a hydrogen bond with the fluorine atom on singly halogenated carbon and a secondary interaction with the hydrogen atom on that same carbon. The angle strain induced in forming the secondary interaction is offset by the favorable electrostatics of the hydrogen bond to fluorine. Comparisons with acetylene complexes of 1,1,2-trifluoroethylene and *cis*-1,2-difluoroethylene show the effects of halogen substitution at the remote carbon on this bonding motif.



I. INTRODUCTION

Our investigations into the nature of intermolecular interactions involving the two lightest halogen atoms, fluorine and chlorine, have led to a deeper understanding of the electrostatic forces and steric factors offered by each to simple protic acids.¹ We have chosen halogen-substituted ethylenes to assess the competition among the nucleophilic halogen atoms and the C=C double bond as hydrogen bond acceptors. In addition, these ethylenes contain at least one electrophilic hydrogen atom, which potentially offers at least a second binding site to the nucleophilic portion of an acid. Working in concert, the nucleophilic and electrophilic sites in the ethylenes allow us to observe how they bind to an acid and reveal to us the cooperation and the compromise between steric factors and electrostatic effects, i.e., given the operative electronic charge distributions, how the two subunits fit together best.

The protic acids we have used for our work are HF, HCl, and HCCH, but we will concentrate on HCCH in this study. In the presence of only one halogen atom on the ethylene, HCCH binds to the F, H pair *cis* to each other in vinyl fluoride (Figure 1a)² but to the geminal Cl, H pair in vinyl chloride (Figure 1b).³ We have argued,⁴ and indeed have shown, through electrostatic potentials mapped onto electron density surfaces of these vinyl halides,³ that because the geminal H is closer than the *cis* H to the halogen atom (two bonds vs three bonds away), it is more electropositive. Therefore, the fact that

HCCH does not bind to the geminal pair formed by the F and H atoms in vinyl fluoride indicates that this configuration is sterically too strained to be favorable: it would require a large deviation from linearity of the hydrogen bond to bring the nucleophilic triple bond close enough to interact with the geminal H atom. Instead, the triple bond interacts with the less electropositive H atom *cis* to the F atom. The situation for vinyl chloride is different. Unlike vinyl fluoride where the most negative potential points away from the F along the C–F bond, it is instead located on a band centered about the larger, more polarizable Cl.³ Consequently, HCCH can form a hydrogen bond with the C–Cl bond at a smaller angle, making possible an interaction between the more electropositive geminal H and the triple bond that does not require too large a distortion of the hydrogen bond from linearity. These two vinyl halides show that, in the absence of additional substituents in the ethylene subunit, HCCH prefers to bind to a F, H pair across the double bond (for simplicity, we call this the “top-binding”

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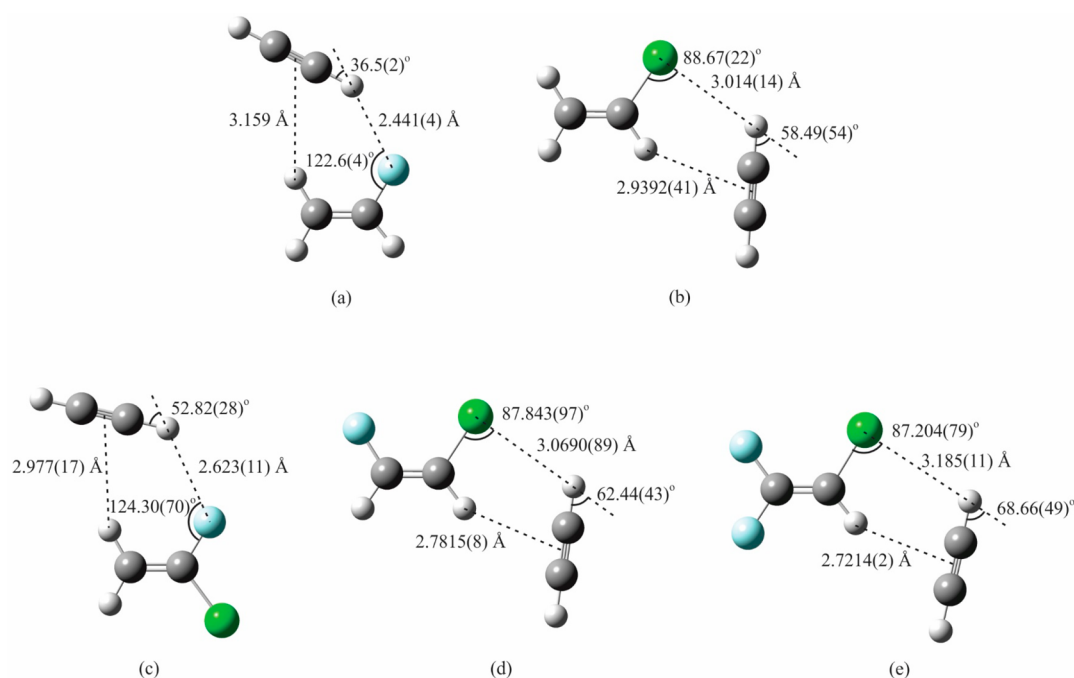


Figure 1. Structure of the HCCH complexes of (a) vinyl fluoride,² (b) vinyl chloride,³ (c) 1-chloro-1-fluoroethylene,⁵ (d) (*Z*)-1-chloro-2-fluoroethylene,⁶ and (e) 2-chloro-1,1-difluoroethylene.⁷ Atom colors: C, dark gray; H, light gray; F, light blue; chlorine, green.

mode) and a Cl, H pair at one end of the double bond (the “side-binding” mode).

