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The molecular structure of and interconversion tunneling in the argon-*cis*-1,2-difluoroethylene complex

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Guided by *ab initio* predictions, the structure of the gas-phase complex formed between *cis*-1,2-difluoroethylene and an argon atom in a pulsed molecular jet is determined using microwave spectroscopy in the 5.7–21.5 GHz region of the spectrum. This is a non-planar, symmetric species, with the argon atom located in the FCCF cavity of the difluoroethylene. The transitions in the microwave spectrum are observed to be split by an interconversion tunneling motion between the two equivalent configurations for the complex with the argon atom located either above or below the difluoroethylene molecular plane. Both one- and two-dimensional discrete variable representation calculations of the tunneling splitting using the *ab initio* interaction potential for the complex suggest that the barrier to interconversion is overestimated by theory. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823494>]

I. INTRODUCTION

Through our studies in recent years on complexes formed between fluorine substituted ethylenes and protic acids and from work reported by the Legon group, we have uncovered many details concerning the intermolecular forces responsible for these complexes. Specifically, the species examined include vinyl fluoride-HX ($X = \text{F},^1 \text{Cl},^{2,3} \text{CCH}^4$), 1,1-difluoroethylene-HX ($X = \text{F},^5 \text{Cl},^6 \text{CCH}^7$), 1,1,2-trifluoroethylene-HX ($X = \text{F},^8 \text{Cl},^9 \text{CCH}^{10}$), and *trans*-1,2-difluoroethylene-HF.¹¹ Two interactions are present in each complex: a hydrogen bond, formed by the acid with a fluorine atom in the substituted ethylene subunit, and a secondary interaction between the nucleophilic portion of the acid and a hydrogen atom in the ethylene subunit. An increase in the number of fluorine substituents in the ethylene subunits has significant effects on the nature of intermolecular interactions, which we observe as changes in the values of the geometric parameters and in some cases, even as a change in bonding mode. In particular, when only one or two F atoms are present in the ethylene subunit, the acid binds across the C=C bond, but in the case of 1,1,2-trifluoroethylene, the acid binds to the F and H atoms at the same end of the double bond. We refer to these arrangements as the top binding (across the C=C bond) and the side binding (at one end of the C=C bond) structures, respectively. These structures are results of a competition between electrostatic and steric factors, and we have argued that the binding of the acid across the C=C bond is sterically more favorable while the side binding configuration is driven by electrostatic factors.¹¹ As trifluoroethylene complexes are the only ones in the list above that adopt a side binding mode, we turn to *cis*-1,2-difluoroethylene, which offers only this mode of binding for an acid in which both primary and sec-

ondary interactions are present, to deepen our understanding of the interplay among opposing factors in intermolecular interactions.

Indeed, *ab initio* calculations carried out for *cis*-1,2-difluoroethylene-HF confirm that the side binding structure is the global minimum on the potential surface that describes the interactions between the subunits. The rotational constants are relatively large; therefore, only about 20 transitions are predicted in our spectral range, making it very difficult to identify them. In fact, our search for this complex led to the observation of many lines, which we must assign before we can attempt to find the spectrum for the HF complex. Not surprisingly, because we use Ar as a buffer gas, most of the lines can be attributed to Ar-*cis*-1,2-difluoroethylene.

Ar-*cis*-1,2 difluoroethylene provides an additional example of an interaction between argon and fluorine-substituted ethylenes, complementing the three previously presented by Kisiel, Fowler, and Legon¹² In particular, it provides a nice point of comparison with the structure of the complex with an alternative disubstituted olefin, Ar-1,1-difluoroethylene, showing the differences due to *cis* versus geminal fluorination. As a structureless probe, argon serves to reveal the electronic distribution of the ethylene subunits, and in the present complex, argon also exhibits tunneling motion between two equivalent non-planar geometries for the molecule. We describe below the rotational spectrum, dynamics, and structure of this complex.

II. AB INITIO AND DVR CALCULATIONS

Holding the geometric parameters of *cis*-1,2-difluoroethylene fixed at their literature values,¹³ *ab initio* calculations at the MP2/6-311++G(2d,2p) level using GAUSSIAN 09¹⁴ give minima corresponding to two distinct structures of Ar-*cis*-1,2-difluoroethylene. Their geometric parameters and rotational constants are shown in Fig. 1 and Table I, respectively. One isomer has a planar configuration

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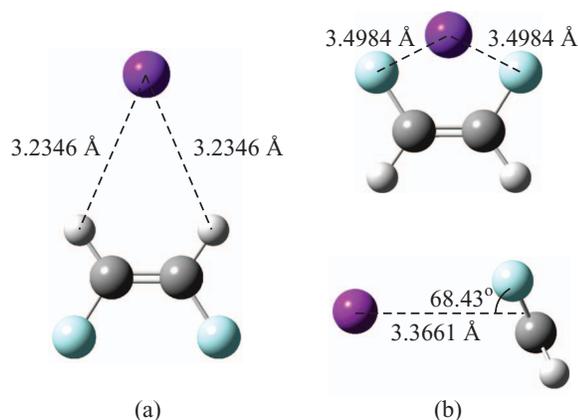


FIG. 1. Structures corresponding to the minima on the *ab initio* potential energy surface of the Ar-*cis*-1,2-difluoroethylene complex: (a) a planar structure and (b) a nonplanar structure shown in two views: the top view shows the difluoroethylene subunit in the plane, while the second view is along the C=C bond. The carbon atoms are dark gray, hydrogen atoms are light gray, fluorine atoms are light blue, and the argon atom is purple.

where Ar is closest to the two hydrogen atoms. Only *a*-type transitions would be expected, since both the *b* and *c* components of the dipole moment vanish by symmetry. The other isomer is nonplanar, with Ar equidistant from the F atoms (Fig. 1(b), top view) and also near the π cloud of the C=C bond (Fig. 1(b), bottom view). Both *a*- and *c*-type transitions are possible for this structure. Additionally, it is 83 cm^{-1} lower in energy than the planar isomer. Thus, under our experimental conditions, we expect to observe only the nonplanar configuration of Ar-*cis*-1,2-difluoroethylene.

