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Molecular Structures and Compositions of *trans*-1,2-Dichlorocyclohexane and *trans*-1,2-Difluorocyclohexane in the Gas Phase: An Electron-Diffraction Investigation

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The structures and compositions of gaseous *trans*-1,2-dichloro- (DCCH) and *trans*-1,2-difluorocyclohexane (DFCH), each of which may exist with the halogen atoms in a diaxial (aa) or diequatorial (ee) conformation, have been investigated by electron diffraction. The analysis was aided by rotational constants from microwave spectroscopy for the ee form of DFCH and by ab initio and density functional theory molecular orbital calculations for all species. The skeletons of the molecules have similar parameter values, but for the Cl–C–C–Cl and F–C–C–F fragments there are significant differences between the corresponding C–C–X bond angles and the X–C–C–X torsion angles in the two systems. There are also significant differences between the values of these parameters in the aa and ee forms of the same system. The composition of DCCH at 100 °C was measured to be 60(4)% aa, and that of DFCH at 70 °C was 42(7)% aa; the uncertainties are estimated 2 σ . From the preferred B3LYP/aug-cc-pVTZ calculations, the predicted theoretical composition is 51.2% aa for DCCH and 40.8% aa for DFCH. (Calculations at the levels B3LYP/6-31G(d) and MP2/6-31G(d) give similar results for DCCH, but both predict more aa than ee for DFCH.) Values ($r_g/\text{\AA}$ and \angle/degree) for some of the more important parameters of the aa/ee forms of DCCH are $\langle\text{C–C}\rangle = 1.525(4)/1.525(6)$, $\text{C–Cl} = 1.806(2)/1.787(2)$, $\angle\text{C}_2\text{–C}_1\text{–Cl} = 107.3(3)/111.5(3)$, $\angle\text{C}_1\text{–C}_2\text{–C}_3 = 113.9(5)/111.6(5)$, $\angle\text{C}_2\text{–C}_3\text{–C}_4 = 111.3(12)/109.9(12)$, and $\text{Cl–C}_2\text{–C}_3\text{–Cl} = 165.3(9)/\text{--}59.4(9)$; and for DFCH $\langle\text{C–C}\rangle = 1.525(6)/1.520(9)$, $\text{C–F} = 1.398(2)/1.390(2)$, $\angle\text{C}_2\text{–C}_1\text{–F} = 106.5(6)/109.2(6)$, $\angle\text{C}_1\text{–C}_2\text{–C}_3 = 111.4(9)/110.9(9)$, $\angle\text{C}_2\text{–C}_3\text{–C}_4 = 113.1(10)/113.1(10)$, and $\text{F–C}_2\text{–C}_3\text{–F} = 171.1(37)/\text{--}67.2(37)$. The structures and compositions are discussed.

Introduction

The *trans*-dihalocyclohexanes may exist as a pair of conformers that readily interconvert by pseudorotation of the carbon skeleton. These conformers are labeled aa or ee in accordance with whether both halogen bonds are axially or equatorially oriented as suggested by Figure 1 for the 1,2 compounds. (There also exist ae forms known as *cis* that cannot be converted to the *trans* forms except by breaking bonds.) A question of interest is the relative stabilities of the two components of the *trans* species. When the substituents are chlorine or bromine in the 1,4 positions, the more stable form is predicted to be aa according to molecular orbital theory.¹ The prediction has been confirmed in the case of 1,4-dichlorocyclohexane by a gas-phase electron-diffraction (GED) study² from which the vapors at 105 °C were found to be 54% (2 σ = 6%) aa, in good agreement with a range of 57–62% predicted from the ab initio and density functional theory (DFT) calculations.¹ In *trans*-1,4-difluorocyclohexane, the aa form is also predicted theoretically to be more stable relative to the ee than in the corresponding chlorine and bromine compounds, but we are not aware of any experimental work on the composition of the fluoro system.

