Exploring the sterically disfavored binding of acetylene to a geminal olefinic hydrogen-fluorine atom pair: The microwave spectrum and molecular structure of *cis*-1,2-difluoroethylene–acetylene

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Abstract

The microwave rotational spectrum of the gas-phase bimolecular heterodimer formed between *cis*-1,2-difluoroethylene and acetylene is obtained using Fourier transform microwave spectroscopy from 5.9 to 21.2 GHz. Rotational constants derived from the analysis of the spectra for the normal isotopologue and singly-substituted ^{13}C isotopologues, obtained in natural abundance, allow the determination of the structure of the complex, which, in the absence of a fluorine-hydrogen atom pair located *cis* to each other, adopts a sterically disfavored geometry ("side-binding") in which the acetylene interacts with a geminal fluorine-hydrogen atom pair. Structural details are found to be similar to previously studied heterodimers with side-binding of acetylene to fluorine while reflecting the degree of halosubstitution. A detailed comparison with the (*Z*)-1-chloro-2-fluoroethylene-acteylene complex reveals information regarding the relaxed steric requirements for hydrogen bonding to chlorine as opposed to hydrogen bonding to fluorine.

I. Introduction

To investigate the nature of intermolecular interactions, we have been conducting a systematic study of complexes formed between haloethylenes and protic acids.[1] Haloethylenes furnish multiple possible sites for an acid to bind, and by varying the number and type of halogen atoms, we can observe how different parts of the molecule compete and cooperate with each other in intermolecular interactions. The consequences can often be succinctly rationalized by the familiar chemical concepts of nucleophilicity, electrophilicity, and steric effects, ideas that are reinforced by quantum chemistry calculations. In this work, we focus on acetylene complexes. For the fluoroethylenes vinyl fluoride and 1,1,2-trifluoroethylene, HCCH forms two interactions in each case to give a planar complex: a hydrogen bond between one of the H atoms in HCCH and an F atom in the ethylene subunit, and a second interaction between the acetylene triple bond and an H atom in the ethylene. For vinyl fluoride, HCCH binds across the double bond, interacting with the F, H pair located *cis* to each other (Fig. 1a),[2] while for 1,1,2-trifluoroethylene, HCCH binds at one end of the double bond, interacting with the geminal F, H pair (Fig. 1b).[3] We have termed these two different motifs "top" and "side" binding, respectively, for HCCH binding across and at one end of the double bond. We can readily explain these two modes of binding. Vinyl fluoride offers two possible sites for the interaction with the acetylene triple bond: the H atoms geminal and *cis* to F. The geminal H atom is closer to the F atom and should be more electropositive, as we have argued previously.[4-5] This can be visualized by mapping the electrostatic potential onto its total electron density surface as in Fig. 2a. Thus, from a purely electrostatic point-of-view, a side-binding configuration for HCCH

should be more favorable. To achieve this configuration, however, the hydrogen bond would have to bend much more from linearity than it does in the top binding, experimental structure to give the same triple bond---H interaction length. The fact that this configuration is not observed suggests that the stronger electrostatic interaction in the side-binding configuration cannot compensate for the unfavorable steric strain. When we change the ethylene subunit to 1,1,2-trifluoroethylene, HCCH once again can bind to it in two different manners. In this case, there are two possible hydrogen bond acceptors: the F atoms geminal and *cis* to the only H atom. Because the geminal F is closer to the electropositive H and therefore, is more nucleophilic (as corroborated by its mapped electrostatic potential surface shown in Fig. 2b), it should form a stronger hydrogen bond with HCCH. This is indeed the configuration observed even though the hydrogen bond has to bend a great deal more from linearity than it would in the top binding mode for the triple bond to forge the second interaction. Here, electrostatic factors of the side-binding configuration outweigh the steric factors of the top binding configuration.

When we change the halogen atom in the singly substituted ethylene from fluorine to chlorine, HCCH interacts with it in the side-binding configuration (Fig. 1c), not top binding as in vinyl fluoride. The change in configuration arises from the vastly different electron density distributions of F and Cl, as demonstrated theoretically in mapped potential surfaces of vinyl fluoride and vinyl chloride (Fig. 2a,c). The most negative potential of F points away from the C–F bond in vinyl fluoride, thus directing the hydrogen bond at a relatively large angle from it. Experimentally, this angle is ~120º for an acid (such as HF, HCl, and HCCH) in adopting a top binding motif[2, 6-17] and ~108º for a side-binding motif.[3, 18-19] This is not the case for vinyl chloride, where the most negative potential of Cl is on a band centered about the atom and approximately perpendicular to the C–Cl bond, making it favorable for the hydrogen bond to

form a small angle with the C–Cl bond. So far, the only top binding mode observed involving Cl in a haloethylene complex is vinyl chloride-HF, where the hydrogen bond forms an angle of 102° with the C–Cl bond.[20] Three complexes, vinyl chloride-HCCH,[4] (*Z*)-1-chloro-2-fluoroethylene-HCCH,[5] and 2-chloro-1,1-difluoroethylene-HCCH[21] adopt side-binding motifs involving Cl, and the hydrogen bond forms an angle of ~89° with the C–Cl bond. The smaller angles formed by the hydrogen bond and C–Cl relaxes the steric requirements, and in the case for the acid partner HCCH, allows the acetylene triple bond to interact with the more electropositive H atom geminal to Cl.

The competition between F and Cl can be observed if both are present in the ethylene subunit. When only top binding modes are available, such as in 1-chloro-1-fluoroethylene,[13] HCCH interacts with the F, H pair across the double bond (Fig. 1d). When only side-binding modes are present, such as in (*Z*)-1-chloro-2-fluoroethylene,[5] however, HCCH interacts with the Cl, H pair at one end of the double bond (Fig. 1e). Given the choice between top binding to F or side binding to Cl in 2-chloro-1,1-difluoroethylene, HCCH once again interacts with the Cl, H pair at one end of the double bond,[21] similar to the case in (*Z*)-1-chloro-2-fluoroethylene. In all three cases, F is the more nucleophilic atom and therefore, it is electrostatically more favorable for HCCH to form a hydrogen bond to it. It follows then that electrostatic factors are dominant in 1-chloro-1-fluoroethylene where HCCH binds to the F atom but not in (*Z*)-1-chloro-2-fluoroethylene or 2-chloro-1,1-difluoroethylene where other factors predominate over the favorable H---F interaction. We are prompted to investigate whether HCCH could adopt a side-binding mode to F in a haloethylene other than 1,1,2-trifluoroethylene. We turn to *cis*-1,2-difluoroethylene-HCCH, where the Cl in (*Z*)-1-chloro-2-fluoroethylene is replaced by an F atom,

to address this question and to further explore the delicate balance between electrostatic and steric factors in the interactions between haloethylenes and HCCH.