With a non-planar equilibrium geometry, the complex can assume two equivalent configurations: Ar can be located on one side or the other of the difluoroethylene plane. This raises the possibility of an observable tunneling splitting between the two. Thus, we turn to theory and determine the minimum energy path connecting the two equivalent configurations. As appropriate for the discrete variable representation (DVR) calculations described in the next paragraph, we use the coordinate system depicted in Fig. 2, where the difluoroethylene subunit defines the *xz* plane and the origin is at its center of mass, which is 0.6462 \AA away from the C=C bond and in the molecular plane. Once again the structure of the *cis*-1,2-difluoroethylene subunit is assumed to be unchanged upon complexation. The position of Ar can therefore be characterized by its distance from the origin, *R*, the polar angle, θ , and the azimuthal angle, ϕ , of *R*. We then carry out a relaxed scan at the MP2/6-311++G(2d,2p) level, changing ϕ in 5° steps from 0° to 360° while optimizing *R* and θ . For each value of ϕ , the optimized value of θ is within 0.03° of 90° . Thus, the minimum energy path lies in the *xy* plane, the

TABLE I. Rotational constants of two isomers of Ar-*cis*-1,2-difluoroethylene (shown in Fig. 1) calculated using GAUSSIAN 09¹⁴ at the MP2/6-311++G(2d,2p) level.

	Planar	Nonplanar
<i>A</i> (MHz)	5930	4781
<i>B</i> (MHz)	959	1669
<i>C</i> (MHz)	825	1375

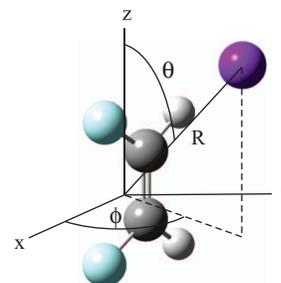


FIG. 2. The coordinate system used to define the position of Ar with respect to the *cis*-1,2-difluoroethylene plane. The origin is the center of mass of the difluoroethylene subunit, which also defines the *xz* plane. *R* is the distance of Ar from the origin, and θ and ϕ are, respectively, the polar and azimuthal angle of *R*.

one perpendicular to the C=C bond and bisecting it. The result of this calculation is shown in Fig. 3, where the structures corresponding to the 3 minima and one of the maxima ($\phi = 0^\circ$ and 360° represent the same configuration) are also displayed. As described earlier, the planar isomer with Ar closest to the two hydrogen atoms in the ethylene subunit ($\phi = 180^\circ$) is a local minimum. The two equivalent, lowest-energy configurations ($\phi = 68.43^\circ$ and 291.57°) are separated by a barrier of only 113 cm^{-1} , which is low enough that tunneling motion between them seems possible. It is notable that the planar configuration with Ar interacting with the two fluorine atoms in the ethylene subunit lies at a potential maximum.

To obtain an estimate of the tunneling splitting in the Ar-*cis*-1,2-difluoroethylene complex, one-dimensional DVR calculations are performed using the *ab initio* minimum energy path. In these calculations, the *cis*-1,2-difluoroethylene is assumed to rotate about its *a* inertial axis, which is parallel to the C=C bond and displaced 0.6462 \AA in the monomer plane towards the fluorine atoms. The center of mass-argon separation, *R*, is fixed at the equilibrium value appropriate to the global minimum of 3.3662 \AA . DVR kinetic energy matrix elements for a $(0, 2\pi)$ interval are taken from Appendix A.4 of Colbert and Miller,¹⁵ with $\hbar^2/2m$ of

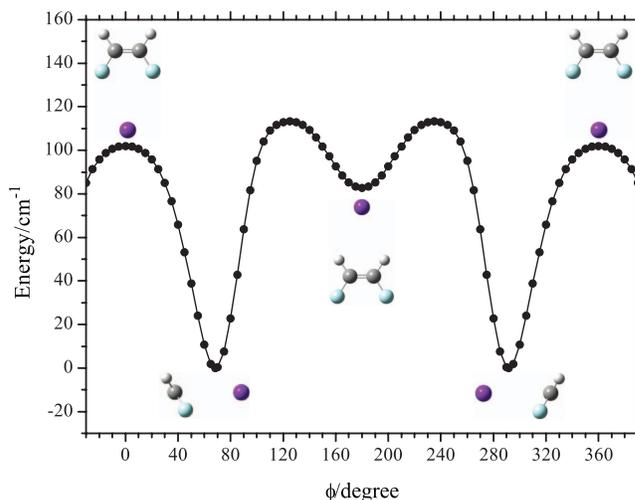


FIG. 3. The minimum energy path for Ar-*cis*-1,2-difluoroethylene in which *R* and θ are optimized and ϕ is varied in 5° steps, calculated at the MP2/6-311G++(2d, 2p) level. The structures of the complex corresponding to some of the extrema are shown. The carbon atoms are dark gray, hydrogen atoms are light gray, fluorine atoms are light blue, and the argon atom is purple.