The theoretical situation is similar for the *trans*-1,2-dihalocyclohexanes (i.e., the aa form is the more stable), but the energy

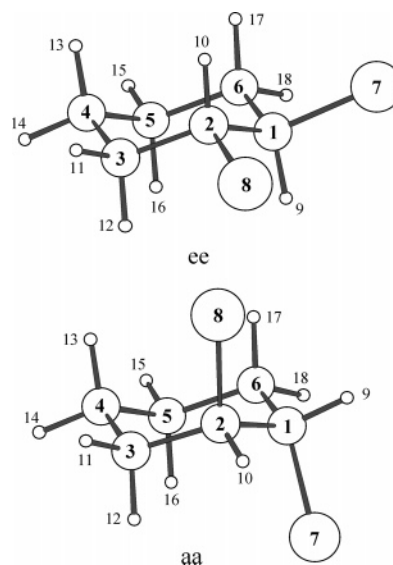


Figure 1. Diagrams of the two forms of the *trans*-1,2-dihalocyclohexanes with atom numbering.

difference in the case of *trans*-1,2-difluorocyclohexane is calculated to be much less than in *trans*-1,4-difluorocyclohexane, possibly because of the “gauche effect”.³ This effect operates in 1,2-difluoroethane, where the F–C–C–F moiety resembles that in 1,2-difluorocyclohexane, to make the gauche form much more stable than the anti. We felt that these circumstances

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merited a GED investigation of the *trans*-1,2-dichloro- and *trans*-1,2-difluorocyclohexanes. It was hoped that the results would help to settle the matter of the relative stabilities of the aa and ee forms from the experimental side. We recognized that the question might not be easy to answer because the two forms in each case are very similar in respect to their interatomic distance distributions and thus provide similar scattering patterns that could be difficult to sort out. Microwave (MW) spectroscopy of the two systems could provide additional data that might narrow the range of models for each that would otherwise be judged acceptable by electron-diffraction criteria alone. However, the amount of the samples of both compounds available for the GED experiments was limited, and at the start of that investigation it was not clear if enough would be left for MW studies. That turned out to be the case for the chloro compound. However, a very small amount of the DFCH sample remained and was sufficient to begin the MW work. A second very small sample was made available to us a bit later.

Experimental Section

Samples. *trans*-1,2-Dichlorocyclohexane (DCCCH) was obtained from Aldrich (99%) and used as received. The corresponding difluoro compound (DFCH) was prepared at the University of Florida according to the procedure of Visser et al.⁴ Into a 50-mL three-necked round-bottomed flask was added a mixture of anhydrous CH_2Cl_2 (20 mL) and cyclohexene (0.82 g, 10 mmol). The mixture was then cooled to -20°C , and 10% F_2 in N_2 , which was passed through a stainless steel tube filled with anhydrous NaF, was slowly bubbled through the mixture under vigorous stirring. When the reaction was finished (monitored by bubbling effluent through saturated NaI aqueous solution) the solvent was removed by distillation and pure *trans*-1,2-difluorocyclohexane (~ 225 mg, 19% yield) was obtained as a white solid by preparative gas chromatography (GC). The ^{19}F NMR spectrum of the product was consistent with that reported in the literature.⁵ The remnants of this material following the GED experiments together with a second sample kindly offered to us by Professor Kenneth Wiberg were used in the MW work.

Electron-Diffraction (GED) Intensity Data. The diffraction experiments were done with the Oregon State apparatus. The vapor temperatures, assumed equal to the nozzle-tip temperatures, were 100°C for DCCCH and 70°C for DFCH. Other experimental conditions were essentially the same for both molecules: r^3 sector; Kodak electron-image film developed for 10 min in D-19 developer diluted 1:1; nominal distances from nozzle tip to film, 750 mm for the "long camera" (LC) and 300 mm for the "middle camera" (MC); beam currents, $0.5\text{--}0.6\ \mu\text{A}$; exposure times, $0.5\text{--}3.0$ min; and 60 kV electron beam accelerating potential. The electron wavelength was calibrated in separate experiments against CO_2 assuming the distance values $r_a(\text{CO}) = 1.1646\ \text{\AA}$ and $r_a(\text{OO}) = 2.3244\ \text{\AA}$. For DCCCH, we selected five films each from the LC and MC distances and scanned each twice; for DFCH, the numbers were three films from each distance each scanned three times. The scans from the individual films were averaged to give 10 sets of scattered intensity data for DCCCH and six for DFCH. The procedures for obtaining the total scattered intensities ($s^4I_t(s)$) and the molecular intensities ($sI_m(s)$) from these data sets have been described in past articles.⁶ The working sets of LC and MC intensity data for each molecule spanned the ranges $2.00 \leq s/\text{\AA}^{-1} \leq 16.50$ and $8.00 \leq s/\text{\AA}^{-1} \leq 39.75$. Figure 2 shows curves of the intensity data for the fluorine compound. The curves for the chlorine compound are similar and may be found in the