II. *Ab Initio* Calculations

Fixing the structures of *cis*-1,2-difluoroethylene[22] and HCCH[23] to the experimental average structures of the free monomers, we explore their interaction potential energy surface to locate possible isomers of the complex using *ab initio* calculations at the MP2/6-311++G(2d,2p) level with Gaussian 16.[24] Three minima are found, and their structures are optimized without and with basis set superposition error (BSSE) correction[25] (Fig. 3). The relative energies of these structures, together with their rotational constants and dipole moment components, are listed in Table I. (The atomic positions for each isomer, in its principal coordinate system, are available as Supporting Information.) The lowest energy isomer [Structure (a)] is nonplanar, with HCCH perpendicular to the ethylene plane and the interactions are between the triple bond and the two H atoms of the ethylene subunit. Because of the symmetry of this isomer, the only nonzero dipole moment component is along the C_2 axis, and only *a* type transitions are expected in its rotational spectrum. The planar, side-binding structure [Structure (b)] is higher in energy by 15.7 cm^{-1} and 10.1 cm^{-1}, respectively, without and with BSSE correction, and should give both *a* and *b* type transitions in the rotational spectrum. The third isomer [Structure (c)] is much higher in energy than the global minimum structure, by 65.7 and 120.1 cm^{-1}, respectively, without and with BSSE correction. Here, HCCH forms a bifurcated hydrogen bond with the two F atoms in the ethylene subunit. This nonplanar isomer should give strong *c* type but weak *a* type transitions, and *b* type transitions are either very weak (predicted when BSSE correction is taken into account) or nonexistent (predicted without BSSE correction). In additional to exhibiting

different types of transitions, the rotational constants of these isomers differ significantly. As a result, they should give different rotational spectra.

III. Experiment

The complex is formed by expanding a mixture of 1% *cis*-1,2-difluoroethylene (SynQuest Laboratories) and 1% HCCH in Ar at a backing pressure of 1 – 2 atm into a Fourier transform microwave spectrometer. We start by using a broadband, chirped pulse spectrometer,[26-28] equipped with two 0.8 mm diameter nozzles, to collect the spectrum in the 5.6 – 18.1 GHz region. The sample is polarized using a chirped microwave polarization pulse of 4 μs duration and 20 – 25 W of power. The resulting free induction decay (FID) is digitized at 50 Gs s^{-1} for 10 μs beginning 0.5 μs after the end of the excitation pulse. Ten FIDs are collected during each 800 μs opening of the pulsed valves, which typically operate at 4 Hz, although this is reduced to 0.8 Hz for overnight operation. 540,000 to 720,000 FIDs are averaged for each segment, and as described previously,[27] 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 spectrum is then analyzed with guidance from the *ab initio* rotational constants. We do not observe a spectrum characteristic of Structure (a), but instead, we find the spectrum for Structure (b), and assign as many transitions as possible for the most abundant isotopologue plus three additional ones, each singly substituted with ^{13}C in natural abundance. We then turn to a narrow band, Balle-Flygare spectrometer to measure more precisely the transitions and to search for and measure weaker ones, including those derived from the fourth singly-substituted ^{13}C isotopologue. The Balle-Flygare instrument[27, 29] utilizes one 0.8 mm pulsed nozzle and operates in the 5 – 21 GHz range. 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 to give a frequency domain spectrum with a 4.8 kHz resolution element.

IV. Results

A. Spectral Analysis

The chirped pulse spectrum has very strong *b* type transitions and weaker *a* type transitions for the most abundant isotopologues of *cis*-1,2-difluoroethylene-HCCH. Figure 4 shows the signal strength for one of the *b* type transitions, $4_{13} - 4_{04}$. When this portion of the spectrum is magnified 50 fold, the same transition in 3 of the 4 isotopologues singly substituted with ^{13}C can be identified amidst many transitions from other species. No *c* type transitions were observed, either in the chirped pulse spectrum or upon searches with the Balle-Flygare instrument, consistent with the planar geometry determined for the molecule.

Analysis of the chirped pulse spectrum gives preliminary spectroscopic constants, facilitating the use of the higher resolution Balle-Flygare instrument to measure transitions that are too weak to observe in the chirped pulse spectrum, including transitions for the remaining ^{13}C containing species. In general, for the minor isotopologues, the transitions for the two species with ^{13}C closest to the hydrogen bond are the strongest and those for the species with ^{13}C farthest away from the hydrogen bond the weakest. Using the labeling system for the C atoms in Fig. 5a, the signal strengths decrease in order for ^{13}C in the positions #3, #1, #2, and #4. We also remeasure the transitions observed in the chirped pulse spectrum with this instrument to obtain higher precision. We use only transitions measured with the Balle-Flygare instrument in the following analysis.

We have observed 98 rotational transitions, accessing J in the range of 0 – 14 and K_a in the range of 0 – 4 for the most abundant isotopologue of *cis*-1,2-difluoroethylene-HCCH. The

number of transitions for each minor isotopologue is only about 1/3 as many, and they sample smaller J and K_a ranges. The spectrum for each species is initially analyzed using the Watson A reduced Hamiltonian in the I^r representation[30] and Pickett's SPFIT program,[31] and the spectroscopic parameters are listed in Table II. For all species, we determine three rotational constants, and for the most abundant isotopologue, 5 quartic and 3 sextic centrifugal distortion constants. For the ^{13}C containing species, we can fit only 3 of 5 quartic centrifugal distortion constants; thus, we fix the rest of the centrifugal distortion constants to the values appropriate for the most abundant species. Tables of observed and calculated transition frequencies with assignments for all isotopologues are available as Supporting Information. The rms deviation for each fit is no more than 2.1 kHz, commensurate with the resolution element of the Balle-Flygare spectrometer.

The rotational constants in Table II give a value of −0.98 for the asymmetry parameter for all 5 isotopologues. The nearness of this value to that of a prolate symmetric top, namely, −1, suggests that the Watson S reduced Hamiltonian[30] might be more appropriate in analyzing the spectrum of each species. We have done so, once again using the I^r representation and present the resulting spectroscopic constants as Supporting Information. In fact, as long as the values of B and C constants are not too close to each other (in our case, they differ by over 80 MHz for each isotopologue), the A reduction Hamiltonian is more efficient with matrix elements connecting only K_a values differing by ±2, which increases to ±6 for the S reduction Hamiltonian when sextic centrifugal distortion constants are included. In our case, for each isotopologue, the A, B, and C constants found using the A reduced Hamiltonian differ from those obtained using the S reduced Hamilton by −0.1 kHz, 17.8 kHz, and −17.7 kHz, respectively. These differences are so small that both sets of rotational constants give the same structure for the complex.

B. Structure Determination

The values of the inertial defect for the 5 isotopologues of *cis*-1,2-difluoroethylene-HCCH are slightly negative, ranging between –0.416 and –0.392 u Å^2, indicative of a planar complex exhibiting out-of-plane vibrational motion. Only three geometrical parameters are necessary to describe the structure of the complex: the distance between the two subunits and the angular orientation of each subunit. The following parameters, although not intuitive and found by trial and error, are used to avoid correlations: the distance of a line defined by C4 and the H atom connected to C2, the angle between this line and the C2–H bond, and the angle formed between this line and the HCCH subunit. (See Fig. 5a for the labeling scheme of the C atoms.) These parameters are fitted to I_a and I_c of each of the isotopologues using Schwendeman's STRFTQ program.[32] The rms deviation of the fit is 0.0220 u Å^2, and the chemically relevant parameters are shown in Figure 5a. HCCH forms a hydrogen bond of 2.6455(92) Å with an F atom in *cis*-1,2-difluoroethylene, and the bond bends by 63.85(34)^o from linearity so that the triple bond interacts with the H atom geminal to F with a length of 2.9654(25) Å. The CF---H angle is 106.24(14)^o.

In addition to the average structure derived above, we can also obtain the absolute values of the coordinates for the carbon atoms using a Kraitchman analysis[33] by treating the most abundant isotopologue as the parent. These coordinates are listed in Table III, together with those determined in the structure fit. The magnitudes of the two set of values agree excellently, differing no more than 3.5%.

V. Discussion

The *cis*-1,2-difluoroethylene-HCCH complex exhibits a planar, side-binding configuration, similar to Structure (b) derived from *ab initio* calculations. The experimental

rotational constants are well predicted by theory, the corresponding values differing by no more than 1.5% when BSSE correction is not taken into account and 1.7% when BSSE correction is included. Interestingly, when the constants calculated without and with BSSE correction are averaged, they differ from the experimental values by no more than 0.2%.