When both F and Cl are present in the ethylene subunit, we are able to observe the manner in which they compete with each other in the interactions with HCCH. Although 1-chloro-1-fluoroethylene offers two top-binding modes—the F, H pair and the Cl, H pair—we have observed only binding to the first pair (Figure 1c).⁵ On the other hand, (*Z*)-1-chloro-2-fluoroethylene offers two side-binding modes—the geminal F, H pair and the geminal Cl, H pair—but this time, the binding is to the latter (Figure 1d).⁶ It appears that given a choice for HCCH, the most stable top-binding configuration is to the more nucleophilic F, but the most stable side-binding configuration is to Cl, the halogen atom that has less stringent steric requirements.

These observations raise the question regarding the competition between a top-binding and a side-binding mode, each to a different halogen atom. We have investigated the complex between 2-chloro-1,1-difluoroethylene and HCCH⁷ where the ethylene offers a top-binding mode to F and a side-binding mode to Cl. Because of the presence of only one H atom in the ethylene, both modes of bonding necessarily involve this atom. The fact that HCCH side-binds to the less nucleophilic Cl (Figure 1e) shows that both the relaxed orientation requirement of Cl and the weaker hydrogen bond (compared to a putative stronger hydrogen bond to F) incur less steric strain for the hydrogen bond in bending to allow the triple bond to interact with the H atom. It is interesting to note that in 2-chloro-1,1-difluoroethylene, the Cl atom, likely because of its proximity to the H atom, is more easily able to draw electron density from it than the F atoms can. As a result, Cl does not appear to be significantly less nucleophilic than the F atoms.⁷

We have one last scenario to consider in the competition between different modes: top-binding to Cl versus side-binding to F. These modes are supplied by (*E*)-1-chloro-1,2-difluoro-

ethylene. We have, so far, been unable to observe a top-binding mode to Cl formed by HCCH but have observed both top-binding and side-binding to F. The top-binding mode is exhibited by vinyl fluoride–HCCH, whereas the side-binding mode has been observed in *cis*-1,2-difluoroethylene–HCCH⁸ and in 1,1,2-trifluoroethylene–HCCH.⁹ For *cis*-1,2-difluoroethylene, the side-binding mode is the only option if HCCH was to bind to an F, H pair. For 1,1,2-trifluoroethylene, the side-binding mode makes possible the interaction to the most nucleophilic F atom (which is closest to the H atom and can draw electron density from it more easily than the other two F atoms can). In this case, experimental results show that electrostatic factors outweigh steric strain. Our studies so far of haloethylene–HCCH complexes therefore suggest that HCCH would likely interact with (*E*)-1-chloro-1,2-difluoroethylene by side-binding to the F, H pair instead of top-binding to the Cl, H pair. Nevertheless, this speculation needs to be confirmed, and more importantly, the detailed structure of the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex needs to be elucidated to help advance a systematic understanding of intermolecular interactions.

II. AB INITIO CALCULATIONS

To aid the search for the microwave spectrum of the most abundant isotopologue of (*E*)-1-chloro-1,2-difluoroethylene–HCCH, we carry out *ab initio* calculations at the MP2/6-311++G(2d,2p) level with GAUSSIAN 16¹⁰ to determine the possible structures of this complex. The geometric parameters of both subunits are set to their averaged, experimental values.^{11,12} To locate HCCH, we use the inertial axis system of (*E*)-1-chloro-1,2-difluoroethylene as the coordinate system and define the plane of the molecule as the *x*–*z* plane. The center of mass of HCCH is then placed at various polar angles and azimuthal angles, while the distance between the two subunits and the orientation of HCCH is allowed to optimize. This relaxed scan is carried out with the polar angle varying from 5

