The Journal of Chemical Physics

RESEARCH ARTICLE | SEPTEMBER 10 2024

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J. Chem. Phys. 161, 104304 (2024)
https://doi.org/10.1063/5.0231236

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The Journal of Chemical Physics ARTICLE pubs.aip.org/aip/jcp

Preserving the symmetry of *cis*-1,2-difluoroethylene in the gas-phase heterodimer with hydrogen chloride: A microwave rotational study revealing a novel structure

Cite as: J. Chem. Phys. 161, 104304 (2024); doi: 10.1063/5.0231236
Submitted: 29 July 2024 • Accepted: 23 August 2024 •
Published Online: 10 September 2024

Helen O. Leung[a] and Mark D. Marshall[a]

AFFILIATIONS

Department of Chemistry, Amherst College, P.O. Box 5000, Amherst, Massachusetts 01002-5000, USA

[a]**Authors to whom correspondence should be addressed:** hleung@amherst.edu and mdmarshall@amherst.edu.
Fax: +1-413-542-2735; **Telephone:** (413) 542-2006

ABSTRACT

The microwave spectra of three isotopologues of the gas-phase heterodimer formed between *cis*-1,2-difluoroethylene and hydrogen chloride are obtained in the 5–21 GHz region using Fourier transform microwave spectroscopy. The molecular structure, determined from the analysis of the spectra and supported by quantum chemistry calculations, has the hydrogen atom of the hydrogen chloride molecule interacting with both fluorine atoms of the fluoroethylene and no interaction between the chlorine atom and the olefin. Although the equilibrium structure has two inequivalent H···F interactions, zero-point motion averages over the two equivalent choices for these interactions, rendering the pairs of like atoms (C, H, and F) of the fluoroethylene equivalent, retaining the C_{2v} symmetry of the olefin. This results in only one unique singly substituted ^{13}C isotopologue and in the observed effects on transition intensities due to nuclear spin statistics. The heterodimer structure allows for a strong, linear hydrogen bond between the HCl donor and the fluoroethylene acceptor that is more important here than in the analogous acetylene containing complex, where the interaction between the π electrons of acetylene and an electrophilic hydrogen atom on the olefin compensates for the loss of linearity required for binding to a geminal F/H pair.

I. INTRODUCTION

Studies of intermolecular interactions involving a protic acid and a fluorine-substituted ethylene with at least one hydrogen atom have provided a wealth of information. The five ethylenes, vinyl fluoride, 1,1-difluoroethylene, *cis*- and *trans*-1,2-difluoroethylene, and 1,1,2-trifluoroethylene, offer multiple nucleophilic and electropositive sites to the acid. By varying the number and location of the fluorine atoms, the properties of the functional groups are modified, allowing us to observe the manner in which they compete or cooperate with each other in binding to the acid. Using three different gas-phase protic acid partners, HF, HCl, and HCCH, 15 possible complexes are expected.[1] The structural details of 12 of these have been reported, and remarkably, they all show regular patterns. First, these complexes are planar or near-planar. Second, the acids invariably bind to an H, F pair of the fluoroethylene. Given a choice, the binding of the acid is to the H, F pair located across the double bond in vinyl fluoride[2–5] and *trans*-1,2-difluoroethylene,[6,7] but to the H, F pair connected to the same C atom in 1,1,2-trifluoroethylene.[8–10] Lacking a choice, the acids bind to the only possible option offered by 1,1-difluoroethylene: the H, F pair across the double bond. Third, and not unexpectedly, the trends for the geometric parameters are nicely correlated with the acid strengths and the electron density distributions in the fluoroethylenes.[1]

The three complexes not yet studied or reported are the HCCH complex of *trans*-1,2-difluoroethylene and the HCl and HF

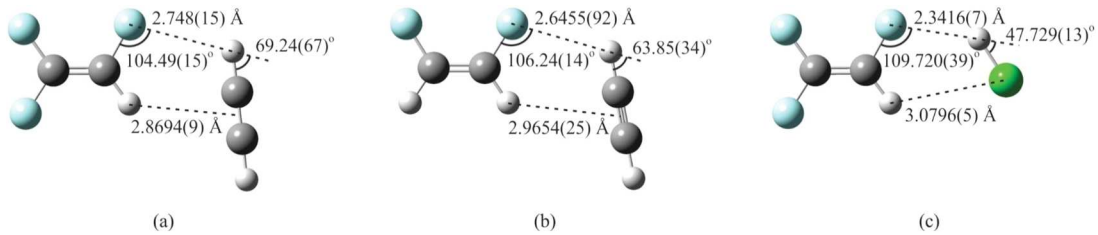

FIG. 1. Structures of (a) 1,1,2-trifluoroethylene–HCCH,[10] (b) *cis*-1,2-difluoroethylene–HCCH,[11] and (c) 1,1,2-trifluoroethylene–HCl.[9] Atom colors: C: dark gray, H: light gray, F: light blue, and Cl: green.