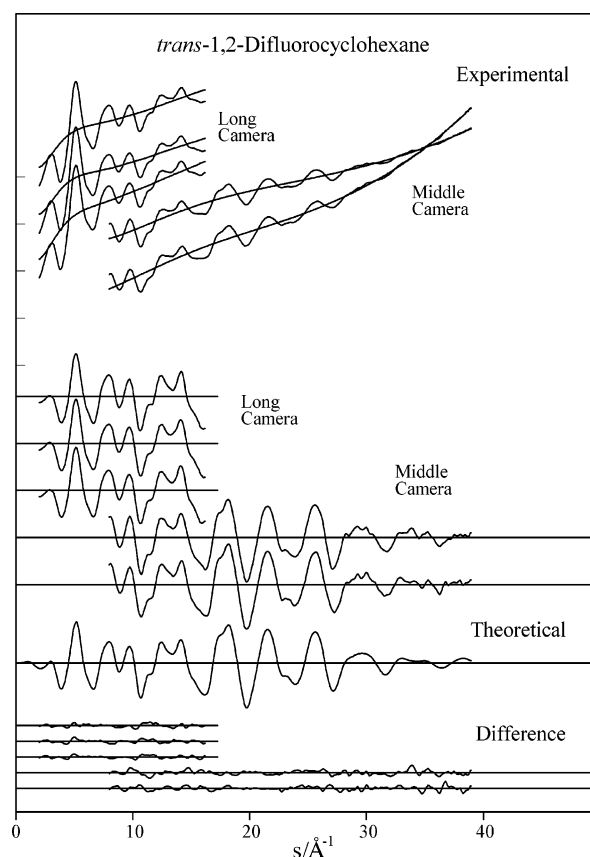


Figure 2. Intensity curves for *trans*-1,2-difluorocyclohexane. The curves on the rising backgrounds are in the form s^4I_{total} and have the molecular parts multiplied 10 times with respect to the backgrounds. The leveled curves below have had the backgrounds removed and were used in the refinements; they are in the form $sI_m(s)$. The difference curves are experimental minus theoretical for the final model shown in Tables 2 and 4.

Supporting Information together with the data themselves for both compounds.

Experimental radial distribution curves are shown in Figures 3 and 4. They were calculated from composites of the LC and MC intensities in the form $sI_m(s)$ after multiplication by $(s^2Z_c/F_c)^2 \exp(-0.002s^2)$, where F_c is the electron-scattering amplitude of carbon. These amplitudes and other quantities used in various calculations were taken from tables.⁷

MW Data. The MW experiments on DFCH were done with the two samples described above. The microwave spectrum was observed in the range 10–18 GHz with the Southern New England Microwave Consortium's pulsed-jet Fourier Transform spectrometer.⁸ About 50 mg of sample was evaporated into a bulb and first-run neon ($\sim 75\%$ Ne, $\sim 25\%$ He) added to 2 atm pressure to yield a mixture containing about 0.15% sample. The nozzle pulsed at 5 Hz. Line widths in the power spectrum were about 20 kHz, and the uncertainties in the reported frequencies are estimated to be less than 2 kHz. Only the equatorial–equatorial conformer was found.

Theoretical Calculations. The radial distribution curves for DCCCH and DFCH from the GED data show eight or nine resolved peaks, due in most cases to the combined effect of several interatomic distances. Even with reasonable assumptions and approximations, such as C_2 symmetry for the molecules and equivalence for all the C–H bond distances and H–C–H bond angles, over a dozen parameters are required to specify the distances in each of the two conformers present in the vapors of each system. Further, there are a host of vibrational amplitude