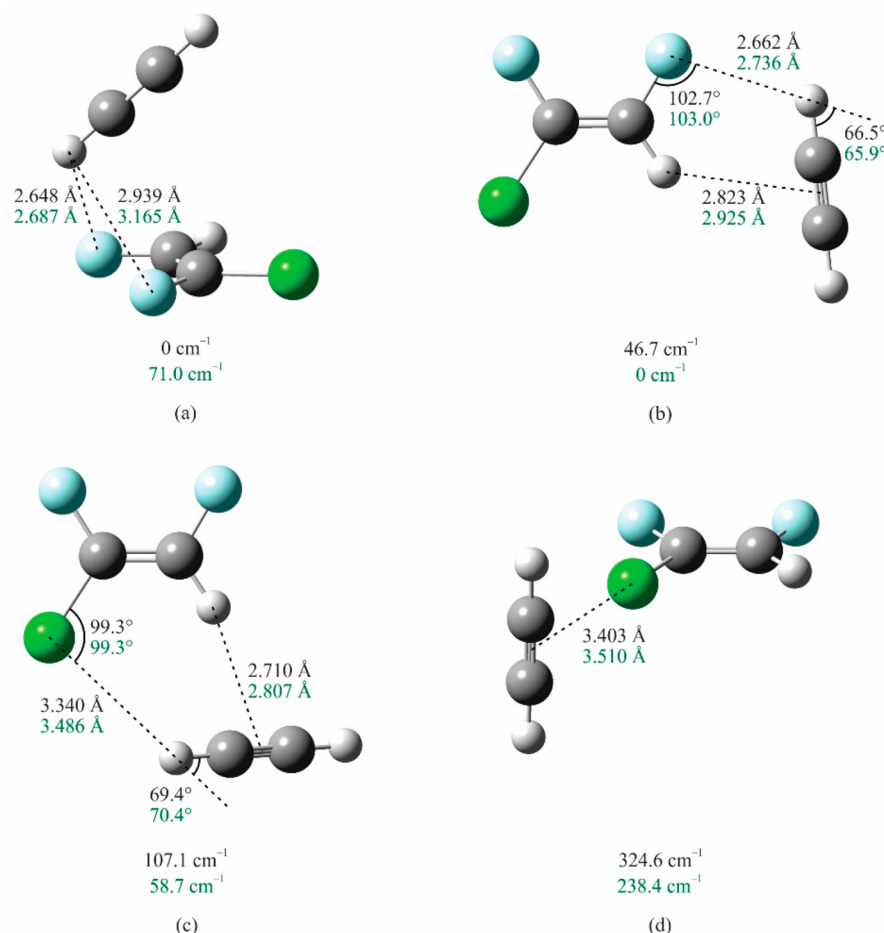


Figure 2. Optimized, *ab initio* structures of four isomers of (*E*)-1-chloro-1,2-difluoroethylene–HCCH. The relative energies without and with BSSE correction are in black and green, respectively. Atom colors: C, dark gray; H, light gray; F, light blue; chlorine, green.

Table 1. Rotational Constants, Dipole Moment Components, and Relative Equilibrium and Zero-Point-Corrected Energies for Four Isomers of (*E*)-1-Chloro-1,2-difluoroethylene–HCCH 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 a		Isomer b		Isomer c		Isomer d	
<i>A</i> /MHz	2090	2119	3137	3143	2322	2320	6619	6545
<i>B</i> /MHz	1464	1345	867	838	1144	1093	676	657
<i>C</i> /MHz	1061	1003	679	662	777	754	635	618
$ \mu_a /D$	0.729	0.693	0.770	0.762	1.826	1.809	1.290	1.287
$ \mu_b /D$	0.479	0.506	1.616	1.615	0.629	0.647	1.363	1.351
$ \mu_c /D$	1.492	1.497	0.000	0.000	0.217	0.207	0.000	0.000
$E_{\text{equil}}^{a,b}/\text{cm}^{-1}$	0.0	71.0	46.7	0.0	107.1	58.7	324.6	238.4
$E_{\text{zpe}}^{a,c}/\text{cm}^{-1}$	0.0	71.3	77.5	0.0	110.0	32.0	314.7	194.2

^aThe energy of the most stable isomer is set to 0 for the structures computed individually with and without BSSE correction. ^bThis equilibrium energy is determined by using the average, experimental structures of (*E*)-1-chloro-1,2-difluoroethylene and HCCH and optimizing the intermolecular degrees of freedom, without and with BSSE correction, individually. ^cA full relaxation of the complex geometry, including the structural parameters of (*E*)-1-chloro-1,2-difluoroethylene and HCCH, is used to compute an equilibrium energy (which differs slightly from that where the subunits are fixed to their respective average structures, as in the preceding line) and a harmonic zero-point correction to this energy, which is applied to both the BSSE-uncorrected and -corrected energies. The counterpoise calculation is performed using the optimized structure obtained without the BSSE correction.

to 175° and the dihedral angle varying from 0 to 180°, both in 10° increments. Because of the planar symmetry of (*E*)-1-chloro-1,2-difluoroethylene, it is unnecessary to place the HCCH center of mass at dihedral angles greater than 180°. After locating four potential minima in the scans over 342

points, we optimize the corresponding structures, which are shown in Figure 2. The rotational constants, dipole moment components, and equilibrium energy for each isomer are listed in Table 1. These isomers are labeled as a, b, c, and d, in order of increasing energy. The atomic coordinates for each isomer

in its principal axis system are available as [Supporting Information](#).

The lowest energy structure of (*E*)-1-chloro-1,2-difluoroethylene–HCCH, Isomer a, shows a nonplanar structure, with HCCH forming a bifurcated interaction with both F atoms. The interaction involving F bonded to C-1 is longer (by 10%), and therefore weaker, than that involving F bonded to C-2. This is a reflection that the former F atom is less nucleophilic, likely because it is closer than the latter to the electronegative Cl atom. With the energy of Isomer a set to 0 cm^{−1}, Isomer b has a planar side-binding to F configuration at 46.7 cm^{−1}, while Isomer c has a slightly nonplanar top-binding to Cl configuration at 107.1 cm^{−1}. Lastly, at a much higher energy of 324.6 cm^{−1}, Isomer d shows an interaction between Cl and the triple bond, a purely dispersive interaction.