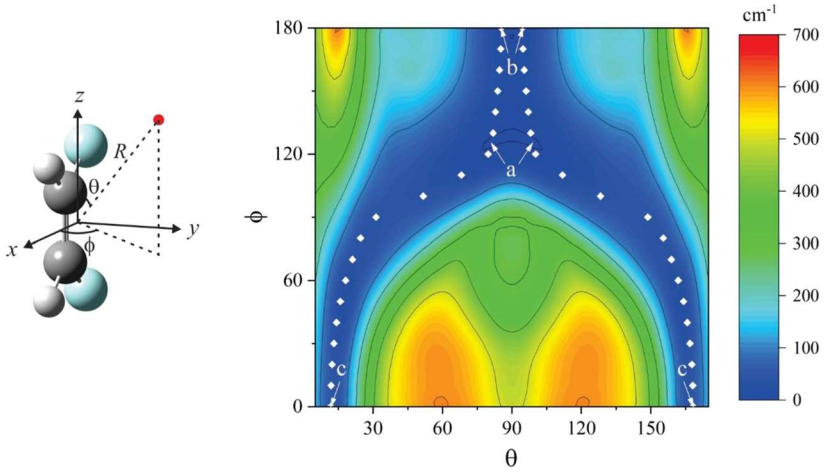

FIG. 2. Left: the spherical polar coordinate system (R, θ, ϕ) used to locate the center of mass of HCl (red circle) with respect to *cis*-1,2-difluoroethylene, lying in the x–z plane with the origin at its center of mass. Right: a contour plot of the potential energy as a function of the angles with R and the orientation of HCl optimized. Three equivalent pairs of minima, labeled *a*–*c*, are located, and the geometry is optimized at each. The corresponding structures are shown in Fig. 4. The white diamonds outline the minimum energy path between minima. Atom colors: C: dark gray, H: light gray, and F: light blue.

complexes of *cis*-1,2-difluoroethylene. Because neither subunit is polar, the dipole moment of the first complex is expected to be very small, making its rotational spectrum challenging to observe. With *cis*-1,2-difluoroethylene as a subunit, the structural study of only one complex has been reported: HCCH predictably binds to one of the H, F pairs at one end of the double bond,[11] with a binding mode the same as that in its 1,1,2-trifluoroethylene counterpart[10] (Fig. 1). Thus far, the binding modes of these fluoroethylene–protic acid complexes are independent of acid identity; therefore, it is reasonable to assume that HCl would bind to *cis*-1,2-difluoroethylene in the same manner as it does to 1,1,2-trifluoroethylene[9] (Fig. 1). Here, we report that such is not the case, and a novel binding mode is uncovered.

II. *AB INITIO* CALCULATIONS

To guide our search for the complex, we turn to theory at the MP2/6-311++G(2d,2p) level with GAUSSIAN 16[12] to construct the interaction potential energy surface formed by the two subunits. Both subunits are fixed at their ground-state geometries.[13,14] We use

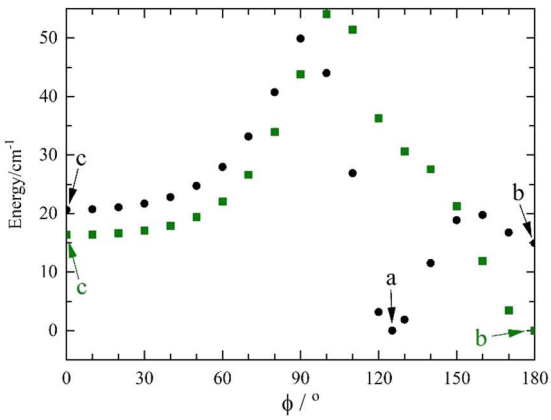

FIG. 3. Minimum energy path between minima as a function of the azimuthal angle (defined in Fig. 2) without (black circles) and with (green squares) BSSE correction. Three minima are present when the BSSE correction is not included, but isomer (a) does not correspond to a potential minimum when the correction is considered.

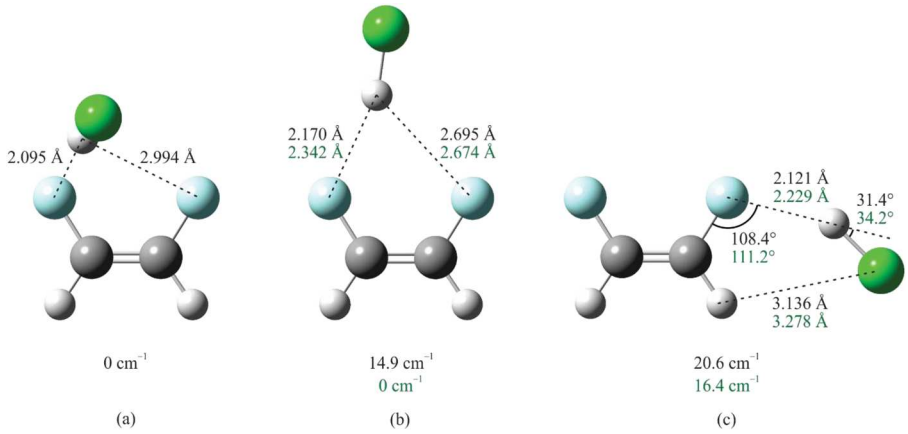

FIG. 4. Optimized structures corresponding to the three minima found in the potential scan for *cis*-1,2-difluoroethylene–HCl. The equilibrium energies and structural parameters are in black and green, respectively, for optimizations performed without and with BSSE correction. Isomer (a) does not correspond to a potential minimum when BSSE correction is included. Atom colors: C: dark gray, H: light gray, F: light blue, and Cl: green.