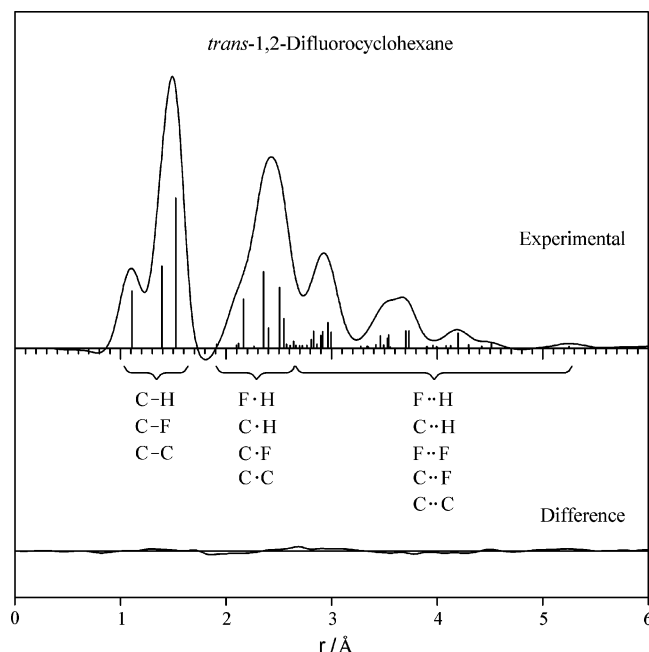


Figure 3. Radial distribution curves for *trans*-1,2-difluorocyclohexane. The vertical lines show the positions of the more important interatomic distances and have lengths proportional to their weights. The damping factor B was equal to 0.0020s².

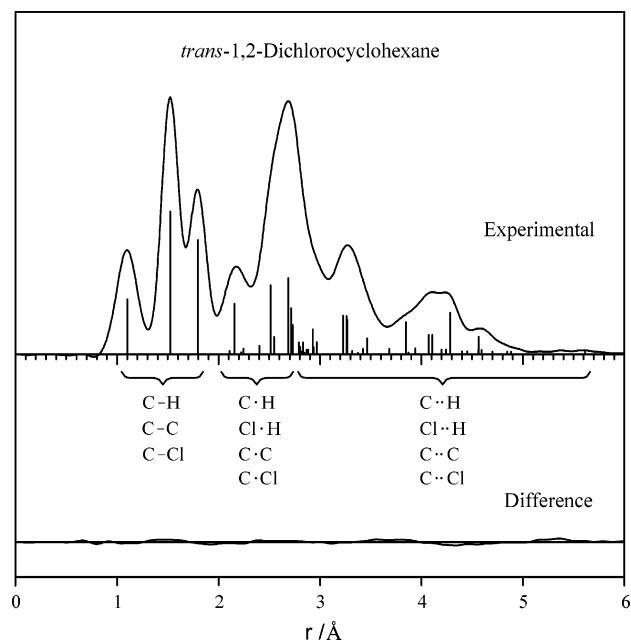


Figure 4. Radial distribution curves for *trans*-1,2-dichlorocyclohexane. See legend to Figure 3.

parameters of which account must be taken to arrive at satisfactory models of the structures, and the projected use of the B_0 rotational constants requires estimates of the differences between the ground-state type of distance reflected by these constants and the thermal average ones obtained from GED. These circumstances require that additional simplifying assumptions be made, and for that purpose, we turned to molecular orbital and normal coordinate calculations. The former provide information about parameter values that cannot be measured, such as the differences between bond lengths that are too similar to be resolved, and the latter provide estimates of vibrational amplitudes and the needed distance differences mentioned above.

Our molecular orbital calculations were carried out with the programs G98W and G03W at the HF and B3LYP levels with

several basis sets. Since we were interested in the *differences* between certain geometrical parameter values, and those between certain vibrational amplitudes, neither of which are as sensitive to deficiencies in the theory as the values themselves, we deemed the results of the B3LYP/6-31G(d) calculations to be satisfactory for our purposes.

The normal coordinate calculations were done with the program ASYM40⁹ based on symmetrized internal coordinates that made use of the Cartesian force fields derived from the B3LYP/6-31G(d) calculations. In addition to the amplitudes mentioned above, the normal coordinate results included the quantities necessary for interconversion of distance types that provide the basis for incorporation of the rotational constants from MW spectroscopy. The relation between these distance types as well as the distances themselves are seen in the tables of structural results presented later.