In our experience, the energy ordering of weakly bound isomers sometimes, but not always, changes when we correct for basis set superposition error (BSSE) and/or zero-point energy. We have not yet found that any of these corrections consistently gives a better prediction of the lowest energy structure. It is, therefore, worthwhile to carry out both corrections to allow us to understand better for which complexes they are useful while, at the same time, bearing in mind that the delicate nature of van der Waals interactions may be too difficult to model to a precision of tens or hundreds of wavenumbers. The four isomers are reoptimized with a BSSE correction,¹³ and the corresponding rotational constants, dipole moment components, and equilibrium energies are listed in [Table 1](#). (The atomic coordinates for each isomer, after BSSE correction, in its principal axis system are available as [Supporting Information](#).) These rotational constants differ from the corresponding ones without BSSE correction by no more than 5% in all but one case (the corrected *B* constant for Isomer a differs from the uncorrected one by 9%). Similarly, the dipole moment components for the uncorrected and corrected structures differ by no more than 6%. The energy ordering for Isomers a, b, and c, however, does switch when BSSE correction is taken into account: The side-binding to the F structure (Isomer b) is now the global minimum (set at 0 cm^{−1}), followed by the top-binding to the Cl structure (Isomer c) at 58.7 cm^{−1}, which in turn is followed by the structure where HCCH forms a bifurcated interaction to the F atoms in (*E*)-1-chloro-1,2-difluoroethylene (Isomer a) at 71.0 cm^{−1}. Finally, Isomer d remains at the highest energy.

Considering only the zero-point energy correction,¹⁴ the energy ordering of the four isomers remains the same as that given by the equilibrium energies (with both subunits fixed at their averaged, experimental structures). With both zero-point energy and BSSE corrections, the energy ordering is the same as that when only the BSSE correction is used. Thus, the BSSE correction is the only one that changes the energy ordering, and the experimental structure of the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex will be useful in establishing the importance of the correction for this complex.

Because the rotational constants of the four isomers are very different, their rotational spectra should be easily distinguishable. Additionally, the dipole moment components suggest that the strongest transitions for Isomers a, b, and c should be, respectively, *c*, *b*, and *a* type transitions, whereas Isomer d should have strong *a* and *b* type transitions.

III. EXPERIMENT

The rotational spectra of (*E*)-1-chloro-1,2-difluoroethylene–HCCH are obtained using a sample with 1% of the haloethylene (SynQuest Laboratories) and 1% HCCH diluted in argon at a backing pressure of 1.5 atm. We use two Fourier transform microwave spectrometers for this work: a broadband chirped pulse (5.6–18.1 GHz) spectrometer^{15–17} and a narrow band, Balle–Flygare (5–21 GHz) spectrometer.^{16,18} Both utilize 0.8 mm diameter pulsed nozzles, two for the broadband and one for the narrow band instrument. We first collect the spectrum with the broadband spectrometer. The sample is polarized using a chirped microwave polarization pulse with a 4 μs duration and 20–25 W of power. The resulting free induction decay (FID) is digitized at 50 Gs s^{−1} for 10 μs beginning 0.5 μs after the end of the excitation pulse. Ten FIDs are collected during each 500 μs opening of the pulsed valves, which typically operate at 4 Hz, although this is reduced to 0.8 Hz for overnight operation. Approximately 400 000–500 000 FIDs are averaged for each segment, and as described previously, the average is Fourier transformed to give a frequency domain spectrum with a resolution element of 23.84 kHz and typical line widths (fwhm) of 225 kHz. The presence of the ³⁵Cl nucleus gives rise to nuclear quadrupole coupling, splitting each rotational transition into a number of hyperfine components. As a result, the transitions are quite weak. Thus, spectra are acquired in 1.5 GHz segments to provide a greater intensity due to the greater microwave power per unit bandwidth.

The chirped pulse spectrum allows us to assign several *b* type transitions for the most abundant isotopologue of (*E*)-1-chloro-1,2-difluoroethylene–HCCH and to determine the rotational constants to fairly good precision. We then turn to our higher-resolution, higher-sensitivity Balle–Flygare Fourier transform microwave spectrometer^{16,18} both to measure the observed transitions to greater precision and to record those not detected by the chirped pulse instrument (either because they are weaker or outside the operation range). We are also able to obtain the spectrum for the ³⁷Cl containing isotopologue in natural abundance and, with the use of an enriched sample of H¹³CCH, the spectra for two species singly substituted with ¹³C. This narrow band instrument delivers the gas pulse parallel to the resonator axis, resulting in a Doppler doubling of each transition. The arithmetic mean of the frequencies for the two components of the doublet provides the rest frequency of the transition. Transitions are measured in the 5.6–19.7 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 element.

IV. RESULTS

A. Spectral Analysis. Using the narrow band spectrometer, we have observed for the four isotopologues of (*E*)-1-chloro-1,2-difluoroethylene–HCCH both *a* and *b* type transitions, ranging from a total of 129 for the normal isotopologue to as low as 66 for one of the ¹³C-substituted versions. The number of corresponding chlorine nuclear quadrupole hyperfine components likewise ranges from a high of 558 to a low of 240. We have accessed *J* from 1 to at least 9 and *K_a* from 0 to at least 3. An example illustrating the quality of our data is illustrated in [Figure 3](#), a composite of two

spectra showing four hyperfine components of the $8_{18}-7_{17}$ transition for the most abundant isotopologue.