the principal axis system of *cis*-1,2-difluoroethylene as a reference; in particular, the origin is at the center of mass of the subunit, and the *a*, *b*, and *c* inertial axes are, respectively, the *z*, *x*, and *y* axes (Fig. 2). A relaxed scan is carried out where the center of mass of HCl is placed at polar angles (θ) between 5° and 175° and azimuthal angles (ϕ) between 0° and 180°, with both its distance from the origin and the HCl orientation allowed to relax. These angles are scanned at 10° intervals, and the resulting potential energy contour is shown in Fig. 2. Because of the symmetry of the complex, the contour plot is symmetric about θ = 90° and the *x*–*z* plane (not shown in the plot). The minimum energy path between minima is depicted in two-dimensions in Fig. 2 and as a function of ϕ in Fig. 3. Three minima, labeled *a*, *b*, and *c* in order of increasing energy, are identified and optimized; the corresponding structures are shown in Fig. 4, with their rotational constants, dipole moment components, and relative energies listed in Table I. All three isomers are comparable in energy, differing by no more than 21 cm^{-1}. The modes of binding for isomers (a) and (b) are similar, with H in HCl interacting with both F atoms. Isomer (a) is nonplanar, with one of the H···F interactions significantly shorter than the other (by 0.9 Å), while the planar isomer (b) shows two H···F interactions differing by 0.5 Å. Isomer (c) has a structure similar to its HCCH counterpart,[11] where HCl forms

TABLE I. Rotational constants, dipole moment components, and relative equilibrium and zero-point corrected energies obtained from *ab initio* calculations at the MP2/6-311++G(2d,2p) level without and with BSSE correction for three isomers of *cis*-1,2-difluoroethylene–HCl.

	No. BSSE correction	BSSE correction[d]	No. BSSE correction	BSSE correction	No. BSSE correction	BSSE correction
	Isomer (a)		Isomer (b)		Isomer (c)	
A/MHz	5119	···	5957	5946	18 918	19 237
B/MHz	1623	···	1473	1392	951	912
C/MHz	1334	···	1181	1128	906	870
$\lvert\mu_a\rvert$/D	2.883	···	4.093	4.053	0.847	0.830
$\lvert\mu_b\rvert$/D	0.795	···	0.489	0.322	1.771	1.763
$\lvert\mu_c\rvert$/D	1.582	···	0.000	0.000	0.000	0.000
E_{equil}[a,b]/cm^{-1}	0.0	···	14.9	0.0	20.6	16.4
E_{zpe}[a,c]/cm^{-1}	29.4	···	0.0	0.0	61.9	83.2

[a]The energy of the most stable isomer is set to 0 for the structures computed, respectively, with and without BSSE correction.
[b]The equilibrium energy is determined by using the average, experimental structures of the two subunits.
[c]A full relaxation of the complex geometry, including the structural parameters of the subunits, is used to compute the equilibrium energy and the zero-point corrected energy. A counterpoise calculation is then performed using this optimized structure, and the BSSE corrected energy is computed as $E_{zpe} - E_{equil} + E_{BSSE}$.
[d]Isomer (a) is not a stable structure, *i.e.*, does not correspond to a local potential minimum when BSSE correction is included.

a hydrogen bond with one of the F atoms and the nucleophilic portion of the acid (Cl in the present case) interacts with the geminal H atom. When zero-point corrected energies are calculated, the energy ordering between isomers (a) and (b) is switched (Table I): isomers (a) and (c) are, respectively, 29 and 62 cm^{-1} higher in energy than isomer (b).

Upon applying a basis set superposition error (BSSE) correction,[15] isomer (a) is no longer at a stable minimum. In addition, the equilibrium energy of isomer (c) is 16 cm^{-1} higher than that of isomer (b), and the energy gap increases to 83 cm^{-1} when zero-point energy is also considered (Table I). According to theory, then, we should expect HCl to bind differently than HCCH to *cis*-1-2-difluoroethylene, and additionally, under our experimental conditions (with an argon expansion), we should be able to observe only isomer (b). With a large dipole moment component along the *a* axis (4.09 D) and a much weaker component along the *b* axis, the rotational spectrum of isomer (b) is predicted to have strong *a* type transitions and much weaker *b* type transitions. Because of the planar symmetry of the isomer, no *c* type transitions are expected. (The atomic positions for each isomer in its principal coordinate system, with and without BSSE correction, are available in the supplementary material.)

III. EXPERIMENT

We begin our experimental work by using a broadband, chirped pulse Fourier transform microwave spectrometer[16–18] to collect the rotational spectrum of the complex, which is formed by expanding a mixture of 1% *cis*-1,2-difluoroethylene (SynQuest Laboratories) and 1% HCl in Ar at a backing pressure of 1–2 atm. After expanding the gas mixture through two pulsed valves, each with a 0.8 mm diameter nozzle, 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. 510 000–900 000 FIDs are averaged for each segment, and as described previously,[17] the average is Fourier transformed to give a frequency domain spectrum with a resolution element of 23.84 kHz and typical linewidths (FWHM) of 225 kHz. We are able to observe and assign rotational transitions due to the most abundant and ^{37}Cl containing isotopologues corresponding to isomer (b), and Fig. 5 shows a portion of the spectrum in the J = 4–3 region displaying three transitions for the most abundant species and one for the ^{37}Cl isotopologue. Because of the presence of a quadrupolar Cl nucleus, each transition is split into several close-lying hyperfine components. To measure these more precisely and to look for weaker transitions, we turn to our narrowband, Balle–Flygare Fourier transform microwave spectrometer,[17,19] which has both a higher resolution and is more sensitive than the chirped pulse spectrometer. The Balle–Flygare instrument uses one 0.8 mm pulsed nozzle and operates in the 5 − 21 GHz range. The time-domain signal is background-corrected, digitized for 2048 data points, and zero-filled to a 4096-point record length before Fourier transformation to give a frequency domain spectrum with a 2.4 kHz resolution element. In the end, in addition to the spectra of the most abundant isotopologue of *cis*-1,2-difluoroethylene–HCl and its ^{37}Cl counterpart, we also observe and analyze the spectrum of one ^{13}C isotopologue in natural abundance. Despite the fact that there are two C atoms in the complex, we cannot detect the spectrum of a second ^{13}C isotopologue. This absence suggests that the internal dynamics in the complex make the C atoms equivalent, and we will discuss this in a later section. In addition, all the observed transitions are *a* type, with no *b* type transitions appearing, consistent with a vanishing *b* component of the dipole moment when averaged over the internal dynamics of the HCl subunit. Finally, the *c* component of the dipole moment is also zero as a consequence of the planar structure of the heterodimer, regardless of the internal dynamics.