Initially, we were puzzled by the absence of the spectrum of Structure (a), the global minimum structure. To explore this further, we correct for zero-point energy in both Structures (a) and (b), but the energy ordering does not change: Structure (b) is at least 24 cm^{-1} higher in energy than Structure (a) with or without BSSE correction.[34] Keeping the same basis set but turning to a higher level of theory, however, the energy ordering does switch: Structure (b) becomes lower in energy than Structure (a) by 40, 39, and 22 cm^{-1} when calculated using MP4, CCSD, and CCSD(T), respectively. Because we use argon as a buffer gas, we expect to see the most stable complex in the expansion, which corresponds to the side-binding configuration for *cis*-1,2-difluroоethylene-HCCH. This implies that the MP2 level of theory does not give the correct energy ordering for Structures (a) and (b). This is, however, not surprising; the two structures are indeed very close in energy, and we cannot expect MP2 to distinguish between their energies. It is remarkable that MP2 has done so well for so long in most of our work.

The value of the CF---H angle, 106.24(14)^{o}, in *cis*-1,2-difluoroethylene-HCCH is characteristic of those observed in other side-binding fluoroethylene complexes,[3, 18-19] consistent with our assertion that this angle reflects the electron density distribution in a C–F bond. Indeed, recently presented symmetry adapted perturbation theory results for a series of protic acid-haloethylene complexes show that *cis*-1,2-difluoroethylene-HCCH has a total binding energy and contributions to that energy from electrostatics and dispersion that are more similar to the side-binding, tri-halospecies than to complexes formed with dihaloethylenes.[1] Although the

fluoroethylene-HCCH complexes have different binding motifs, it is still useful to compare them. As the number of F atoms increases in fluoroethylenes, the nucleophilicity of the F atom involved in the hydrogen bond should decrease, as there is less polarizable electron density in the ethylene subunit, and additionally, the density has to be shared among more F atoms. This effect should manifest as an increase in the hydrogen bond length formed with a given acid. Indeed, with HCCH as a partner, the length of the hydrogen bond formed with vinyl fluoride,[2] *cis*-1,2-difluoroethylene, and 1,1,2-trifluoroethylene[3] increases from 2.441(4) Å to 2.6455(92) Å to 2.748(15) Å (Figs. 1 and 5a). Using the same reasoning, an increase in the number of F atoms should render the hydrogen atoms in the ethylene subunit more electropositive, thus strengthening the bond between an H atom in the ethylene subunit and the nucleophilic portion of an acid. Once again, using HCCH as a partner, the length of this bond decreases from 3.159 Å to 2.9654(25) Å to 2.8694(9) Å when the ethylene partner changes from vinyl fluoride[2] to *cis*-1,2-difluoroethylene to 1,1,2-trifluoroethylene.[3] It is interesting to compare the structures of the HCCH complexes of *cis*-1,2-difluoroethylene and 1,1-difluoroethylene (Figure 5) because these ethylene subunits contain the same number of F atoms. The hydrogen bond lengths agree with each other, namely, 2.6455(92) Å and 2.646(11) Å, respectively, and the triple bond---H interaction lengths in these complexes, 2.9654(25) Å and 3.005(21) Å, are very similar,[11] differing by only approximately twice the higher uncertainty. It therefore appears that the electronic distributions about the F and H atoms in the ethylene subunits that interact with HCCH are roughly the same even though the atoms are arranged differently in the two difluoroethylenes.

In our earlier study of the (*Z*)-1-chloro-2-fluoroethylene-HCCH complex,[5] we explored the interaction potential of the two subunits using the MP2/6-311++G(2d,2p) level of theory.

Four minima were obtained. The F binding configuration is 115 cm^{-1} higher in energy than the Cl binding configuration when BSSE correction is not taken into account (or 80 cm^{-1} higher when the correction is made). There is one structure for (*Z*)-1-chloro-2-fluoroethylene-HCCH with an energy intermediate to these two configurations, and it is equivalent to Structure (a) in this current study where the acetylene triple bond interacts with the two H atoms in (*Z*)-1-chloroethylene. This structure is slightly lower in energy than the F side-binding configuration, by 8 cm^{-1} without or with BSSE correction. [A structure similar to Structure (c) shown earlier where HCCH forms a bifurcated hydrogen bond with the halogen atoms, F and Cl in the case of (*Z*)-1-chloro-2-fluoroethylene, becomes very high in energy when BSSE correction is taken into account.] At the time, we had no experimental data to rationalize why HCCH side binds to Cl instead of F, and we used theoretical findings to make our argument. Now, with the structure of *cis*-1,2-difluoroethylene-HCCH determined, we can compare experimental results and return to the question of why a side-binding configuration to F in (*Z*)-1-chloro-2-fluoroethylene is not observed.

The mapped electrostatic potential of (*Z*)-1-chloro-2-fluoroethylene (Fig. 2d) indicates that the maximum electron density is in a region more or less in between the two halogen atoms. The electron densities for this mixed halogen molecule at F and at Cl, respectively, are similar to what is found in each of its vinyl halide counterparts (vinyl fluoride and vinyl chloride, Fig. 2a,c), albeit somewhat diminished. We therefore assume that if HCCH were to bind to the F atom in (*Z*)-1-chloro-2-fluoroethylene, it would assume the same structural parameters as observed for *cis*-1,2-difluoroethylene-HCCH. There are two interactions in each of these two complexes, and spectroscopic evidence suggests that the hydrogen bond is more important than that the triple bond---H interaction in stabilizing the complex. As described previously, the

signal strengths for the *cis*-1,2-difluoroethylene-HCCH isotopologues singly substituted with ^{13}C decreases in the order of ^{13}C in the positions #3, #1, #2, and #4. The effective reduced masses for intermolecular vibrations depend non-trivially upon masses and distances,[35] but frequently appear to result in higher zero-point energies for isotopologues with a heavier isotopic substitution farther from the intermolecular bond.[4, 11, 13, 36] This greater energy results in a decreased population, weakening the rotational transition intensity. Both C3 and C1 are close to the hydrogen bond; thus, they give stronger transitions. Although C4 is close to the H---triple bond, it gives the weakest signal, indicating that this interaction is secondary to the hydrogen bond. In fact, although we did not remark upon it at the time, the same phenomenon was also observed when we studied (*Z*)-1-chloro-2-fluoroethylene-HCCH.[5]

The length of the H---Cl hydrogen bond in (*Z*)-1-chloro-2-fluoroethylene-HCCH is 3.0690(89) Å, which is 0.424 Å longer than the H---F hydrogen bond, or 1.5 times the difference between the van der Waals radii of Cl and F. As a result, the H---Cl bond is weaker than the H---F bond. (Roughly speaking, if the two hydrogen bonds were to have similar strength, the H---Cl bond should only be 0.28 Å longer the H---F bond; the fact that it is an additional 0.14 Å longer indicates that it is weaker).