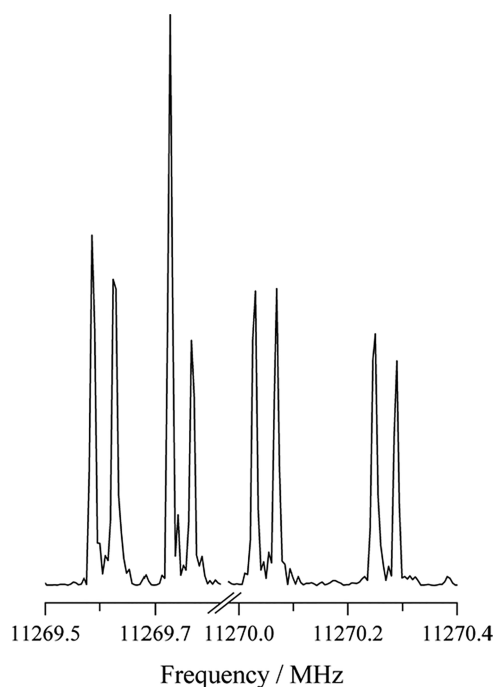


Figure 3. $8_{18}-7_{17}$ rotational transition for the most abundant isotopologue of (*E*)-1-chloro-1,2-difluoroethylene–HCCH observed in two segments, linked together by a break in the frequency scale, using a Balle–Flygare Fourier transform microwave spectrometer. Four ^{35}Cl quadrupole hyperfine components, each split into a Doppler doublet, corresponding respectively, to $F' - F'' = 15/2 - 13/2$, $17/2 - 15/2$, $13/2 - 11/2$, and $19/2 - 17/2$ in order of increasing frequency.

The narrow band spectrum for each isotopologue is analyzed using the Watson *A*-reduced Hamiltonian,¹⁹ with the inclusion

of a chlorine nuclear quadrupole coupling interaction and Pickett's nonlinear SPFIT program.²⁰ We have determined all three rotational constants and five quartic centrifugal constants and, for the nuclear quadrupole coupling tensor, χ_{aa} and $\chi_{bb} - \chi_{cc}$. The individual diagonal components of the tensor are then evaluated using the Laplace condition, $\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$. Additionally, as shown below, the rotational constants are consistent with a planar complex; thus, the only nondiagonal component of the nuclear quadrupole coupling tensor is χ_{ab} , and we have also determined its magnitude. These 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 smaller than 2 kHz, less than half of the resolution element of the spectrum.

A comparison between the experimental rotational constants of the most abundant isotopologue and those predicted by theory shows excellent agreement with the constants of Isomer b. Additionally, we have found that *b* type transitions are in general stronger than *a* type, which is also consistent with Isomer b.

B. Structure Determination. The values of the inertial defect for the four isotopologues range from -0.0008 to 0.012 u Å². The nearness of them to zero indicates that the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex is planar and exhibits little effect from either in- or out-of-plane zero-point vibrational motions. The asymmetry parameter of each isotopologue is between -0.863 and -0.855 , which, in fact, justifies the use of the Watson *A*-reduced Hamiltonian for spectral analyses.

Before determining the average structure of the complex, we first establish the positions of the Cl atom in (*E*)-1-chloro-1,2-difluoroethylene and the C atoms in HCCH by calculating their Kraitchman substitution coordinates using the most abundant species as the parent.²¹ We are also able to assign relative signs to these coordinates to give reasonable atomic distances (Table 3). The *b* coordinate of one of the C atoms is

Table 2. Spectroscopic Constants^a for Four Isotopologues of (*E*)-1-Chloro-1,2-difluoroethylene–HCCH^{b,c}

	C ³⁵ ClFCHF–HCCH	C ³⁷ ClFCHF–HCCH	C ³⁵ ClFCHF–H ¹³ CCH	C ³⁵ ClFCHF–HC ¹³ CH
<i>A</i>	3174.268000(55)	3112.26250(11)	3174.578416(87)	3147.71022(16)
<i>B</i>	848.665544(25)	838.537102(38)	830.023458(56)	828.046838(76)
<i>C</i>	669.634435(18)	660.551364(27)	657.990823(40)	655.578147(60)
$\Delta_J/10^{-3}$	0.81561(14)	0.80500(25)	0.76760(39)	0.79891(52)
$\Delta_{JK}/10^{-3}$	−3.4837(11)	−3.6138(20)	−3.2596(20)	−3.3843(38)
$\Delta_K/10^{-3}$	29.5833(32)	29.0284(88)	29.3252(53)	28.766(13)
$\delta_J/10^{-3}$	0.234971(63)	0.23407(11)	0.21674(19)	0.22612(22)
$\delta_K/10^{-3}$	2.7914(48)	2.6811(83)	2.736(12)	2.790(21)
χ_{aa}	11.55005(83)	8.2817(17)	11.5407(20)	12.5006(23)
χ_{bb}	−49.31426(92)	−38.0466(13)	−49.3017(16)	−50.2625(19)
χ_{cc}	37.76422(81)	29.7650(14)	37.7610(16)	37.7619(20)
$ \chi_{ab} $	41.319(14)	37.817(11)	47.358(27)	46.698(29)
no. of rotational transitions	129	89	84	66
no. of <i>a</i> type	52	38	32	28
no. of <i>b</i> type	77	51	52	38
no. of hyperfine components	558	327	305	240
<i>J</i> range	1–12	1–10	1–9	1–9
<i>K_a</i> range	0–4	0–3	0–4	0–3
rms/kHz	1.62	1.46	1.76	1.87