Structure Analyses

Models. Models of the structures for the DCCH and DFCH systems require specification of a large number geometrical parameters. The main reasons are that each system consists of two conformers that have very similar but not identical bond lengths and bond angles and that many of the same quantities *within* each conformer are also similar but not identical. These conditions make the structure analyses impossible without several simplifying assumptions. Those we adopted were identical for each system and include C_2 symmetry for each species, equivalent C–H bond lengths and H–C–H bond angles for each system, and bisection of each C–C(H)–C plane by its H–C–H plane. There is no doubt about the validity of the symmetry assumption which is confirmed both by the theoretical and MW results (described below), and whatever variation might exist in the C–H bond lengths or H–C–H angles should have only a negligible effect on the values derived for the more important parameters. The other assumptions were all drawn from the results of the molecular orbital calculations obtained at the B3LYP/6-31G(d) level. The most important among these was the specification of the aa form in terms of the ee by invoking the distance and angle differences obtained from theory. The simplification obtained by this procedure was an evaluation of the structure of each system, and its composition, via refinement of only the parameters of the ee form and its mole fraction. The list of geometrical parameters for the ee forms were as follows (the atom numbering is shown in Figure 1): $r(\text{C–H})$; $r(\text{C–X})$; $r(\text{C}_1\text{–C}_2)$; $\Delta r(\text{C}_2\text{–C}_3) = r(\text{C}_1\text{–C}_2) - r(\text{C}_2\text{–C}_3)$; $\Delta r(\text{C}_3\text{–C}_4) = r(\text{C}_1\text{–C}_2) - r(\text{C}_3\text{–C}_4)$; $\angle(\text{H–C–H})$; $\angle(\text{C}_2\text{–C}_1\text{–H}_9)$; $\angle(\text{C}_1\text{–C}_2\text{–X})$; $\angle(\text{C}_1\text{–C}_2\text{–C}_3)$; $\angle(\text{C}_2\text{–C}_3\text{–C}_4)$; $\angle(\text{C}_6\text{–C}_1\text{–C}_2\text{–C}_3)$; $\angle(\text{C}_1\text{–C}_2\text{–C}_3\text{–C}_4)$; $\angle(\text{X–C–C–X})$; $\angle(\text{H}_9\text{–C}_1\text{–C}_2\text{–H}_{10})$; and X , the mole fraction. The aa parameter values, in angstroms for distances and degrees for angles, were tied to the ee by the following differences (ee – aa). For DCCH/DFCH, $\Delta[r(\text{C–H})] = 0.0009/0.0009$; $\Delta[r(\text{C–X})] = 0.0196/-0.0088$; $\Delta[\langle r(\text{C–C}) \rangle] = 0.0006/-0.0009$; $\Delta[\Delta r(\text{C}_1\text{–C}_2)] = 0.0072/0.0104$; $\Delta[\Delta r(\text{C}_2\text{–C}_3)] = -0.0051/-0.0045$; $\Delta[\Delta r(\text{C}_4\text{–C}_5)] = -0.0005/0.0003$; $\Delta[\angle(\text{H–C–H})] = 0.53/-0.44$; $\Delta[\angle(\text{C}_2\text{–C}_1\text{–H}_9)] = -0.63/-1.19$; $\Delta[\angle(\text{C}_1\text{–C}_2\text{–X})] = 4.14/2.61$; $\Delta[\angle(\text{C}_1\text{–C}_2\text{–C}_3)] = -2.26/-0.52$; $\Delta[\angle(\text{C}_2\text{–C}_3\text{–C}_4)] = -1.40/0.01$; $\Delta[\angle(\text{C}_6\text{–C}_1\text{–C}_2\text{–C}_3)] = 7.99/1.35$; $\Delta[\angle(\text{C}_1\text{–C}_2\text{–C}_3\text{–C}_4)] = -6.25/-1.29$; $\Delta[\angle(\text{X–C–C–X})] = -224.65/-238.34$; and $\Delta[\angle(\text{H}_9\text{–C}_1\text{–C}_2\text{–H}_{10})] = 232.05/226.85$. (The dihedral angles are positive if the forward group is rotated counterclockwise from the eclipsed position.) Account was taken for vibrational anharmonicity in the bonds by inclusion of the usual terms $at^4s^2/6$ in the intensity function with a assumed equal to 2.0

TABLE 1: Rotational Assignment,^a Rotational Constants, and Centrifugal Distortion Constants of *trans*-ee-1,2-DFCH