Eq. (A12) replaced with $F = A + \frac{16.8576 \text{ cm}^{-1} \text{ amu } \text{Å}^2}{\mu R^2}$, where $A = 0.7038 \text{ cm}^{-1}$ is the rotational constant about the a axis of *cis*-1,2-difluoroethylene,¹³ μ is the reduced mass (24.603 amu) of the complex, and R is the (fixed) distance between the argon atom and the center of mass of the difluoroethylene monomer. The constant, 16.8576, appearing in the expression for F corresponds to the value $h/8\pi^2c$ in the units given.

As is well-known, the potential energy matrix in DVR is diagonal, with these elements equal to the value of the potential energy at the corresponding grid point, which in principle are available directly from the *ab initio* calculation. However, the requirement for an evenly spaced grid with an odd number of points¹⁵ means that the two equivalent potential wells are not sampled at symmetrically related angles. This has two disadvantages. First, it is not possible to take advantage of the symmetry in the potential to reduce the number of points that must be calculated and second, the round-off errors and other forms of imprecision in the numerical representation of the potential render the two wells slightly inequivalent, and the tunneling is quenched with the wave functions collapsing to a single well. To avoid this problem, the minimum energy path was fit to a 15-term cosine expansion that was used to generate the values of the potential at the $(2n + 1)$ grid points. Subsequently, we have found that the original formulation of DVR on a $(0, 2\pi)$ interval given by Meyer¹⁶ allows for an even number of grid points on the interval, which successfully addresses both disadvantages of using an odd number of points. In test calculations with several potentials, including the 15-term cosine expansion used here for Ar-*cis*-1,2-difluoroethylene, we have found that the two methods give equivalent results for converged levels. Using the Colbert-Miller formulation with 71 equally spaced grid points, we find two-closely spaced levels $\sim 19 \text{ cm}^{-1}$ above the global minima of the minimum energy path and well below the top of the barrier to interconversion. These tunneling levels have a converged splitting of 0.023 MHz that would lead to observable effects in the microwave spectrum.

III. EXPERIMENT

We synthesize *cis*-1,2-difluoroethylene from the dechlorination of 1,2-dichloro-1,2-difluoroethane.¹⁷ The products contain a *cis/trans* mixture of 1,2-difluoroethylene, which is used directly in our experiment without a separation of the isomers. The rotational spectra of two naturally occurring isotopologues of Ar-*cis*-1,2-difluoroethylene (Ar-*cis*-CHFCHF and Ar-*cis*-CHF¹³CHF) are collected in the 5.7–21.5 GHz region using a pulsed molecular beam, Fourier transform microwave spectrometer, which has been previously described in Ref. 18. To form the complex, a mixture of 1% *cis/trans*-1,2-difluoroethylene in argon at a stagnation pressure of approximately 2 atm is expanded through a 0.8 mm diameter pulsed nozzle mounted behind one of the mirrors that forms the Fabry-Pérot cavity. The time domain signals are digitized at a sampling frequency of 10 MHz and corrected for background, and then signal averaged and doubled in length via zero-filling before Fourier transformation to a frequency domain signal. A greater number of data points in the time domain are collected for stronger transitions and fewer for weaker transitions. Typically, the resolution element for the frequency domain signals is 1.2 kHz for the most abundant species and 4.8 kHz for the ¹³C-containing species. Because the molecular beam is parallel to the mirror axis, each transition appears as a Doppler doublet. The rest frequency of the transition is the mean frequency of the two Doppler components.

IV. RESULTS

A. Spectral analysis and group theory

Both a - and c -type transitions are observed for two isotopologues of Ar-*cis*-1,2-difluoroethylene, consistent with the spectrum of a nonplanar complex. Most transitions, when resolvable, show doubling beyond the expected Doppler doubling. (A typical line is $\sim 6 \text{ kHz}$ full width at half maximum.) A sample a -type rotational transition is shown in Fig. 4(a).

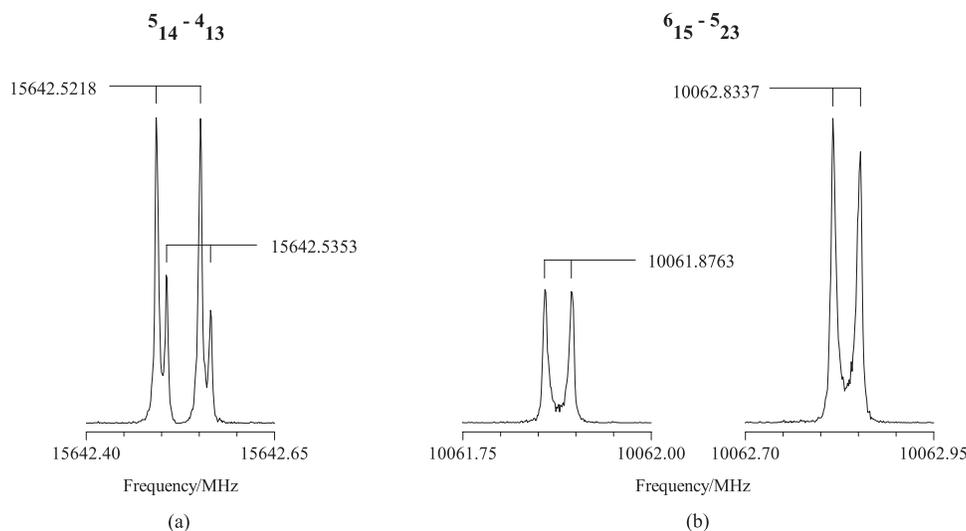


FIG. 4. A typical a type transition and b type transition. Due to the Doppler effect, each line appears as a doublet with indicated rest frequency. Two Doppler doublets are observed for each rotational transition due to tunneling motion.