^aIn MHz, unless as otherwise noted. ^b1σ standard deviations in the parameters are given in parentheses. ^cThe nuclear quadrupole coupling constants of chlorine are fitted as $1.5\chi_{aa}$ and $(\chi_{bb} - \chi_{cc})/4$, and the Laplace condition is used to calculate the individual hyperfine constants.

Table 3. Coordinates of the Chlorine Atom in (*E*)-1-Chloro-1,2-difluoroethylene and the Carbon Atoms in HCCH Determined from a Kraitchman Analysis and a Structure Fit of Four Isotopologues of CCIFCHF–HCCH

	<i>a</i> /Å	<i>b</i> /Å
(i) substitution coordinates ^{a,b}		
Cl	1.90608(79)	−1.2808(12)
C	−3.66584(41)	undetermined
C	−3.85387(39)	−1.1813(13)
(ii) from structure fit		
Cl	1.9129	−1.2790
C	−3.6750	0.0103
C	−3.8661	−1.1828

^aCostain errors²⁶ in the parameters are given in parentheses.

^bAlthough only the absolute values of the substitution coordinates can be determined from the Kraitchman analysis, the relative signs for the *a* and *b* coordinates are assigned using physically reasonable atomic distances.

nonphysical, suggesting that it lies very close to the *a* axis. The positions of these coordinates indeed agree with those for Isomer b (as presented in Supporting Information).

To find the average structure of the complex, we assume the structures of the subunits do not change upon complexation. As a result of the planarity of the complex, we need only three geometric parameters to define its structure: a distance between the two subunits and one angle for each subunit as described below. We choose these to be the distance between the centers of the C=C bond and the C≡C bond, and the angles made by the line connecting these centers with, respectively, HCCH and the C=C bond. These geometric parameters are fit to I_a and I_c of each of the four isotopologues using Schwendeman's STRFTQ program.²² (Only two of three moments of inertia are independent in a planar species.) The rms deviation of the fit is 0.035 u Å², and the chemically relevant parameters are shown in Figure 4a. Specifically, HCCH forms a hydrogen bond of 2.7659(88) Å with the F atom connected to C-2 in (*E*)-1-chloro-1,2-difluoroethylene. This bond forms an angle of 104.829(66)° with the C–F bond and bends by 70.55(38)° to bring the triple bond of HCCH to 2.8865(2) Å from the geminal H atom. The coordinates of the Cl atom and the two C atoms from the fit are listed in Table 3. The agreement between the average coordinates and the corresponding Kraitchman coordinates is remarkable—the greatest absolute difference is 0.012 Å and the greatest relative difference is 0.36%—a confirmation that the complex indeed is very rigid and exhibits little zero-point motion. Additionally, the *b* coordinate of one of the C atoms in HCCH indeed is very small (0.0103 Å). Thus, it is not surprising that the different zero-point motions of the species containing ¹³C in

this position and the parent species, even if small, can make the substitution coordinate of this atom ill-determined and assume a nonphysical value, as shown in Table 3.

C. Nuclear Quadrupole Coupling Constants. The principal nuclear quadrupole coupling constants, χ_{xx} , χ_{yy} , and χ_{zz} (named in order of increasing magnitude), for the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex, determined from the experimental constants, are 37.3781, 37.7642, and −75.1423 MHz, respectively, with the *y* axis parallel to the *c* inertial axis and the *x* and *z* axes in the plane of the complex. These values are very similar to the corresponding constants for the (*E*)-1-chloro-1,2-difluoroethylene monomer (37.7309, and 37.8434, −75.5741 MHz, the *y* axis is also in the same direction as that for the complex), differing by only 0.9, 0.2, and 0.6%. It thus appears that the zero-point motions of the complex and the monomer are very similar and that HCCH does not cause any significant perturbation to the electric field gradient of the (*E*)-1-chloro-1,2-difluoroethylene subunit upon complexation, which is not surprising given the distance between the acetylene molecule and the chlorine atom.

The *z* principal electric field gradient axis in (*E*)-1-chloro-1,2-difluoroethylene–HCCH and the C–Cl bond in the substituted ethylene both form similar angles with the *a* inertial axis (61.37 and 61.86°, respectively), indicating that the *z*-axis lies practically along the C–Cl bond. Furthermore, the magnitude of the asymmetry parameter for the nuclear quadrupole coupling constants, $|η| = |(\chi_{xx} - \chi_{yy})/\chi_{zz}|$, is 0.0051; thus, the charge distribution about the *z* axis is very cylindrical.