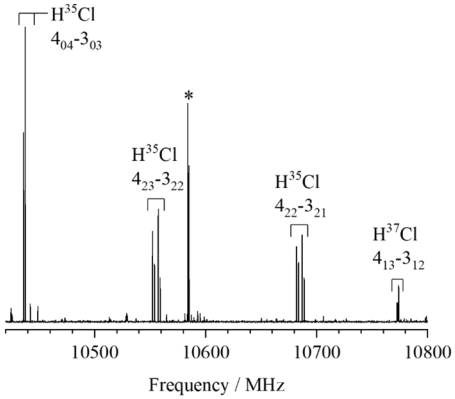

FIG. 5. A 380 MHz portion of the chirped pulse spectrum of *cis*-1,2-difluoroethylene–HCl showing four *a*-type rotational transitions: three for the most abundant isotopologue and one for the ^{37}Cl isotopologue. The transition at 10 585 MHz, indicated by *, is due to Ar-*cis*-1,2-difluoroethylene.

IV. RESULTS

A. Spectral analysis

The spectral analysis of each of the three isotopologues is carried out using the narrowband data. For the most abundant species and the ^{37}Cl isotopologue of *cis*-1,2-difluoroethylene–HCl, over 170 hyperfine components in 36 rotational transitions are analyzed. The J range sampled is 1–8, whereas the K_a range is 0–3. For the minor ^{13}C isotopologue, only 47 hyperfine components in 12 rotational transitions are observed, with a smaller J range (2–6) and K_a range (0–1). The spectrum of each species is fitted using the Watson A reduced Hamiltonian in the I^r representation[20,21] with the inclusion of chlorine nuclear quadrupole coupling interaction. Using Pickett's SPFIT program,[22] we determine the rotational constants, the diagonal components of the nuclear quadrupole coupling tensor, and 3–6 centrifugal distortion constants. For the most abundant species, when all quartic centrifugal distortion constants except Δ_K are fitted, the rms deviation is 2.8 kHz. The inclusion of Δ_K in the fit decreases the deviation to 2.4 kHz, but the correlation between the A rotational constant and Δ_K is significant (−0.986). The addition of yet another parameter, the sextic centrifugal distortion constant Φ_{JK}, decreases the rms deviation to 1.38 kHz, but with a similar correlation (0.983) between A and Δ_K. (The inclusion of Φ_{JK} without Δ_K increases the rms deviation to 2.3 kHz). This lowering of the rms deviation is significant. Furthermore, the rotational constants

TABLE II. Spectroscopic constants (in MHz, unless otherwise noted) for three isotopologues of *cis*-1,2-difluoroethylene–HCl.[a,b]

	CHFCHF–H^{35}Cl	CHFCHF–H^{37}Cl	^{13}CHFCHF–H^{35}Cl
A	5997.6262(55)	5997.5647(39)	5967.061(19)
B	1464.204 90(13)	1417.391 95(11)	1447.765 62(14)
C	1177.728 32(11)	1147.231 540(94)	1165.921 18(11)
$\Delta_J/10^{-3}$	2.890 11(76)	2.734 12(60)	2.8305(14)
$\Delta_{JK}/10^{-3}$	38.706(11)	36.7359(80)	37.574(92)
$\Delta_K/10^{-3}$	−10.28(57)	−10.28[c]	−10.28[c]
$\delta_J/10^{-3}$	0.516 23(48)	0.476 35(38)	0.502 21(90)
$\delta_K/10^{-3}$	28.696(38)	27.315(36)	28.696[c]
$\Phi_{JK}/10^{-6}$	−2.70(14)	−2.58(10)	−2.70[c]
χ_{aa}	−51.5206(12)	−40.621 27(93)	−51.5129(77)
χ_{bb}	25.2374(15)	19.8966(14)	25.2388(87)
χ_{cc}	26.2832(13)	20.7247(12)	26.2740(79)
No. of rotational transitions[d]	36	36	12
No. of hyperfine components	189	170	47
J range	1–8	1–8	2–6
K_a range	0–3	0–3	0–1
rms/kHz	1.38	1.03	0.87

[a] 1σ standard deviations in the parameters are given in parentheses.
[b] The nuclear quadrupole coupling constants of chlorine are fitted as 1.5 χ_{aa} and $(\chi_{bb} - \chi_{cc})/4$, and the Laplace condition is used to calculate the individual hyperfine constants.
[c] Fixed at the value appropriate to the ^{35}Cl-containing isotopologue.
[d] All transitions are *a*-type.

derived from the two fits—the one that includes Δ_K and Φ_{JK} and the one that does not—differ by only 0.1 MHz for A and less than 1 kHz for B and C. The two sets of rotational constants yield the same structure for the complex; thus, we decide to keep both Δ_K and Φ_{JK} in the fit. This effect of Φ_{JK} and the arguable need to include it in a fit of transitions with such a limited quantum number range is unusual but could be an artifact of the large amplitude motion discussed below. The transitions for the ^{37}Cl containing isotopologue are not sensitive to Δ_K, while those for the ^{13}C isotopologue are not sensitive to either Δ_K or Φ_{JK}. Accordingly, the undeterminable constants are fixed to those appropriate to the most abundant species. All spectroscopic parameters can be found in Table II, and tables of observed and calculated transition frequencies with assignments for all isotopologues are available in the supplementary material. The rms deviation for each fit is no more than 1.4 kHz, smaller than the resolution element of the Balle–Flygare spectrometer.