The triple bond---H interaction in the (*Z*)-1-chloro-2-fluoroethylene complex is 2.7815(8) Å, which is 0.18 Å shorter, and therefore stronger than its *cis*-1,2-difluoroethylene counterpart, which is 2.9654(25) Å. It is, however, difficult to ascertain the degree of strengthening of this bond in (*Z*)-1-chloro-2-fluoroethylene versus the degree of weakening of the hydrogen bond in this complex, but we can look to the literature for guidance. The triple bond---H interaction is present for the HCCH complexes of HF,[37] HCl,[38] and HCN,[39] and the interaction lengths are, respectively, 2.196, 2.415, and 2.593 Å, reflecting the order of decreasing gas phase acid

strength. The corresponding interactions lengths for (*Z*)-1-chloro-2-fluoroethylene-HCCH and *cis*-1,2-difluoroethylene-HCCH are longer, so much so that this bond in (*Z*)-1-chloro-2-fluoroethylene-HCCH, while compensating for the weaker hydrogen bond, is not contributing a significant amount of electrostatic stabilization to the complex. Thus, from an electrostatic point of view, binding of HCCH to the F atom in (*Z*)-1-chloro-2-fluoroethylene should be electrostatically more stable for each of the individual interactions. The fact that it this binding is not observed suggests that F binding is strained, and thus, overall is energetically unfavorable compared to Cl binding. In other words, HCCH fits better at the geminal Cl, H end of the double bond.

The argument that F binding is a strained configuration in (*Z*)-1-chloro-2-fluoroethylene-HCCH can be further supported. Since the H---F bond in *cis*-1,2-difluoroethylene-HCCH is stronger than the H---Cl bond in (*Z*)-1-chloro-2-fluoroethylene-HCCH, it should be bent less from linearity. This is because it is more difficult to bend a stronger bond and additionally, the complex would not have as much of a need for another interaction to stabilize it. Yet, the deviations from linearity of these hydrogen bonds are very similar [63.85(34)^o vs 62.44(43)^o], suggesting that the F binding configuration is in need of further stabilization, likely because the CF---H angle of ~106^o is more strained than the CCl---H angle of ~88^o, a result of the different electronic distribution at the F and Cl atoms. It is interesting to note that even though the H atom geminal to F should be more electropositive than that geminal to Cl (Fig. 2d), the triple bond---H interaction for *cis*-1,2-difluoroethylene-HCCH is longer than that for (*Z*)-1-chloro-2-fluoroethylene-HCCH, a result of the complicated balance between electrostatic and steric factors.

VI. Conclusions

The microwave rotational spectrum of *cis*-1,2-difluoroethylene-HCCH has been obtained and analyzed, and the molecular structure of this gas-phase heterodimer has been determined. Lacking a hydrogen atom *cis* to the hydrogen bond accepting fluorine atom, this haloethylene does not offer the "top-binding" configuration to the acetylene observed in complexes with vinyl fluoride,[2] 1,1-difluoroethylene,[11] or 1-chloro-1-fluoroethylene.[13] Consequently, the *cis*-1,2-difluoroethylene-HCCH complex adopts the sterically strained "side-binding" geometry previously observed in 1,1,2-trifluoroethylene[3] and (*E*)-1-chloro-1,2-difluoroethylene[40] for hydrogen bonding to a fluorine atom. The level of theory, MP2/6-311++G(2d,2p), that has previously served as a reliable guide for predicting the global minimum structure for protic acid-haloethylene heterodimers, does not do so for *cis*-1,2-difluoroethylene-HCCH, even after correcting for basis set superposition error and zero-point energy. Higher levels of calculation, MP4, CCSD, or CCSD(T), using the same basis set are necessary to reproduce the experimental observation. A closer comparison of structural parameters reveals that C–F···H angle in *cis*-1,2-difluoroethylene-HCCH is similar to that in other side-binding to fluorine complexes[3, 18-19] while the hydrogen bond and secondary interaction lengths are in line with those observed in 1,1-difluoroethylene-HCCH, which adopts the sterically favored (and solely available) top-binding motif.[11]

Characterization of the structural details for the side binding of acetylene to a fluoroethylene provides information regarding the observed propensity for HCCH to form a hydrogen bond to the less electronegative chlorine atom when given a choice between side binding to fluorine versus chlorine in (*Z*)-1-chloro-2-fluoroethylene-HCCH.[5] Were this complex to have a hydrogen bond to fluorine, the electron distributions of the two haloethylenes suggest

that it would adopt a similar geometry to that in *cis*-1,2-difluoroethylene. The difference between the hydrogen bond lengths to chlorine in (*Z*)-1-chloro-2-fluoroethylene-HCCH and to fluorine in *cis*-1,2-difluoroethylene-HCCH is greater than the difference in the van der Waals radii of the two halogens, indicating that the observed hydrogen bond to chlorine in (*Z*)-1-chloro-2-fluoroethylene-HCCH is weaker than would be the bond to fluorine. However, the relaxed steric requirements for bonding to chlorine allows for an enhancement of the secondary interaction between the geminal hydrogen atom and the acetylenic triple bond with a lowest cost in bond bending strain. Simply put, acetylene fits better on the chlorine side of (*Z*)-1-chloro-2-fluoroethylene-HCCH than it does on the fluorine side. As is the case for favoring top binding, in vinyl fluoride, the opportunity for an enhanced electrostatic interaction to the geminal hydrogen atom is outweighed by unfavorable steric requirements.

Supplementary Material

Please see the supplementary material for the Cartesian coordinates of all atoms in the *ab initio* predicted optimized structures in Fig. 3 (Table S1), observed transition frequencies with assignments and residuals (observed minus calculated) for five isotopologues of *cis*-1,2-difluoroethylene-HCCH (Tables S2-S6), and spectroscopic constants obtained using the Watson *S*-reduced Hamiltonian for these five isotopologues (Table S7).

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Table I. The relative energies, without and with BSSE correction, rotational constants, and dipole moment components for three isomers of *cis*-1,2-fluoroethylene-HCCH (shown in Fig. 3) obtained from *ab initio* calculations.

	Structure (a)		Structure (b)		Structure (c)	
	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction	No BSSE Correction	BSSE Correction
A/MHz	5076	5076	11664	11784	4471	4502
B/MHz	1392	1325	1082	1048	1784	1651
C/MHz	1164	1117	990	962	1483	1387
$\lvert\mu_a\rvert$ / D	2.708	2.699	1.018	0.999	0.688	0.801
$\lvert\mu_b\rvert$ / D	0.000	0.000	2.237	2.246	0.000	0.031
$\lvert\mu_c\rvert$ / D	0.000	0.000	0.000	0.000	2.420	2.388
Energy[a]/ cm^{-1}	0	0	15.7	10.1	65.7	120.1

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

Table II. Spectroscopic constants (in MHz, unless otherwise noted) for five isotopologues of the *cis*-1,2-fluoroethylene-HCCH complex.[a,b] See Fig. 5a for the labeling scheme of the C atoms.

	CHFCHF–HCCH (most abundant)	CHF^{13}CHF–HCCH (^{13}C1)	^{13}CHFCHF–HCCH (^{13}C2)	CHFCHF–H^{13}CCH (^{13}C3)	CHFCHF–HC^{13}CH (^{13}C4)
A	11705.66697(35)	11678.68329(61)	11538.15510(78)	11668.43706(54)	11601.35226(94)
B	1066.27667(13)	1065.80015(14)	1059.85138(16)	1047.24162(13)	1038.28714(19)
C	978.01549(12)	977.454979(89)	971.43530(11)	961.730707(91)	953.70149(13)
Δ_J / 10^{-3}	1.45299(48)	1.45295(87)	1.4369(10)	1.38497(87)	1.4163(12)
Δ_{JK} / 10^{-3}	–27.9085(77)	–27.644(27)	–27.148(36)	–26.618(20)	–28.298(46)
Δ_K / 10^{-3}	866.595(68)	[866.595]	[866.595]	[866.595]	[866.595]
δ_J / 10^{-3}	0.171395(46)	0.17066(54)	0.16904(64)	0.15808(54)	0.16579(85)
δ_K / 10^{-3}	8.881(55)	[8.881]	[8.881]	[8.881]	[8.881]
Φ_J / 10^{-6}	–0.0080(15)	[–0.0080]	[–0.0080]	[–0.0080]	[–0.0080]
Φ_{JK} / 10^{-6}	0.723(44)	[0.723]	[0.723]	[0.723]	[0.723]
Φ_{KJ} / 10^{-6}	–27.64(39)	[–27.64]	[–27.64]	[–27.64]	[–27.64]
No. of rotational transitions	98	32	31	34	29
No. of *a* type	58	19	18	21	17
No. of *b* type	40	13	13	12	12
J range	0 – 14	0 – 8	0 – 8	0 – 8	0 – 8

K_a range	0 – 4	0 – 2	0 – 1	0 – 2	0 – 1
rms / kHz	1.05	1.55	1.80	1.55	2.12

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

[b]Values in brackets are fixed to the corresponding values appropriate for the most abundant isotopologue.