<i>N</i>	<i>J'</i>	<i>K_p'</i>	<i>K_o'</i>	<i>J''</i>	<i>K_p''</i>	<i>K_o''</i>	freq _{obs} /MHz	obsd – calcd/MHz
1	2	1	2	1	1	1	5576.6897	–0.0016
2	2	1	1	1	1	0	7005.1294	–0.0001
3	3	0	3	2	0	2	8439.5309	0.0011
4	4	0	4	3	0	3	10806.0421	0.0001
5	4	1	4	3	1	3	10713.0302	0.0006
6	4	1	3	3	1	2	13071.5000	0.0008
7	4	2	3	3	2	2	12322.6797	0.0000
8	4	2	2	3	2	1	14072.8902	–0.0002
9	4	3	2	3	3	1	13021.2429	–0.0001
10	4	3	1	3	3	0	13520.2401	0.0007
11	5	0	5	4	0	4	13202.4205	–0.0003
12	5	1	5	4	1	4	13174.7459	0.0001
13	5	1	4	4	1	3	15500.5073	–0.0009
14	5	2	4	4	2	3	15035.0252	0.0006
15	5	2	3	4	2	2	17378.5902	0.0000
16	5	3	3	4	3	2	16169.2087	–0.0017
17	5	3	2	4	3	1	17409.4730	0.0019
18	5	4	2	4	4	1	16418.6990	–0.0013
19	5	4	1	4	4	0	16599.5762	–0.0007
20	6	0	6	5	0	5	15621.8551	–0.0002
21	6	1	6	5	1	5	15614.6042	0.0002
22	6	1	5	5	1	4	17806.5696	0.0007
<i>A</i> /MHz							2701.0809(6) ^b	
<i>B</i> /MHz							1929.87597(24)	
<i>C</i> /MHz							1215.50543(15)	
<i>D_J</i> /kHz							0.0892(21)	
<i>d₁</i> /kHz							–0.0316(17)	
<i>κ</i>							–0.03838	
rmsd/kHz							0.928	

^a The spectrum was fit with an S-reduction Hamiltonian in the III-r representation. ^b Numbers in parentheses are one standard deviation in the last digit.

Å^{–1}. Possible nonbond anharmonicity was ignored. Each system model contained slightly more than 100 interatomic distances and included all interactions except those of type H···H.

MW Results. The molecular orbital and preliminary GED studies provided accurate molecular models to predict rotational

spectra of the polar ee and the rather nonpolar aa conformer of DFCH. The ee form has *C*₂ symmetry, and the dipole moment is directed along the molecule's a principal axis. Strong a-type lines were readily observed close to the predicted frequencies. The assignments and analysis are summarized in Table 1 together with the values of the A, B, and C rotational constants, the asymmetry parameter *κ*, and the centrifugal distortion constants *D_J* and *d₁*.

Electron-Diffraction Results. The GED structure refinements were carried out with our usual least-squares method,¹⁰ which fits theoretical molecular intensities in the form *sI_M(s)*¹¹ to the observed intensities, and theoretical values of rotational constants to the observed ones if available, by adjustment of the model parameters. The fitting was done simultaneously on all data sets, i.e., the 10 sets derived by subtracting the backgrounds from the curves of Figures 2 and 3. Because the MW rotational constants were being included as auxiliary data for the ee form of DFCH, both its structure and that of the aa form were specified by the distance type *r_α*^o, which provides a common meeting ground for the otherwise different distance types implicit in the MW and GED data.¹² Without rotational constants for DCCH it was convenient to specify the structures of its components in *r_α* space. With use of the harmonic corrections to the *α* values obtained from the theoretical force fields, the observed *B₀* values for the ee form of DFCH were converted to *B_z* values for the fitting process. The corrections *B_z* – *B₀* in MHz are, respectively, equal to 0.030, –0.070, and 0.120 for A, B, and C.