V. DISCUSSION

With argon as the carrier gas, the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex is expected to relax to the lowest energy structure.^{23–25} Because the experimental structure is consistent with Isomer b, BSSE correction is essential in this case to give the correct, global minimum configuration. The values of the predicted *A* rotational constant, with and without BSSE correction, are smaller than the experimental constant for the most abundant isotopologue by 37 and 31 MHz, respectively. The values of the predicted *B* and *C* rotational constants, calculated without the BSSE correction, are 18 and 9 MHz greater than the experimental constants, respectively, while those calculated with the BSSE correction are smaller by 11 and 8 MHz, respectively. It is interesting to note that when the values of the predicted *B* constant with and without BSSE correction are averaged, they are only 4 MHz greater than the experimental value. When the same is done to the values of the predicted *C* constant, it is only 1 MHz greater than the experimental value. In any event, with or without BSSE correction, theory is able to predict rotational constants to within 2% of their observed values. Of course, this still presents

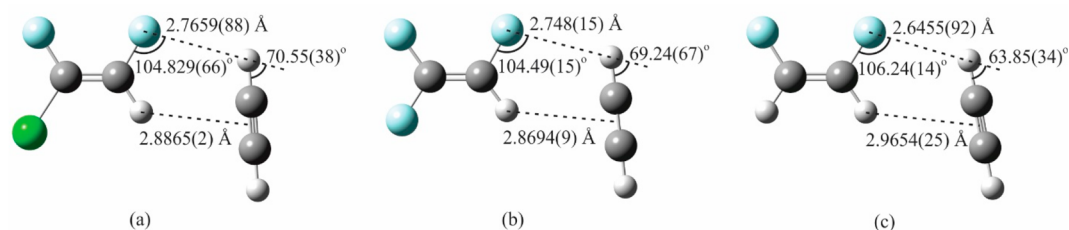


Figure 4. Experimental structure of (a) (*E*)-1-chloro-1,2-difluoroethylene–HCCH (this work), (b) 1,1,2-trifluoroethylene–HCCH,⁹ and (c) *cis*-1,2-difluoroethylene–HCCH.⁸

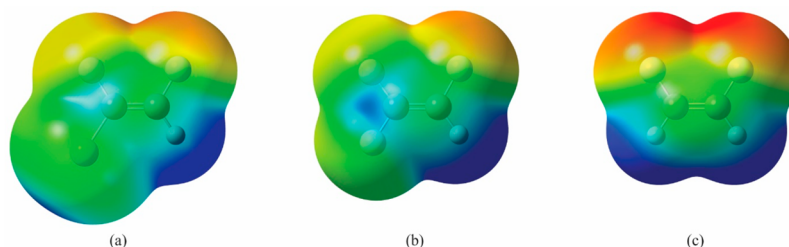


Figure 5. Electrostatic potential mapped onto the total electron density isosurface for (a) (*E*)-1-chloro-1,2-difluoroethylene, (b) 1,1,2-trifluoroethylene, and (c) *cis*-1,2-difluoroethylene. The same value of electron density and identical color scales are used for the surfaces. Blue represents positive electrostatic potential, and red represents negative electrostatic potential.

a large search range for transitions in the microwave region; thus, the broadband spectrum provided by the chirped pulse spectrometer is particularly valuable in guiding the search for transitions, allowing us to obtain the spectrum of the most abundant species expeditiously and subsequently to search for those of the other isotopologues using the narrow band, Balle–Flygare instrument.

Once again for HCCH, a top-binding configuration to Cl is not observed. Instead, the (*E*)-1-chloro-1,2-difluoroethylene–HCCH complex adopts the sterically strained side-binding configuration to the F atom connected to C-2 (Figure 4a). The structure of this complex is remarkably similar to its 1,1,2-trifluoroethylene counterpart (Figure 4b). The hydrogen bond length for (*E*)-1-chloro-1,2-difluoroethylene–HCCH is longer by 0.0179 Å and bends more from linearity by 1.31° than the trifluoroethylene complex. However, each of these differences is within 2σ of the larger uncertainty for the corresponding parameters, suggesting that the hydrogen bond in the present complex is not significantly weaker than that in 1,1,2-trifluoroethylene–HCCH despite the longer bond and greater deviation from linearity. On the contrary, the interaction between the triple bond and the H atom for (*E*)-1-chloro-1,2-difluoroethylene–HCCH is longer by a statistically significant amount (0.0171 Å). The values of the CFH angle for these two complexes also agree well, differing by 0.34°, an amount only slightly greater than 2σ of the larger uncertainty.