Table III. The coordinates of four C atoms in the *cis*-1,2-difluoroethylene-HCCH complex determined from a Kraitchman analysis and a structural fit. See Fig. 5a for the labeling scheme for the C atoms.

	C1	C2	C3	C4
(i) Substitution coordinates[a]				
$\lvert a \rvert$ / Å	0.4621(32)	1.70044(88)	2.94603(51)	3.58671(42)
$\lvert b \rvert$ / Å	0.3171(47)	0.7974(19)	0.3763(40)	0.6347(24)
(ii) From structural fit				
a / Å	–0.4778	–1.7070	2.9549	3.5968
b / Å	–0.3063	–0.7955	0.3901	–0.6336

[a]Costain errors[41] in the parameters are given in parentheses.

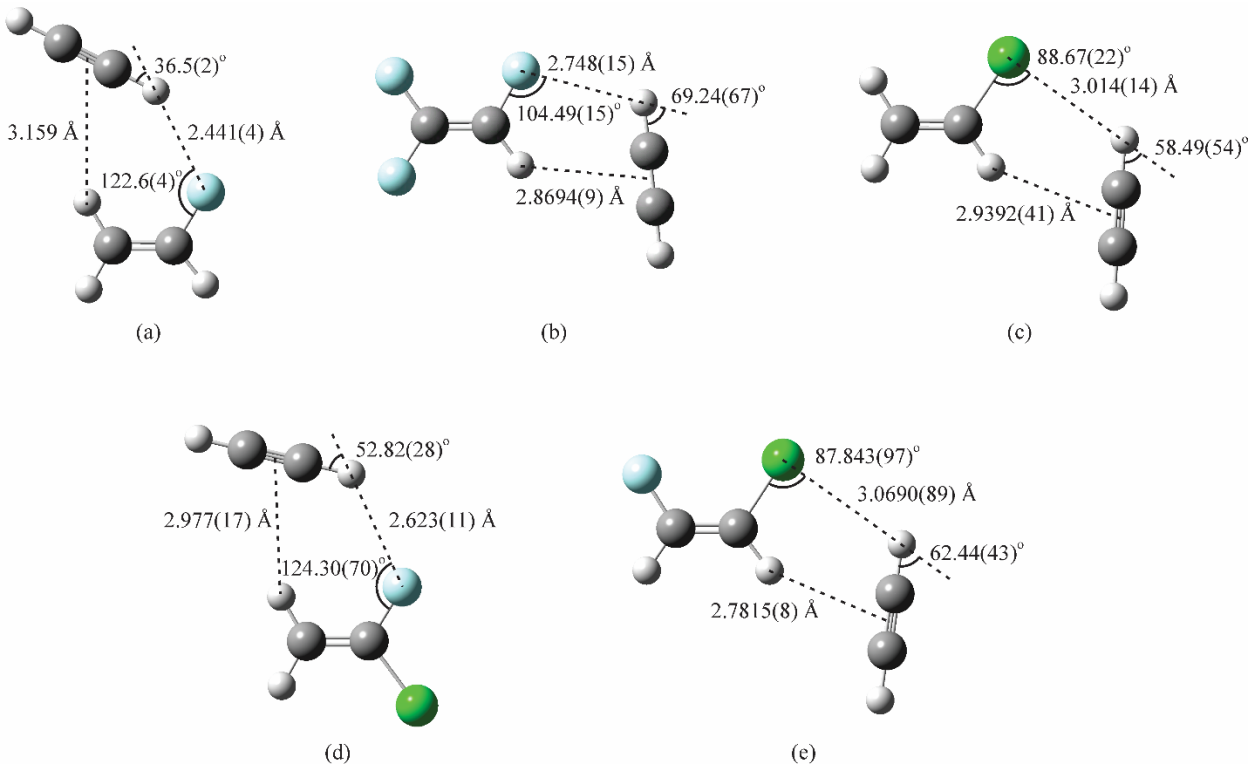

Figure 1. Structures of (a) vinyl fluoride-HCCH[2], (b) 1,1,2-trifluoroethylene-HCCH[3], (c) vinyl chloride-HCCH,[4] (d) 1-chloro-1-fluoroethylene-HCCH,[13] and (e) (*Z*)-1-chloro-2-fluoroethylene-HCCH.[5] Atom colors: C, dark gray; H, light gray; F, light blue; Cl: green.

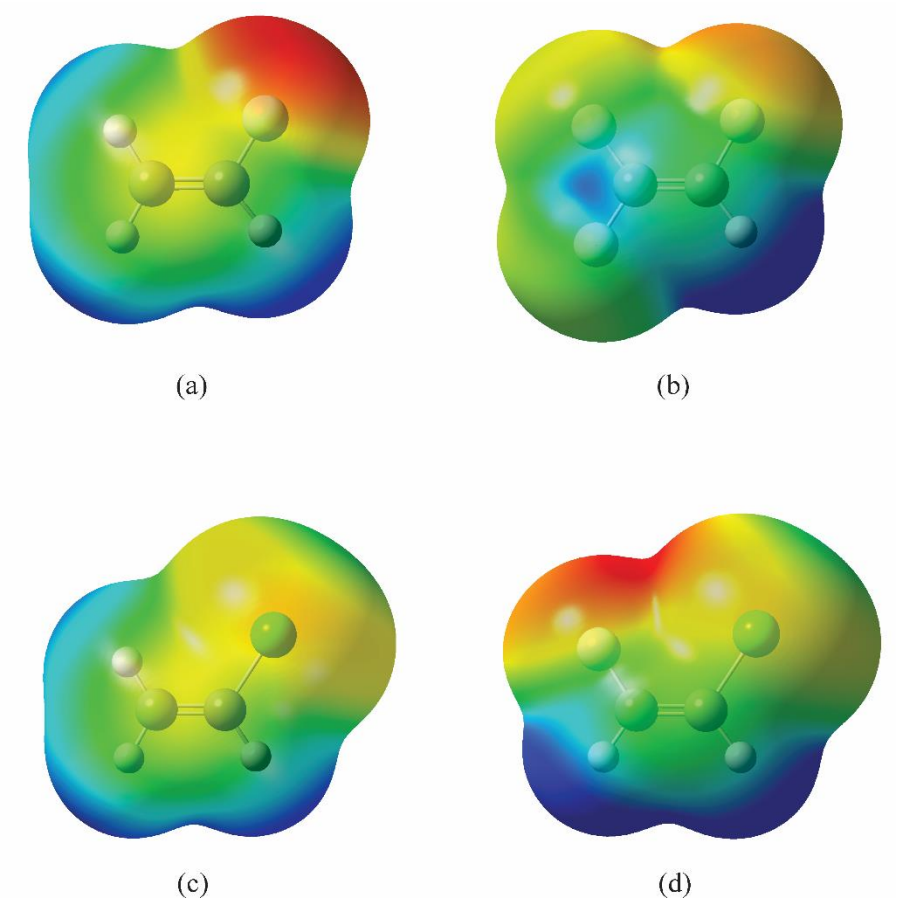

Figure 2. Electrostatic potential, mapped onto a total electron density isosurface for (a) vinyl fluoride, (b) 1,1,2-trifluoroethylene, (c) vinyl chloride, and (d) (*Z*)-1-chloro-2-fluoroethylene. The same value of electron density is used for the isosurfaces, and identical color scales are used. Blue represents positive electrostatic potential, and red, negative electrostatic potential.