TABLE III. Coordinates of the C and Cl atoms for structures (i) and (ii) obtained from the structure fits and the Kraitchman substitution coordinates for Cl and a C atom.

	C-1	C-2	Cl
Substitution coordinates[a]			
$\|a\|$/Å	1.984 64(76)		2.412 93(62)
$\|b\|$/Å	0.6641(23)		0.021(70)
Structure (i)			
a/Å	−2.0779	−1.8730	2.4120
b/Å	0.5165	−0.7905	0.0800
Structure (ii)			
a/Å	−2.0802	−1.8695	2.4117
b/Å	0.5072	−0.7989	0.0621

[a] Costain errors[29] in the parameters are given in parentheses.

B. Structure determination

Each isotopologue of the *cis*-difluoroethylene–HCl complex has an asymmetry parameter between −0.889 and −0.881 and an inertial defect between −0.311 and −0.299 u Å^2. Thus, it is a planar, near prolate asymmetric top that exhibits out-of-plane vibrational motion. With the most abundant species as the parent, we determine the Kraitchman substitution coordinates[23] for both Cl and ^{13}C using the rotational constants of the minor isotopologues and list them in Table III. The Cl atom lies on the *a* inertial axis of the complex.

Next, we determine the average structure of the complex using the moments of inertia of the isotopologues. Because of the planar symmetry, only two of three moments of inertia for each isotopologue are independent. Restricting the structures of the subunits to be the same as those of the free monomers,[13,14] the structure of the complex can be specified using only three geometrical parameters: the distance between the two subunits and the angular orientation of each subunit. Nevertheless, these cannot be determined solely from

the experimental values of the moments of inertia. As such, we turn to the nuclear quadrupole coupling constants of HCl to establish the orientation of this subunit.

Assuming that the weak intermolecular interactions do not perturb the electric field gradient of the chlorine nucleus, the nuclear quadrupole coupling constant χ_{aa} of ^{35}Cl in *cis*-1,2-difluoroethylene–H^{35}Cl is simply a $\langle P_2 \rangle$ projection of that in the H^{35}Cl monomer,[24] namely,

$$\chi_{aa,\text{complex}} = \frac{3\langle \cos^2\theta_a \rangle - 1}{2} \chi_{aa,\text{monomer}}, \quad (1)$$

where θ_a is the angle formed by the H^{35}Cl subunit and the *a* inertial axis in the complex. Using the projection equation, the value of θ_a, or more precisely, $\cos^{-1}\sqrt{\langle \cos^2\theta_a \rangle}$, is determined to be 23.471 93(96)°. When the HCl subunit is fixed to reproduce this angle, we are able to use Schwendeman's STRFTQ program[25] to fit the distance between H in HCl and the center of the C=C bond ("X") in the difluoroethylene together with the angle formed by H, X, and one of the C atoms using I_a and I_c of the isotopologues. Because we believe internal dynamics may scramble the identity of the C atoms, we decided to use I_a and I_c obtained only from the most abundant and ^{37}Cl isotopologues in the structure fit. Two fits are consistent with the χ_{aa} value of ^{35}Cl in the complex, and the rms deviations are 0.0059 and 0.0066 u Å^2, respectively. The fitted parameters, together with physically relevant bond lengths, are given in Table IV; the corresponding structures are displayed in Fig. 6. (The atomic positions of both structures are given in the supplementary material.) When the moments of inertia of ^{13}C are included in either fit, regardless which of the two C atoms is assumed to include the substitution, the rms deviation of the fit increases to over 0.1 u Å^2 but with practically no change in the geometric parameters. The same is true when we assume both singly substituted ^{13}C species have the same moments of inertia. This indeed suggests that the internal dynamics in the complex render the two carbon atoms equivalent so that the ^{13}C substitution samples both atomic positions, or equivalently that the ground vibrational state wave function has a significant amplitude at both minima with only a small barrier between the two. Thus, the isotopic substitution data cannot be used in a fit to a single structure and it is reasonable to exclude it.

TABLE IV. Geometric parameters for two possible structures of *cis*-1,2-difluoroethylene–HCl and their relative energies.[a]

	Structure (i)	Structure (ii)
Parameters used in structure fit[b]		
H···X/Å	3.223 293(29)	3.288 552(32)
∠H···X C-1/° [c]	104.150(11)	86.528(12)
∠Cl H···X/° [d]	151.2894	143.8923
Derived parameters[c]		
H···F-1/Å	2.9360(3)	2.4455(4)
∠H···F-1 C-1/°	100.647(10)	119.353(13)
∠Cl H···F-1/°	118.0867(9)	176.0121(17)
H···F-2/Å	2.0730(3)	2.6595(4)
∠H···F-2 C-2/°	131.648(15)	111.799(12)
∠Cl H···F-2/°	178.2086(38)	111.1640(6)
rms/u Å^2	0.0059	0.0066
Relative energy		
No BSSE correction/cm^{-1}	0	142.3
With BSSE correction/cm^{-1}	0	74.2

[a]Calculated at the MP2/6-311++G(2d,2p) level.
[b]X represents the center of the C=C bond.
[c]C-1 and F-1 correspond to the C and F atoms on the right of the double bond of *cis*-1,2-difluoroethylene shown in Fig. 6, whereas C-2 and F-2 correspond to those on the left.
[d]The value is fixed to reproduce θ_a, the angle between H^{35}Cl and the *a* inertial axis of the complex.