The similarity between these two complexes can be explained by mapping the electrostatic potential onto the total electron density surface for each substituted monomer. For both (*E*)-1-chloro-1,2-difluoroethylene (Figure 5a) and 1,1,2-trifluoroethylene (Figure 5b), the F atom connected to C-2 is the most nucleophilic atom, while the geminal hydrogen is the only electropositive atom. These two atoms form the most optimal sites for HCCH to bind. In fact, a qualitative examination of these two surfaces shows that these F atoms in the two substituted ethylene subunits are similarly electro-negative, while the H atom in (*E*)-1-chloro-1,2-difluoroethylene is slightly less electropositive than that in 1,1,2-trifluoroethylene. These surfaces are therefore consistent with the experimental findings: the interactions involving the hydrogen bonds are similar, but those between the triple bond and the hydrogen atom are somewhat different, with that in the (*E*)-1-chloro-1,2-difluoroethylene complex slightly weaker (and therefore with a longer interaction length). It is interesting to note that the F atom geminal to the Cl atom in (*E*)-1-chloro-1,2-difluoroethylene is more negative than its counterpart in 1,1,2-trifluoroethylene; F is more likely to be able to withdraw electron density from a geminal Cl atom than from a geminal F atom.

The only other haloethylene–HCCH complex that exhibits a side-binding to F mode is *cis*-1,2-difluoroethylene–HCCH.⁸ In the absence of a third halogen atom, such as that in both (*E*)-1-chloro-1,2-difluoroethylene and 1,1,2-trifluoroethylene, the intermolecular interaction lengths are significantly different when the dihaloethylene complex (Figure 4c) is compared with the trihaloethylene complexes. The F atoms in *cis*-1,2-difluoroethylene are more nucleophilic, as shown by the electrostatic potential of the molecule mapped onto its electron density surface in Figure 5c. As a result, the hydrogen bond in the *cis*-1,2-difluoroethylene–HCCH complex (Figure 4c) has a length of 2.6455(92) Å, significantly shorter (by 0.1 Å) than those in the trihaloethylene complexes. This stronger bond bends by 63.85(34)°, less than that observed in the trihaloethylene complexes and, as a result, forms an appreciably longer (by 0.08–0.1 Å)—hence weaker—interactions between the triple bond and the geminal H. Turning this around, although the hydrogen bond is weaker in each of the trihaloethylene complexes, energetically it costs less for it to bend more from linearity, and the second interaction between the geminal H and the triple bond is more stabilizing than that for the *cis*-1,2-difluoroethylene complex.

In (*E*)-1-chloro-1,2-difluoroethylene, the acetylene is offered the alternatives of either forming a C–Cl⋯H hydrogen bond in the “top-binding” arrangement, in which the second interaction is to a hydrogen atom *cis* to the Cl atom hydrogen bond acceptor or adopting the “side-binding” configuration with a C–F⋯H hydrogen bond where the H atom involved in the second interaction is geminal to the halogen. We have argued previously^{3,4} that the latter is sterically unfavorable, while the former has yet to be observed as a lowest energy configuration for a haloethylene–acetylene heterodimer. That is, when complexing with haloethylenes, the more favorable arrangements for acetylene are top-binding to fluorine or side-binding to chlorine, which are not possible with (*E*)-1-chloro-1,2-difluoroethylene.

VI. CONCLUSIONS

The microwave rotational spectrum of (*E*)-1-chloro-1,2-difluoroethylene–HCCH has been obtained and analyzed, and the structure of this gas-phase heterodimer determined. The experimental structure is extremely well predicted by *ab initio* quantum chemistry calculations at the MP2/6-311++G(2d,2p) level. Although corrections for basis set superposition error are essential for correctly predicting the lowest energy configuration for this species, the observed spectroscopic constants are nearly equally well predicted by calculations including this correction or not. The observed configuration is a planar geometry with a hydrogen bond together with a second interaction between a nucleophilic

portion of the acid (the HCCH triple bond here) and a hydrogen atom on the haloethylene as has been observed for the majority of similar complexes.¹ With the two more favored motifs not possible in (*E*)-1-chloro-1,2-difluoroethylene, top-binding to fluorine or side-binding to chlorine, the sterically challenging side-binding to fluorine is preferred over the still unobserved top-binding to chlorine. Indeed, the observed structure is nearly unchanged from that of the analogous species 1,1,2-trifluoroethylene–HCCH,⁹ with little effect from the substitution of F by Cl on the remote carbon.

In examining the binding modes for acetylene to fluorine and chlorine in haloethylenes, we have seen top-binding to fluorine preferred over top-binding to chlorine in 1-chloro-1-fluoroethylene–HCCH,⁵ side-binding to chlorine preferred over side-binding to fluorine in (*Z*)-1-chloro-2-fluoroethylene,⁶ side-binding to chlorine over top-binding to fluorine in 2-chloro-1,1-difluoroethylene,⁷ and, finally in this work, side-binding to fluorine preferred over top-binding to chlorine. In each of these cases, only one mode of binding is available for each halogen. The still uncharacterized (*E*)-1-chloro-2-fluoroethylene–HCCH complex is unique in offering all four combinations of top and side-binding to both fluorine and chlorine. It would be interesting to see what is the preferred mode when all four are available. However, this species has a small dipole moment, presenting a challenge for rotational spectroscopy, although preliminary quantum chemistry calculations do suggest they should be observable using the higher sensitivity of the Balle–Flygare spectrometer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c05169>.

Tables of observed and calculated transition frequencies for four isotopologues of the (*E*)-1-chloro-2-fluoroethylene–HCCH complex, the atomic coordinates for the theoretical structures shown in Figure 1, and the complete citation for Gaussian 16 (ref 10) (PDF)

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Notes

The authors declare no competing financial interest.

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