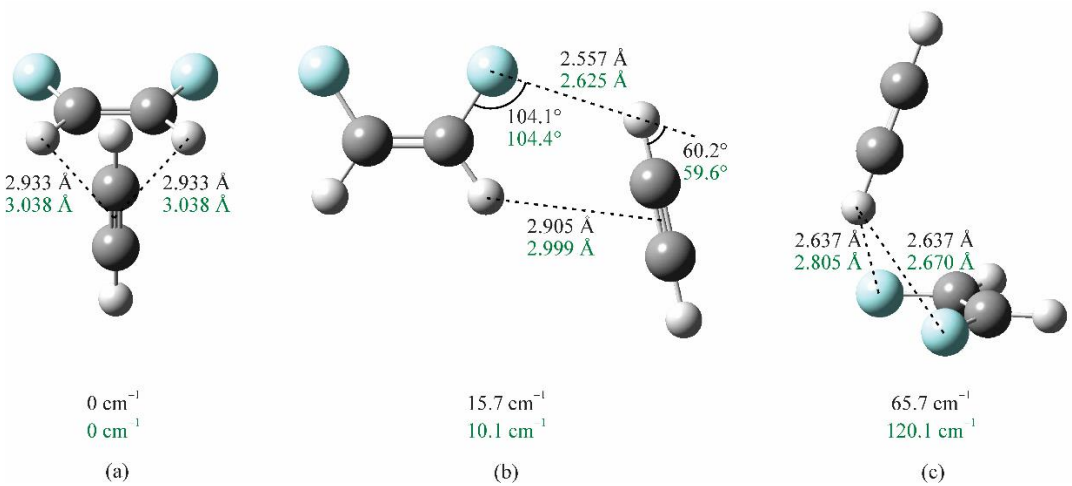

Figure 3. The optimized structures and relative energies of three isomers of *cis*-1,2-difluoroethylene-HCCH determined by *ab initio* calculations using MP2/6-311++G(2d,2p) model chemistry. The values in black and green represent those resulting from calculations without and with BSSE correction, respectively. Using higher levels of theory [MP4, CCSD or CCSD(T)], the energy ordering of structures (a) and (b) is reversed, and indeed structure (b) is experimentally observed. Atom colors: C, dark gray; H, light gray; F, light blue.

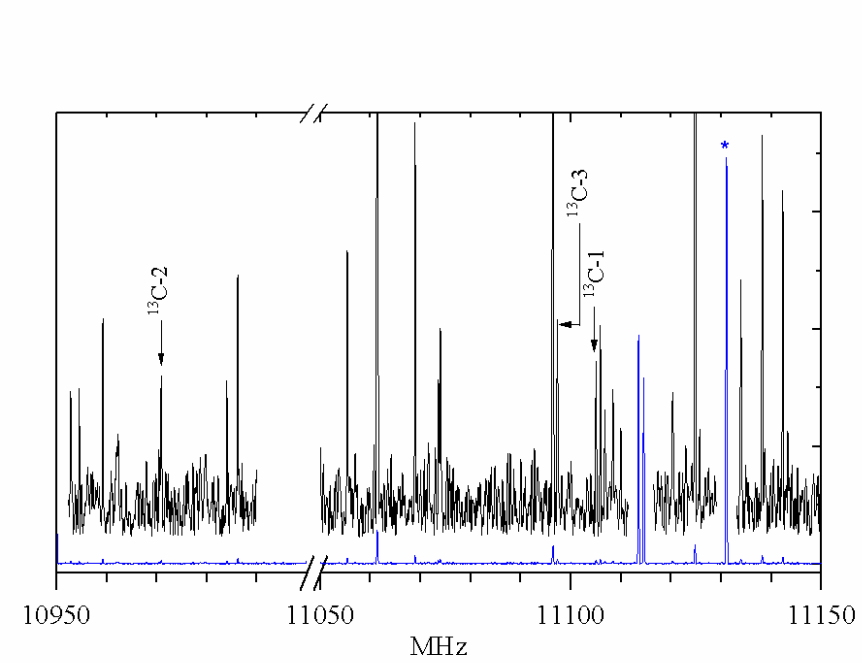

Figure 4. A portion of the chirped pulse spectrum (blue trace) showing the $4_{13} - 4_{04}$ transition (marked by a blue star) of the most abundant isotopologue of *cis*-1,2-difluoroethylene-HCCH. The two transitions near 11113 MHz are due to Ar-*cis*-1,2-difluoroethylene.[42] Under 50 fold magnification (black trace), the $4_{13} - 4_{04}$ transitions due to three isotopologues of the HCCH complex singly substituted with ^{13}C are also observed. The numbering system for the carbon atoms is shown in Fig. 5a.

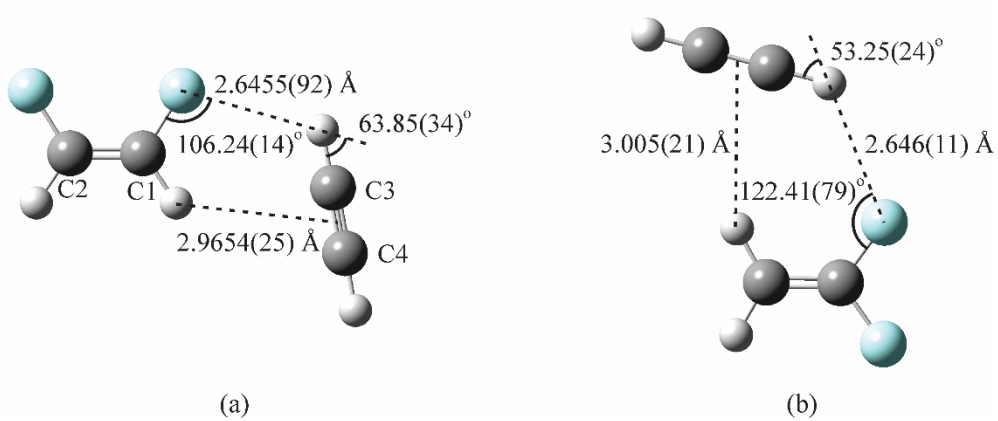

Figure 5. Structures of (a) *cis*-1,2-difluoroethylene-HCCH (this work) and the labeling scheme for the carbon atoms, and (b) 1,1-difluoroethylene-HCCH.[11] Atom colors: C, dark gray; H, light gray; F, light blue.