TABLE II. Character table for the molecular symmetry (permutation-inversion) group of Ar-*cis*-CHFCHF.

	E	$(H_1H_2)(F_1F_2)(C_1C_2)$	E^*	$(H_1H_2)(F_1F_2)(C_1C_2)^*$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	-1	1
B_2	1	-1	1	-1

The two sets of Doppler doublets of the $5_{14}-4_{13}$ transition, with one set much stronger than the other, are separated by only 14 kHz. On the other hand, for *c*-type transitions the two sets of doublets are more widely separated (by ~ 1 MHz). An example is shown in Fig. 4(b) where once again, one set of Doppler doublets, this time of the $6_{15}-5_{23}$ transition, is stronger than the other set.

As discussed above, this complex is expected to display the effects of tunneling between two equivalent configurations, and we turn to group theory to aid in the assignment of transitions. The doubling of transitions and the difference in tunneling splittings for *a*- and *c*-type transitions suggest that we have two tunneling states for each rotational level. Furthermore, *a* type transitions with smaller tunneling splittings arise from transitions within the same tunneling state, whereas *c* type transitions with larger tunneling splittings arise from transitions across tunneling states. The two equivalent frameworks for Ar-*cis*-CHFCHF are shown in Fig. 3 ($\phi = 68.43^\circ$ and 291.57°), and the appropriate molecular symmetry group is isomorphic to C_{2v} (see Table II for the character table). With two identical H nuclei (H_1 and H_2), F nuclei (F_1 and F_2), and C nuclei (C_1 and C_2), the overall wave function for the complex must be symmetric with respect to $(H_1H_2)(F_1F_2)(C_1C_2)$, the operation that interchanges two pairs of fermions and one pair of bosons; in other words, it must have either A_1 or A_2 symmetry. The overall wave function is a product of the electronic, vibrational, rotational, nuclear spin, and tunneling wave functions, $\psi = \psi_{\text{elec}}\psi_{\text{vib}}\psi_{\text{rot}}\psi_{\text{spin}}\psi_{\text{tun}}$. The ground electronic and vibrational wave functions are totally symmetric, and the irreducible representations for ψ_{rot} , ψ_{spin} , and ψ_{tun} (only the ground and first excited tunneling states, $v_{\text{tun}} = 0$ and 1, are relevant to this work) are listed in Table III. The statistical weights of the spin states are 10 and 6, respectively, when the spin symmetries are A_1 and B_2 .

The allowed combinations of ψ_{rot} , ψ_{spin} , and ψ_{tun} are listed in Table IV. To summarize, for even values of K_a , the ground and exciting tunneling states have statistical weights of 10 and 6, respectively; for odd values of K_a , the weights are reversed; that is, the ground tunneling state has a weight

TABLE III. Symmetry properties for factors in the overall wave function with respect to the permutation of the H, F, and C nuclei in Ar-*cis*-CHFCHF.

	ψ_{rot}	ψ_{spin}	ψ_{tun}
$K_a = \text{even}, K_c = \text{even}: A_1$		A_1 (stat. wt. = 10)	$v_{\text{tun}} = 0: A_1$
$K_a = \text{even}, K_c = \text{odd}: A_2$		B_2 (stat. wt. = 6)	$v_{\text{tun}} = 1: B_1$
$K_a = \text{odd}, K_c = \text{even}: B_2$			
$K_a = \text{odd}, K_c = \text{odd}: B_1$			

TABLE IV. Allowed combinations of ψ_{rot} , ψ_{spin} , and ψ_{tun} .

	ψ_{rot}	ψ_{spin}	ψ_{tun}
$K_a = \text{even}, K_c = \text{even/odd}: A_1/A_2$		A_1 (stat. wt. = 10)	$v_{\text{tun}} = 0: A_1$
$K_a = \text{odd}, K_c = \text{even/odd}: B_2/B_1$		A_1 (stat. wt. = 10)	$v_{\text{tun}} = 1: B_1$
$K_a = \text{odd}, K_c = \text{even/odd}: B_2/B_1$		B_2 (stat. wt. = 6)	$v_{\text{tun}} = 0: A_1$
$K_a = \text{even}, K_c = \text{even/odd}: A_1/A_2$		B_2 (stat. wt. = 6)	$v_{\text{tun}} = 1: B_1$

of 6 and the excited tunneling state has a weight of 10. Electric dipole transitions connect only spin states with the same symmetry. Thus, each rotational transition is split into two components. For an *a*-type transition one component connects two rotational levels in the ground tunneling state while the other connects two in the excited tunneling state (or “bottom-to-bottom” and “top-to-top”). For the *c*-type transitions, the components connect pairs of rotational levels with one level in the ground tunneling state and the other in the excited tunneling state (or “bottom-to-top” and “top-to-bottom”). The intensity ratio of the two components is 10:6, as given by the statistical weight of the levels involved. Specifically, for an *a*-type transition, the stronger component connects two rotational levels in the ground tunneling state for an even value of K_a'' but two rotational levels in the excited tunneling state for an odd value of K_a'' . The two components are separated by the difference of tunneling splittings and, therefore, are similar in frequency (and may even be unresolvable). For a *c*-type transition, the higher frequency component (which connects the ground tunneling state of the lower rotational level and the excited tunneling state of the upper rotational level) is stronger for an even value of K_a'' , but it is weaker for an odd value of K_a'' . These two components are separated by the sum of the tunneling splittings and are easily resolved.