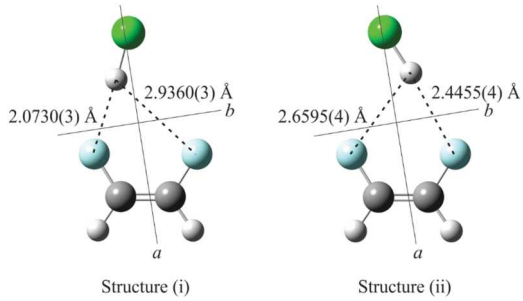

FIG. 6. Two structures of *cis*-1,2-difluoroethylene–HCl consistent with experimental spectroscopic constants, but theory shows that structure (i) is lower in energy. The *a* and *b* inertial axes are indicated for each structure. C-1 and F-1 correspond to the C and F atoms on the right of the double bond of *cis*-1,2-difluoroethylene, whereas C-2 and F-2 correspond to those on the left. Atom colors: C: dark gray, H: light gray, F: light blue, and Cl: green.

With the exception of the *b* coordinate of the H atom in HCl, structures (i) and (ii) are practically identical (within 0.02 Å). In particular, the distances between the Cl atom in HCl and the atoms of the difluoroethylene are practically the same in the two structures. The only differences between the structures are whether the HCl bond points toward F-2 [structure (i)] or F-1 [structure (ii)] and the accompanying H···F distances (see Fig. 6). For a comparison with the substitution coordinates, we list the coordinates for the C and Cl atoms from the structure fits for both structures in Table III together with the Kraitchman coordinates for Cl and the single result available for C. Indeed, the Cl coordinates for both structures agree excellently with those determined using the Kraitchman analysis. Interestingly, the Kraitchman coordinates for the C atom are very nearly the root mean square of the coordinates for the two C atoms in the two structures. The Kraitchman equations are based on changes in moments of inertia (or equivalently, planar moments) that are mass weighed sums of the squares of coordinates and are averaged over the zero-point motion of the molecule. This further suggests that we are observing an effective average structure in which the two carbon atoms are equivalent.

Because the zero-point motion of DCl is significantly different from HCl, we did not attempt to use it to locate the H atom of HCl in the complex. We can, however, turn to theory to determine which of the two possible structures is more likely. At the

MP2/6-311++G(2d,2p) level, structure (ii) is 142 cm^{-1} higher in energy without BSSE correction and 74 cm^{-1} higher in energy with BSSE correction than structure (i). These energy differences are significant; thus, structure (i) represents the experimental structure of *cis*-1,2-difluoroethylene–HCl.

V. DISCUSSION

Combining theory and experiment, we have determined the structure of *cis*-1,2-difluoroethylene–HCl. Although experimental data suggest two possible structures, structure (ii) can be eliminated on energetic grounds. The two H···F distances in structure (ii) are more nearly equal than those in structure (i): 2.4455(4) and 2.6595(4) Å vs 2.0730(3) and 2.9360(3) Å. It is instructive to compare these lengths with those in other haloethylene–HCl complexes. HCl binds across the C=C bond to H and F atoms located on different C atoms in vinyl fluoride,[3,4] 1,1-difluoroethylene,[26,27] *trans*-1,2-difluoroethylene,[7] and (*E*)-1-chloro-2-fluoroethylene,[28] and the respective H···F bond lengths are 2.123(1), 2.330 94(36), 2.200 30(53), and 2.194 81(34) Å. The binding mode of HCl to 1,1,2-trifluoroethylene[9] is different; the acid interacts with the H and F atoms connected to the same C atom, with a H···F distance of 2.3416(7) Å. The H···F distances in structure (ii) are longer, and in some cases, significantly more so, than these other haloethylene–HCl complexes, further demonstrating that this configuration where HCl appears to interact more or less equally with both F atoms is high in energy.

The shorter H···F bond in structure (i) has a length of 2.0730(3) Å and deviates from linearity by only 1.8°, while the other H···F bond is not only significantly longer [2.9360(3) Å], but also bends much more from linearity (61.9°). The shorter, almost linear bond is, therefore, the one that confers stability to the complex; it is also shorter than the H···F bonds in the haloethylene–HCl complexes mentioned earlier. Using this structure, the rotational constants of the two isotopologues singly substituted with ^{13}C are predicted to be 5980, 1447, 1165 and 5955, 1451, 1167 MHz. Although these two sets of constants may seem quite similar, if there were indeed two distinct, singly substituted ^{13}C isotopologues, they would give rise to well separated lines in the microwave spectrum. We are, however, able to observe only one spectrum, which suggests one of two scenarios. In the first, zero-point effects leading to lower energy for the isotopologue with HCl forming the shorter bond to the F atom connected to ^{13}C would lead to the second isotopologue having weaker transitions, perhaps too weak to observe. In the second scenario, as we have suggested earlier, the two C atoms in *cis*-1,2-difluoroethylene–HCl are equivalent. In other words, the two minima labeled as isomer (b) in Fig. 2 are indistinguishable, and in the ground vibrational state, both are sampled on the timescale of molecular rotation and microwave spectroscopy.