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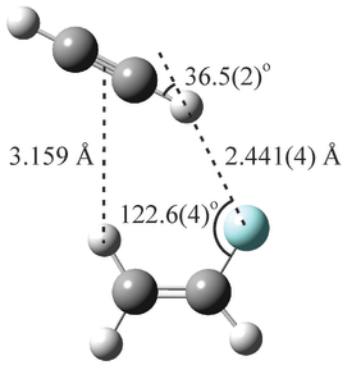
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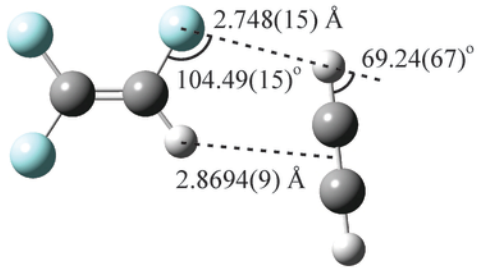
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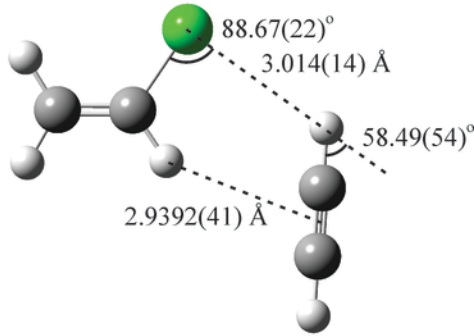
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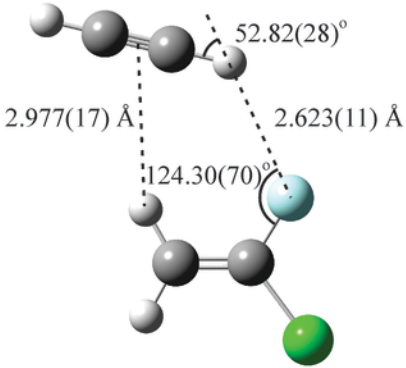
(c)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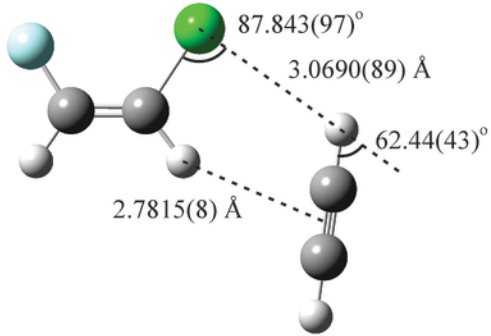
(d)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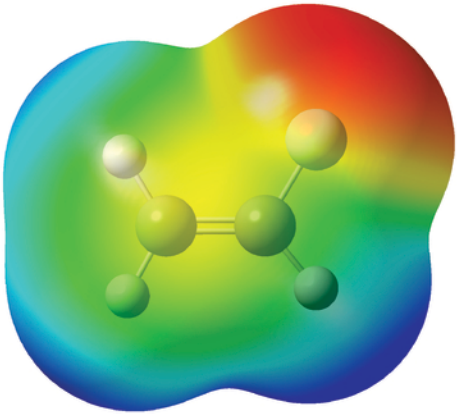
(e)



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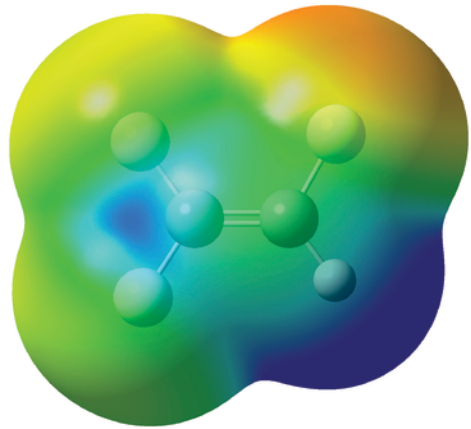

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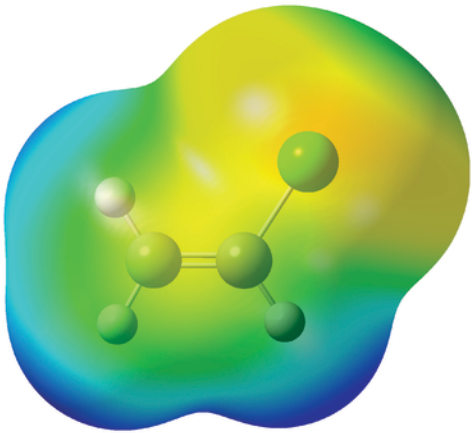

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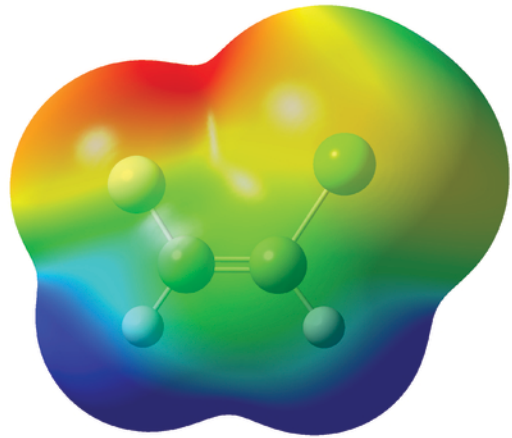

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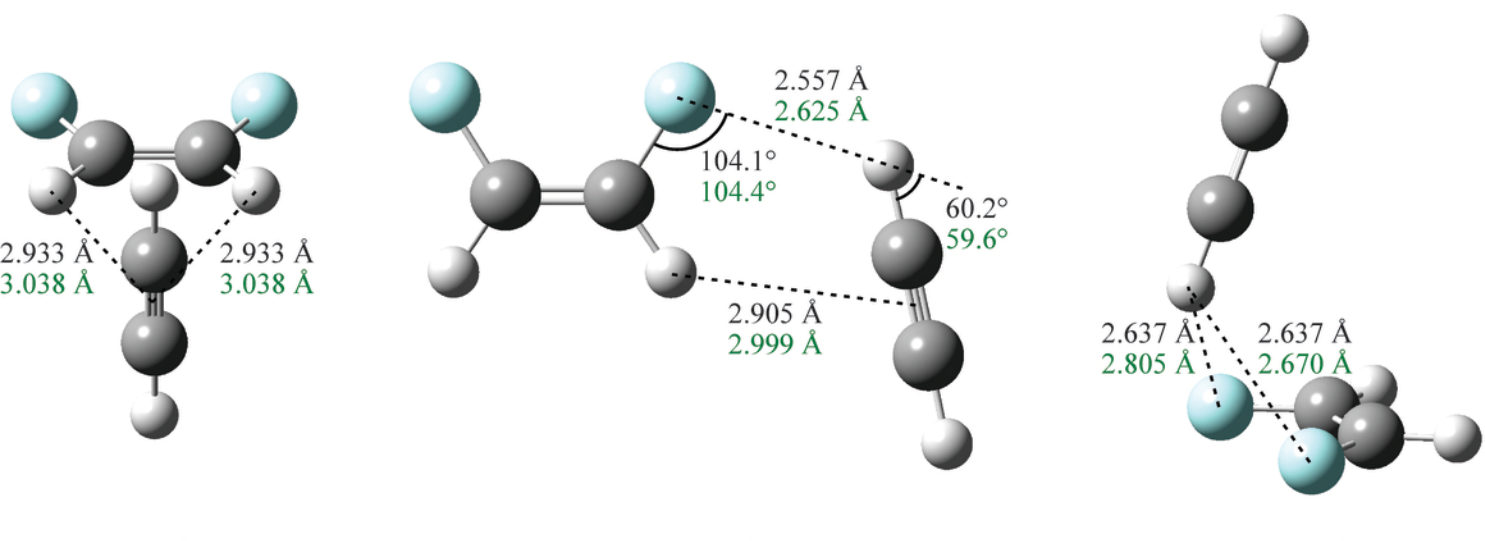

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(a)

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(b)