The appropriate molecular symmetry group for Ar-*cis*-CHF¹³CHF is isomorphic to C_s (Table V). The C_{2v} group used for the most abundant isotopologue is homomorphic onto the C_s group, with the A_1 and B_2 (A_2 and B_1) representations of the C_{2v} group correlating with the A' (A'') representation of the C_s group. There is, however, no symmetry operation in the C_s group that permutes equivalent nuclei. Thus, nuclear spin statistics are no longer relevant. Nevertheless, the selection rules given above still apply: each transition is split into two components, with *a*-type transitions occurring within a tunneling state and *c*-type transitions connecting the ground and excited tunneling states.¹⁹

Using the simple fact that the higher frequency component of a *c*-type transition connects the ground tunneling state in the lower rotational level with the excited tunneling state in the upper rotational level, we readily assign all the *c*-type transitions for both isotopologues. The spectroscopic constants

TABLE V. Character table for the molecular symmetry (permutation-inversion) group of Ar-*cis*-CHF¹³CHF.

	E	E^*
A'	1	1
A''	1	-1

TABLE VI. Spectroscopic constants^{a,b} (in MHz, except as otherwise noted) for the ground and first excited tunneling states for two isotopologues of Ar-*cis*-1,2-difluoroethylene.

	Ar- <i>cis</i> -CHFCHF		Ar- <i>cis</i> -CHF ¹³ CHF	
	A ₁	B ₁	A'	A''
ΔE (MHz)	0.53192(56)		0.46401(99)	
A (MHz)	4874.77050(42)	4874.76759(38)	4841.04179(68)	4841.03975(68)
B (MHz)	1648.038948(88)	1648.037148(91)	1633.52546(25)	1633.52344(25)
C (MHz)	1352.712838(75)	1352.713017(73)	1342.44377(23)	1342.44451(23)
Δ_J (kHz)	9.56453(92)	9.56574(93)	9.3565(27)	9.3585(27)
Δ_{JK} (kHz)	80.848(20)	80.893(19)	78.909(18)	78.952(18)
Δ_K (kHz)	-66.194(73) ^c	-66.194(73) ^c	-63.94(13) ^d	-63.94(13) ^d
δ_J (kHz)	1.72612(56)	1.72819(57)	1.6782(18)	1.6764(18)
δ_K (kHz)	49.465(23)	49.515(23)	48.145(90)	48.093(90)
Φ_{JK} (Hz)	-10.14(33)	-9.98(32)	-10.14 ^e	-9.98 ^f
Φ_{KJ} (Hz)	23.5(15)	26.3(14)	23.5 ^e	26.3 ^f
No. of rot. transitions	55		37	
No. of <i>a</i> type	29		18	
No. of <i>c</i> type	26		19	
No. of components	108		73	
<i>J</i> range	0–7		1–6	
<i>K_a</i> range	0–3		0–2	
rms (kHz)	0.77		1.17	

^aA-reduction, *I'*-representation.²⁰^b1 σ standard deviations in the parameters are given in parentheses.^cConstrained to be the same for both tunneling states in the fit.^dConstrained to be the same for both tunneling states in the fit.^eFixed at the value appropriate to the A₁ state of the most abundant isotopologue.^fFixed at the value appropriate to the B₁ state of the most abundant isotopologue.

determined from these lines allow us to assign with confidence the *a*-type transitions. Additionally, for the most abundant species, the relative intensities for the two components in each transition are in accord with the expectations discussed above. We have assigned 55 rotational transitions for the most abundant isotopologue and 37 for the ¹³C-containing isotopologue. Both tunneling components are included for most transitions, with the exception of the 1₁₀-0₀₀ and 2₂₀-2₁₂ transitions in the most abundant species and the 2₂₀-2₁₂ transition in the ¹³C-containing isotopologue. In each of these transitions, extensive, unassigned splitting is observed in one of the components, which is not used in the analysis. These splittings, which are not instrumental in origin, might be due to magnetic hyperfine interactions that are different in the two tunneling states, although neither the spin-rotation nor nuclear spin-spin interactions are expected to be resolvable for this complex, let alone have a marked tunneling state variation. It is also possible that the extra lines are due to another species in the jet expansion.