To examine the barrier separating the two configurations of isomer (b), we scan the minimum energy path as a function of θ near the values appropriate to these configurations, once again using theory at the MP2/6-311++G(2d,2p) level (Fig. 7). The barrier to interconversion between the two equivalent structures is 13.8 cm^{-1} when BSSE correction is not included but reduces to 1.2 cm^{-1} with BSSE correction. Indeed, it may very well be that for some levels of theory, the barrier actually vanishes. Nevertheless, these values are sufficiently small that the zero-point motion of

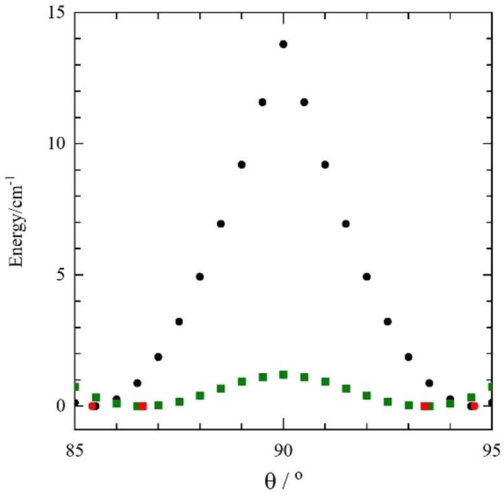

FIG. 7. Minimum energy path as a function of the polar angle (defined in Fig. 2) without (circles) and with (squares) BSSE correction. The optimized angles for isomer (b) are displayed in red.

HCl in the complex would certainly extend over the two equivalent configurations. The interconversion of these configurations involves the interchange of two pairs of fermions (the two hydrogen atoms and two fluorine atoms); the resulting nuclear spin statistics should show a 6:10 intensity ratio between odd and even K_a transitions. Although the Balle–Flygare spectrometer has a large dynamic range, it is difficult to control instrumental effects to get precise intensity information. Nevertheless, an examination of the 5_{15}–4_{14} and 5_{05}–4_{04} transitions in the ^{37}Cl isotopologue is helpful. Figure 8 shows four quadrupole hyperfine components for each of these transitions. The transition frequency for each component, after averaging the frequencies of the two halves of the corresponding doublet, is displayed as a red line, with the intensity given as the average of the two halves of the doublet. (In the case of the transitions around 12 099 MHz, where the higher frequency half of one doublet overlaps with the lower frequency half of another, the intensity is taken

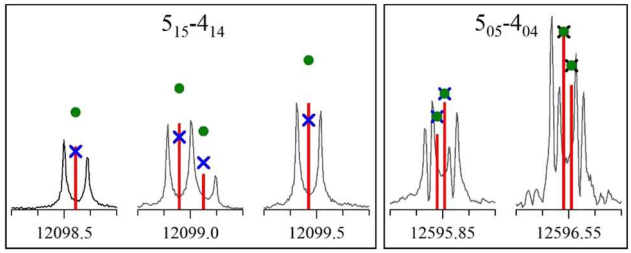

FIG. 8. Narrowband spectrum of two rotational transitions for the *cis*-1,2-difluoroethylene–$H^{37}Cl$ isotopologue, each showing the Doppler doublets of four nuclear quadrupole hyperfine components and using the same intensity scale. The frequencies and intensities of the two segments of a Doppler doublet are averaged and displayed in red. The predicted intensity of each transition, relative to the strongest transition at 12 596.540 MHz, is marked with a green circle when spin statistics is not taken into account and a blue cross when it is.

to be that of the non-overlapping half.) Scaling the predicted intensity of the strongest transition ($F' - F''$ = 13/2–11/2) of 5_{05}–4_{04} at 12 596.540 MHz to be the same as that observed, we calculate the predicted intensities of the transitions displayed in Fig. 8. It appears that the observed intensities for the 5_{15}–4_{14} transitions are weaker than expected when spin statistics are not included, and in fact, are best matched when spin statistics are included. This observation supports the conclusion that the C atoms in the *cis*-1,2-difluoroethylene–HCl complex are equivalent.

An examination of the intensities of several transitions of the three isotopologues in the narrowband spectrum also supports this. Were the C atoms not equivalent, we would expect the intensity ratio of the same hyperfine component to be 100:33:1 for the most abundant, ^{37}Cl, and each of the two distinguishable ^{13}C isotopologues, respectively. In the absence of spin statistics, the ratio would be 100:33:2 for substitution at either of the two equivalent carbon atoms. However, the substitution of one ^{12}C by ^{13}C, even though there are two equivalent locations for the substitution, reduces the molecular symmetry group from C_{2v}(M) to C_s(M) and renders the hydrogen and fluorine atoms distinguishable. Consequently, all sixteen nuclear spin states can be paired with every rotational level. This enhances the population of the singly substituted ^{13}C isotopologues by not only the symmetry factor of two for the two equivalent substitution sites but also by an additional factor of 16/10 and 16/6 for even and odd values of K_a, respectively. Consequently, the isotopologue intensity ratio for *a* type transitions becomes 31:10:1 for even K_a values (and 19:6:1 for odd K_a values). For the 6 hyperfine components examined (two each in the 4_{04}–3_{03}, 5_{05}–4_{04}, and 6_{06}–5_{05} rotational transitions), the ^{35}Cl isotopologue is 32–62 times stronger than their counterparts for the ^{13}C isotopologue, whereas the ^{37}Cl isotopologue is 17–22 times stronger than their counterparts for the ^{13}C isotopologue. Although the ratio does not match 31:10:1, the stronger than expected transition intensities for the ^{13}C isotopologue do suggest that large amplitude motion in the complex renders the atoms to one side of the double bond in the *cis*-1,2-difluoroethylene subunit equivalent to their counterparts on the other side. Once again, we stress that intensity data from the narrowband spectrometer are not quantitatively reliable, as demonstrated by the fact that the intensity ratios of a transition between the most abundant and the ^{37}Cl isotopologue range from 1.9:1 to 2.8:1 in the six hyperfine components examined. The smaller ratio deviates greatly from the expected 3:1 ratio.