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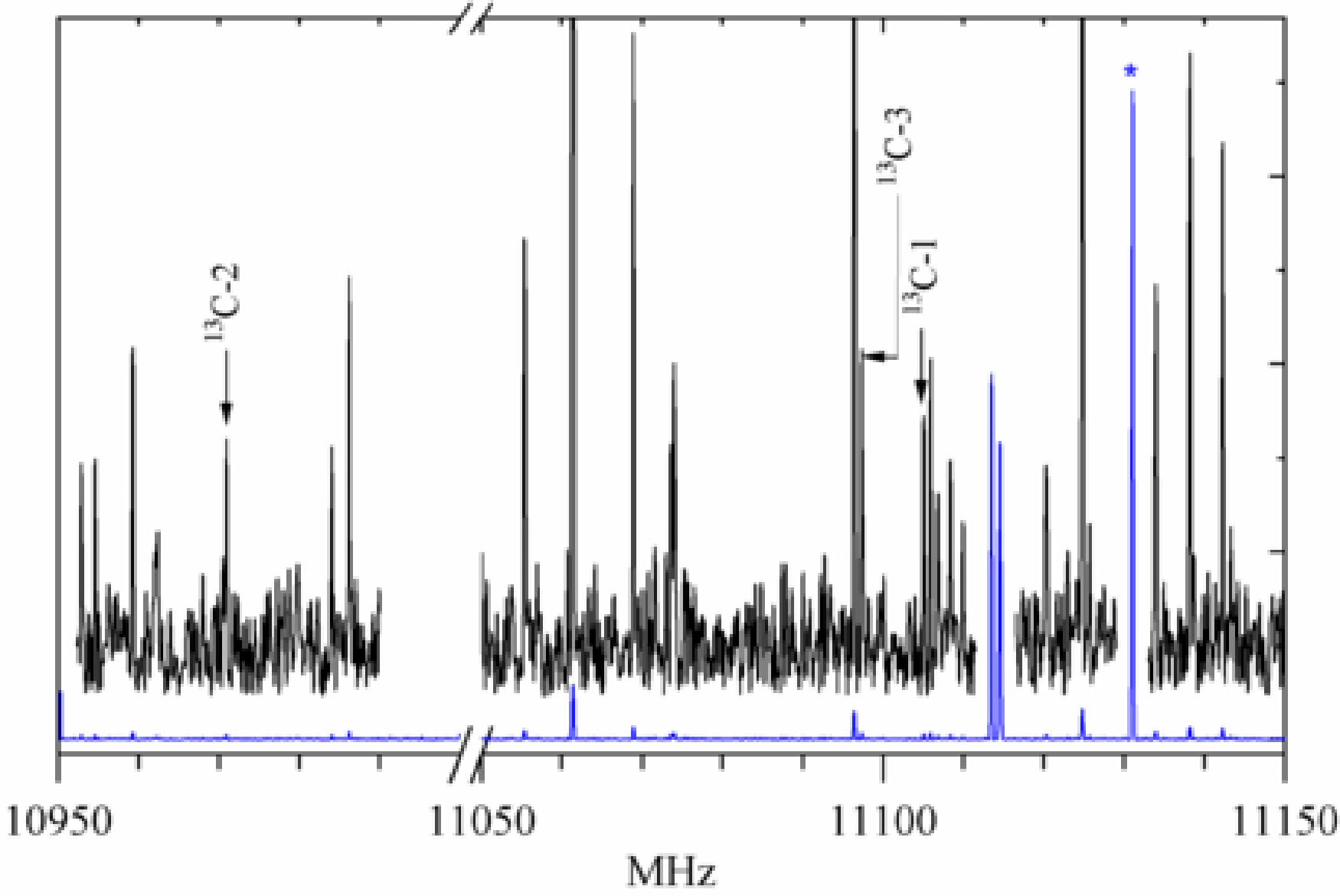
(c)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^{13}C-3
^{13}C-1
*
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11050
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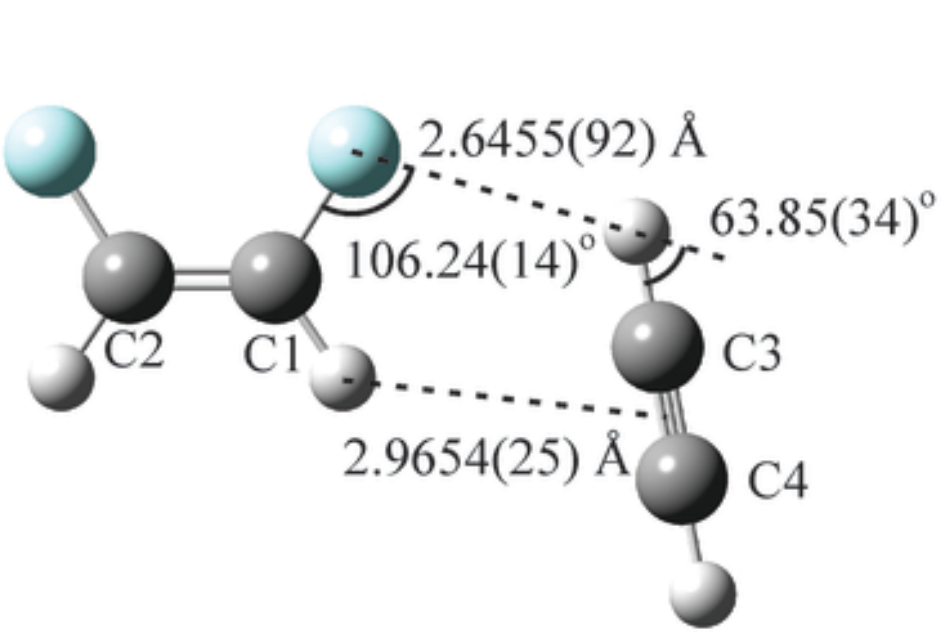
MHz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106.24(14)°
C2
C1
C3
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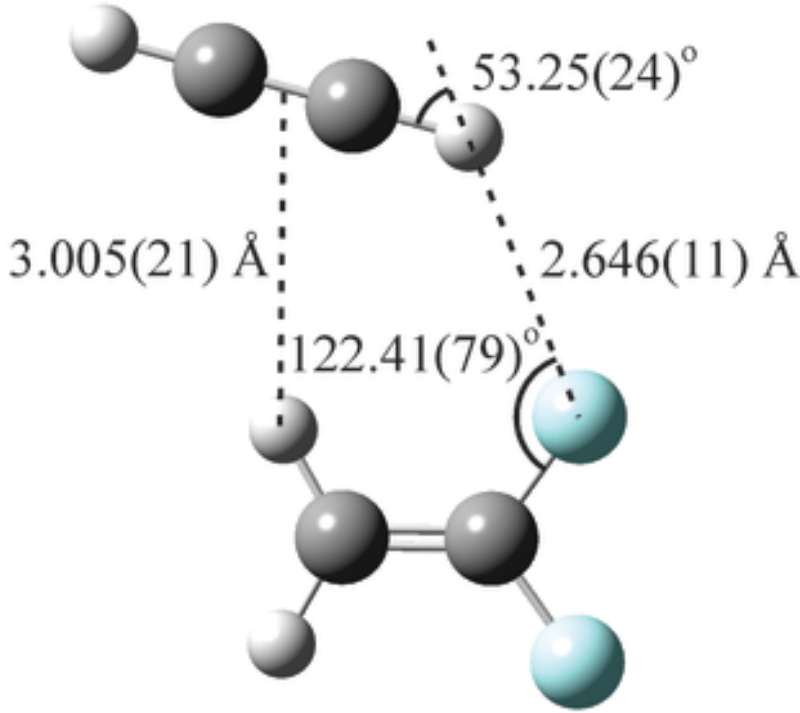
C4

(a)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