The transitions for each isotopologue are analyzed using the Watson *A*-reduced Hamiltonian (as appropriate for the value of Ray's asymmetry parameter, $\kappa = -0.83$, that is ultimately determined) in the *I'* representation²⁰ and the spectroscopic constants are derived using Pickett's nonlinear least squares program, SPFIT.²¹ In addition to 3 rotational constants and 5 quartic centrifugal constants (and in the case of the most abundant species, 2 sextic centrifugal distortion constants) for each tunneling state, we have also determined the tunneling splitting, $\Delta E = 0.53191(56)$ MHz, for the most abundant isotopologue, which decreases, as expected,

to 0.46401(99) MHz for the heavier, ¹³C-containing species (Table VI). The rms error of each fit is only about 1 kHz, much smaller than a typical line width. Tables of observed and calculated transition frequencies with assignments for the two isotopologues are available as supplementary material.²²

B. Structure determination

The Ar-*cis*-1,2-difluoroethylene complex has an inertial defect of -37 amu \AA^2 , and thus is nonplanar, consistent with the observation of both *a* and *c* type transitions. Additionally, the intensity of each rotational transition in the ¹³C-containing isotopologue is twice as strong as expected based on the natural abundance of ¹³C, indicating that the two carbon atoms must occupy symmetrically equivalent positions. In other words, the complex possesses a symmetry plane containing argon and bisecting the C=C bond, as predicted by theory.

We are able to determine a partial substitution structure of Ar-*cis*-1,2-difluoroethylene in the principal coordinate system of the most abundant isotopologue using a Kraitchman analysis.²³ Treating the Ar-*cis*-CHF¹³CHF complex and the *cis*-CHFCHF monomer as containing a single substitution in Ar-*cis*-CHFCHF, taken as the parent, (with ¹³C and with a hypothetical Ar atom of zero mass as substitutions, respectively), the absolute values of the substitution coordinates of the C and Ar atoms and their Costain errors [$\sigma(r) = 0.0015\text{\AA}^2/|r|$]²⁴ are determined (Table VII). The relative signs for most of these coordinates can also be deduced. Because of the symmetry of the complex, the magnitudes of the

TABLE VII. Coordinates of singly substituted atoms in Ar-*cis*-CHFCHF from a Kraitchman analysis (Ar-¹²CHF¹²CHF as parent, see text for details) and from a fit to the moments of inertia of two isotopologues of Ar-*cis*-1,2-difluoroethylene.

	C	C	Ar
Substitution coordinates ^{a,b}			
<i>a</i> (Å)	1.56125(96)	1.56125(96)	-2.08554(72)
<i>b</i> (Å)	0.6586(23)	-0.6586(23)	Nonphysical ^c
<i>c</i> (Å)	0.5486(27)	0.5486(27)	±0.077(19)
Fit to moments of inertia			
<i>a</i> (Å)	1.6235	1.6235	-2.0854
<i>b</i> (Å)	0.6615	-0.6615	0.0000
<i>c</i> (Å)	0.5127	0.5127	0.0765

^aCostain errors in the parameters are given in parentheses.

^bNote that only the magnitudes of the substitution coordinates are given by a Kraitchman analysis. The signs are obtained by imposing physically reasonable bond lengths and interaction distance between the subunits.

^cThe coordinate is imaginary, 0.0057i(0.2629j), as is often the case for an atom with a vanishing (or nearly vanishing) coordinate.

substitution coordinates for the two C atoms are the same; the only possible differences are the signs. Furthermore, to give a reasonable C=C bond length in the complex, the two C atoms must have opposite signs for their *b* coordinates while those for the *a* coordinates and for the *c* coordinates must be the same. The length thus determined is 1.3172(33) Å, which agrees very well with the value of 1.323 Å for the *cis*-CHFCHF monomer. The location of the Ar atom is determined by recognizing that the *a* inertial axis for a van der Waals complex is approximately the axis connecting the two subunits; thus, Ar lies more or less on the *a* axis, so that the values of its *b* and *c* coordinates should be very nearly zero. Indeed, the value for the *b* substitution coordinate is nonphysical and imaginary and that for the *c* substitution coordinate is small. Furthermore, the *a* coordinate of Ar must have a different sign from those of the C atoms to satisfy the center of mass condition. This gives the distance of Ar from the center of mass, but does not specify its position with respect to the difluoroethylene subunit.

By simply reversing the roles of Ar-*cis*-1,2-difluoroethylene and *cis*-1,2-difluoroethylene in the Kraitchman analysis, we can determine the Ar position unambiguously in the principal axis system of the monomer. Taking *cis*-1,2-difluoroethylene as the parent, and the complex as containing a single substitution of ⁴⁰Ar for a hypothetical zero-mass atom, the resulting *a* coordinate for argon has a non-physical, imaginary value, suggesting that the actual *a* coordinate is zero. In other words, since the *a* axis of *cis*-1,2-difluoroethylene is parallel to the C=C bond, the argon atom is located in the plane bisecting this bond. The *c* coordinate (and its Costain uncertainty) is 2.99431(50) Å, which represents the distance of the argon atom out of the ethylene plane, and the *b* coordinate, representing the displacement of the argon atom from a position directly above the difluoroethylene center of mass to one either closer to or away from the fluorine atoms, is 1.58923(94) Å. The latter choice gives a Ar-C distance of 3.20 Å, 10.6% smaller than the sum of the van der Waals radii of the two atoms of 3.58 Å²⁵ and is thus an unlikely

structure. The only reasonable structure then agrees with that of the global minimum given by theory.