The *cis*-1,2-difluoroethylene–HCl complex is the first fluoroethylene–HX (HX = HF, HCl, HCCH) complex that shows a dependence of the binding mode on acid identity. To understand this new configuration, we map the electrostatic potential onto the total electron density surface of the difluoroethylene (Fig. 9). The most negative portion of the molecule is, not surprisingly, around the F atoms, and the HCl molecule binds in this region with a linear hydrogen bond. According to theory, this is a more energetically favored configuration than that where HCl binds to the geminal F, H pair [isomer (c)]. In this latter configuration, the bending of the hydrogen bond from linearity must be so destabilizing that the Cl···H interaction cannot compensate for it. This is not the case for *cis*-1,2-difluoroethylene–HCCH.[11] Using the same level of theory [MP2/6-311++(2d,2p)], the configuration with HCCH interacting with both F atoms (a nonplanar structure similar to isomer (a) in Fig. 1) is 65.7 and 120.1 cm^{-1}, respectively, without and with BSSE correction, higher in energy than when HCCH binds to the F, H pair bonded to the same C atom in the difluoroethylene subunit. It appears then that the interaction of HCCH with a second F atom is less than the stabilization afforded by the interaction between the triple bond of HCCH and the electropositive H atom geminal to the hydrogen-bonded F atom. This is likely a consequence of the lower energetic requirement to bend the hydrogen bond of HCCH, a weaker acid than HCl.

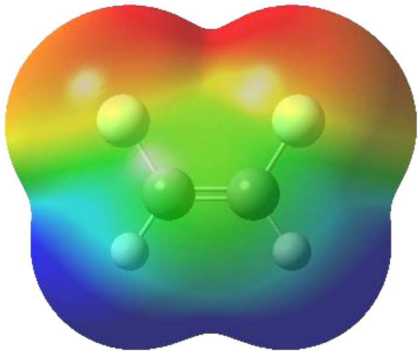

FIG. 9. Electrostatic potential, mapped onto a total electron density isosurface for *cis*-1,2-difluoroethylene. Blue represents positive electrostatic potential, and red represents negative electrostatic potential.

VI. CONCLUSIONS

The microwave spectra for three isotopologues, ^{35}Cl, ^{37}Cl, and a single ^{13}C isotopologue, of the gas-phase heterodimer formed between *cis*-1,2-difluoroethylene and HCl have been obtained and analyzed. A molecular structure for the heterodimer is found that is consistent with the observed spectra and quantum chemistry calculations. This structure is remarkable in several ways. First, it has a mode of binding different from that observed for the analogous *cis*-1,2-difluoroethylene–acetylene complex, or indeed any other previously characterized protic acid–fluoroethylene heterodimer. Furthermore, it does not include an interaction between the nucleophilic portion of the acid (the Cl atom in this case) and a hydrogen atom of the fluoroethylene. In addition, the large amplitude in-plane motion of the HCl subunit samples both of the two equivalent Cl–H···F binding sites, rendering not only the two fluorine atoms equivalent but also the two carbon atoms and two olefinic hydrogen atoms. Consequently, there is only one unique, singly substituted ^{13}C isotopologue, consistent with observation and supported by observed spin statistics effects on transition intensities.

The observed structure allows for a nearly linear hydrogen bond between the hydrogen atom of the HCl donor and a highly electronegative fluorine atom acceptor while also interacting, although to a lesser extent, with a second fluorine atom. Indeed, as noted above, two equivalent bonding arrangements, in which the roles of the fluorine atoms are switched, are sampled on the time scale of the experiment due to the zero-point motion of HCl. Presumably, this second H···F interaction is more important in the case of *cis*-1,2-difluoroethylene–HCl than for *cis*-1,

2-difluoroethylene–HCCH, as is also the loss of stability accompanying the departure of the hydrogen bond from linearity necessary for bonding to the geminal H, F pair as observed in the acetylene complex.

SUPPLEMENTARY MATERIAL

See the supplementary material for the Cartesian coordinates of all atoms in the *ab initio* predicted optimized structures in Fig. 4 and the two structures consistent with experimental spectroscopic constants in Fig. 6 (Table S1), and observed transition frequencies with assignments and residuals (observed minus calculated) for three isotopologues of *cis*-1,2-difluoroethylene–HCl (Tables S2–S4).

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-2309942. We thank Dr. Philip R. Bunker for discussions regarding the molecular symmetry groups appropriate for the normal and singly substituted ^{13}C isotopologues of *cis*-1,2-difluoroethylene–HCl and nuclear spin statistics considerations.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Helen O. Leung: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Mark D. Marshall**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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