Using the substitution structure as a guide, we proceed to determine the structural parameters of the complex more precisely. Making the usual assumption that the structure of a subunit remains unchanged upon complexation and by restricting the Ar atom to the plane bisecting the C=C bond (that is, $\theta = 90^\circ$ in Fig. 2), only two parameters (*R* and ϕ) are necessary to characterize this complex. We fit these parameters to the three moments of inertia from each of the two isotopologues of Ar-*cis*-1,2-difluoroethylene, giving a rms deviation of 0.113 amu Å². Since the corresponding values of moments of inertia for the ground and excited tunneling states agree to within $1.4 \times 10^{-4}\%$ in each isotopologue, the structure of the complex is the same regardless whether it is derived from the ground or excited tunneling state: $R = 3.38950(40)$ Å and $\phi = 62.25(18)^\circ$. This structure gives a distance of 3.4735(35) Å between Ar and each F atom. These parameters can be compared with those predicted by *ab initio* theory in the lower and upper portions, respectively, of Fig. 1(b). The coordinates of the C atoms and the Ar atom derived from the fit are listed in Table VII; they agree well with the substitution coordinates and suggest that the positive sign is the correct choice for the *c* coordinate of Ar.

V. DISCUSSION

The experimentally determined tunneling splitting for Ar-*cis*-1,2-difluoroethylene is approximately 20 times that predicted using one-dimensional DVR calculations on the *ab initio* minimum energy path. These splittings, however, depend quite sensitively on the height and shape of the barrier to interconversion. One approach is a simple scaling of the *ab initio* result, and multiplying each point on the minimum energy path in Fig. 3 by 0.6926 (so that the barrier to interconversion is 78.26 cm⁻¹) results in a predicted splitting of 0.532 MHz, in agreement with experiment. Thus, it appears that at this level of theory, the energy of the planar configuration with the argon atom on the fluorine side of the difluoroethylene is overestimated. Alternatively, the width of the barrier is narrower than that predicted by theory, and indeed the experimental value of $\phi = 62.25^\circ$ is over 6° smaller than the (equilibrium) value from *ab initio* calculations.

Additionally, since the optimized value of *R* varies between 3.71 Å and 3.37 Å over the interval $\phi = 0^\circ$ to 70° , we considered the possibility of coupling between the angular and radial motions along the tunneling path as a contribution to this discrepancy. We performed two-dimensional DVR calculations in plane polar coordinates (see Appendix for a description of this method) using a grid of *ab initio* points calculated using GAUSSIAN 09¹⁴ at the MP2/6-311++G(2d,2p) level. For each value of $R = 2.5$ Å to 4.5 Å in 0.1 Å steps, the interaction potential between argon and *cis*-1,2-difluoroethylene was fit to a 15-term cosine series in ϕ as described earlier and used to generate the potential energy at 61 equally spaced angles on a (0, 2 π) interval. Using the unscaled *ab initio* potential in the 2D-DVR calculation predicts a tunneling splitting of 0.017 MHz, much less than the experimental value, but not so different from the 1D

calculation. Scaling the energy of each grid point by 0.6771 relative to the lowest energy point is necessary to obtain the experimental tunneling splitting of 0.532 MHz. It would appear that for Ar-*cis*-1,2-difluoroethylene, radial-angular coupling is a small effect, and that it is the shape of the *ab initio* potential that is responsible for the disagreement between the predicted and experimental splitting.

On the other hand, the experimental, average structure of Ar-*cis*-1,2-difluoroethylene agrees very well with the equilibrium structure determined theoretically. Specifically, the experimental value of the distance between Ar and the center of mass of *cis*-1,2-difluoroethylene differs from the theoretical value by only 0.7% (0.023 Å) and the difference is similarly 0.7% (0.025 Å) for the Ar-F distance. The values for the angle ϕ show a greater variation: the experimental value differs from the theoretical one by 9.0% (6.2°) as noted above in considering the shape of the barrier to interconversion. However, as this is also the coordinate most closely associated with that responsible for the large amplitude motion connecting the two equivalent configurations of the complex, it would be expected to be significantly affected by averaging over this motion.

It is useful to compare our results for Ar-*cis*-1,2-difluoroethylene with its other fluoroethylene counterparts. Ar-vinyl fluoride, Ar-1,1-difluoroethylene, and Ar-1,1,2-trifluoroethylene have previously been studied by Kisiel, Fowler, and Legon¹² Although all three of these species also have non-planar structures with two equivalent positions for the argon atom on either side of the fluoroethylene plane, only Ar-vinyl fluoride displays the splitting due to tunneling between the two configurations, as observed for Ar-*cis*-1,2-difluoroethylene in the present case. The projections of the argon atom position into the fluoroethylene plane for these complexes are shown in Fig. 5. As observed by Kisiel, Fowler,

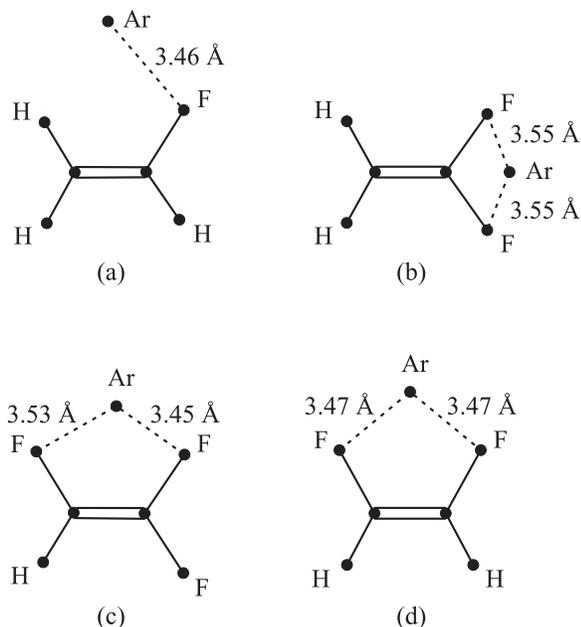


FIG. 5. The structures of (a) Ar-vinyl fluoride (Ref. 12), (b) Ar-1,1-difluoroethylene (Ref. 12), (c) Ar-1,1,2-trifluoroethylene (Ref. 12), and (d) Ar-*cis*-1,2-difluoroethylene (this work) with the position of Ar projected into each ethylene plane.

and Legon¹² Ar positions itself to maximize interactions with the largest number of preferably heavy atoms, which is also the case for Ar-*cis*-1,2-difluoroethylene. This also rationalizes the structure of Ar-1,1,2-trifluoroethylene, where binding in the XCCF cavity, as Kisiel *et al.* denote it,¹² allows for contact with four heavy atoms (FCCF), just as in Ar-*cis*-1,2-difluoroethylene, whereas the alternative, XCF binding location would only provide three (FCF). On the other hand for Ar-1,1-difluoroethylene, the XCCF cavity would supply HCCF for binding to the argon, but the observed XCF structure gives one carbon and two fluorine atoms. From Fig. 5, we note that the value for the Ar-F distance is strikingly similar for these complexes, ranging from 3.45 to 3.55 Å. Restricting the comparison to complexes where the argon atom binds in the XCCF cavity, or analogous to the “top” configuration in our description of complexes with protic acids,¹¹ the consistency is even more remarkable, varying only between 3.45 and 3.47 Å. Similar results were seen in our earlier report of the Ar-(*Z*)-1-chloro-2-fluoroethylene complex,²⁶ where once again the Ar binds to the XCCF cavity, maximizing interactions with preferably heavy atoms and having an Ar-F distance of 3.46 Å. The Ar-C distances are more variable among these species and are in the range of 3.56–3.95 Å for Ar-vinyl fluoride, Ar-1,1-difluoroethylene, and Ar-1,1,2-trifluoroethylene. The corresponding value for Ar-*cis*-1,2-difluoroethylene of 3.7345(14) Å falls near the middle of this range and is similar to the 3.77 Å distance obtained for Ar-(*Z*)-1-chloro-2-fluoroethylene.

VI. CONCLUSIONS

We have determined the structure of the gas-phase complex formed between *cis*-1,2-difluoroethylene and the argon atom. As predicted by *ab initio* calculations, this is a non-planar, symmetric species, with the argon atom located in the FCCF cavity. This is consistent with the suggestion of Kisiel, Fowler and Legon¹² that the observed structure will maximize the number of contacts of the argon atom with preferably heavy atoms. This structure corresponds to, and shows excellent agreement with, the lower of two minima found on the *ab initio* potential surface for the complex. On the other hand, a comparison of the experimentally observed tunneling splitting to that predicted by the DVR calculations suggests that the *ab initio* surface significantly overestimates the barrier to interconversion between the two equivalent configurations corresponding to the argon atom located on either side of the *cis*-1,2-difluoroethylene molecular plane.

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APPENDIX: 2-D DVR IN PLANE POLAR COORDINATES

In plane polar coordinates, (r, ϕ) , the Hamiltonian is typically written as

$$\hat{H} = -\frac{\hbar^2}{2m} \left[\left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right] + V(r, \phi), \quad (\text{A1})$$

but for DVR, the kinetic energy needs to have the form

$$r^{-1/2} \frac{\partial^2}{\partial r^2} r^{1/2} + f(r). \quad (\text{A2})$$

It can be shown that the choice $f(r) = 1/(4r^2)$ allows the Hamiltonian to be expressed as

$$\hat{H} = -\frac{\hbar^2}{2m} \left[\left(r^{-1/2} \frac{\partial^2}{\partial r^2} r^{1/2} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{1}{4r^2} \right] + V(r, \phi), \quad (\text{A3})$$

so that analogies to Eqs. (2.11)–(2.13) of Colbert and Miller¹⁵ may be used with the volume element $rdrd\phi$ to arrive at

$$H_{ik,i'k'} = T_{ii'}^r \delta_{kk'} + T_{kk'}^\phi \frac{\delta_{ii'}}{r_i^2} + \delta_{ii'} \delta_{kk'} \left[V(r_i, \phi_k) - \frac{\hbar^2}{8mr_i^2} \right], \quad (\text{A4})$$

where the kinetic energy matrix elements, $T_{ii'}^r$ and $T_{kk'}^\phi$, are taken from Eqs. (A8) and (A12), respectively, of Colbert and Miller.¹⁵ Alternatively, if an even number of angular grid points is desired, Eq. (2.11') of Meyer¹⁶ may be used. When applied to the large amplitude motion in Ar-*cis*-1,2-difluoroethylene, the effective mass for the radial motion is $\mu = m_{\text{Ar}} m_{\text{DFE}} / (m_{\text{Ar}} + m_{\text{DFE}})$, where m_{Ar} and m_{DFE} are the masses of the argon atom and the difluoroethylene molecule, respectively, and in the angular kinetic energy matrix element, the term $\hbar^2/2m$ is replaced by

$$F = A + \frac{16.8576 \text{ cm}^{-1} \text{ amu } \text{\AA}^2}{\mu R_i^2}, \quad (\text{A5})$$

where A is the moment of inertia of *cis*-1,2-difluoroethylene about its a inertial axis.

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