Preliminary refinements revealed that the difference parameters Δ*r*(*C*₁–*C*₂), Δ*r*(*C*₂–*C*₃), and Δ*r*(*C*₃–*C*₄) were highly correlated with other parameters and could not be refined. For DCCH they were, respectively, given the theoretical values of 0.0046, –0.0007, and –0.0022 Å, and for DFCH 0.0103, 0.0038, and –0.0057 Å. The preliminary refinements also suggested that the H–C–H angle be refined subject to a predicate

TABLE 2: Experimental (*r_α*/Å, *r_α*^o/Å) and Theoretical (*r_e*/Å) Distances and Angles (∠/degree) in DCCH and DFCH

parameters	DCCH ^a				DFCH ^a			
	ee		aa		ee		aa	
	<i>r_α</i>	<i>r_e</i>	<i>r_α</i>	<i>r_e</i>	<i>r_α</i> ^o	<i>r_e</i>	<i>r_α</i> ^o	<i>r_e</i>
Structure-Defining								
<i>r</i> (C–H)	1.090(3)	1.096	1.089(3)	1.095	1.106(3)	1.098	1.105(3)	1.097
<i>r</i> (C ₁ –C ₂)	1.516(5)	1.530	1.523(5)	1.536	1.512(6)	1.520	1.523(6)	1.532
Δ <i>r</i> (C ₂ –C ₃)	[–0.005]	–0.005	[0.007]	0.007	[–0.006]	–0.006	[0.008]	0.008
Δ <i>r</i> (C ₃ –C ₄)	[–0.007]	–0.007	[0.001]	0.001	[–0.016]	–0.016	[–0.005]	–0.005
<i>r</i> (C–X)	1.780(2)	1.825	1.800(1)	1.845	1.386(2)	1.396	1.395(2)	1.405
∠(H–C–H)	107.5(32)	106.7	107.6(32)	106.8	105.2(44)	106.6	105.6(44)	107.1
∠C ₂ –C ₁ –H ₉	103(11)	109.4	104(11)	110.0	108(17)	108.6	109(17)	109.8
∠C ₂ –C ₁ –X	111.5(3)	111.4	107.3(3)	107.2	109.2(6)	109.0	106.5(6)	106.4
∠C ₁ –C ₂ –C ₃	111.6(5)	111.1	113.9(5)	113.4	110.9(9)	111.7	111.4(9)	112.2
∠C ₂ –C ₃ –C ₄	109.9(12)	111.6	111.3(12)	113.0	113.1(10)	111.6	113.1(10)	111.6
∠C ₆ –C ₁ –C ₂ –C ₃	56.6(21)	54.8	48.6(21)	46.9	53.9(25)	54.5	52.6(25)	53.1
∠C ₁ –C ₂ –C ₃ –C ₄	–55.9(10)	–55.4	–49.7(10)	–49.2	–55.3(14)	–54.7	–54.1(14)	–53.5
∠X–C–C–X	–59.4(9)	–62.1	165.3(9)	162.5	–67.2(37)	–64.4	171.1(37)	173.9
∠H ₉ –C ₁ –C ₂ –H ₁₀	170(42)	169.6	–62(42)	–62.5	181(15)	168.8	–46(15)	–58.1
χ ^b	0.40(4)		0.60(4)		0.58(7)		0.42(7)	
<i>R</i> ^c	0.107				0.081			
Calculated								
<i>r</i> (C ₂ –C ₃)	1.522(5)	1.535	1.516(5)	1.529	1.518(6)	1.527	1.515(6)	1.523
<i>r</i> (C ₃ –C ₄)	1.523(5)	1.537	1.522(5)	1.536	1.528(6)	1.536	1.529(6)	1.537
<i>r</i> (C ₄ –C ₅)	1.526(27)	1.533	1.522(28)	1.537	1.531(32)	1.537	1.532(32)	1.537
∠C ₂ –C ₃ –H ₁₁	109.9(9)	109.6	109.5(9)	109.2	109.6(11)	109.6	109.5(11)	109.5
∠C ₃ –C ₄ –H ₁₃	109.5(8)	109.8	109.3(8)	109.6	110.3(9)	109.8	110.1(9)	109.6
∠C ₃ –C ₄ –C ₅	111.2(14)	110.8	112.0(15)	111.4	110.3(12)	111.0	110.5(13)	111.3
∠H ₉ –C ₁ –X ₇	107(23)	105.2	107.5(15)	104.0	114(14)	107.3	101.3(59)	107.4
∠C ₂ –C ₃ –C ₄ –C ₅	56.2(18)	55.9	53.7(18)	53.4	55.3(19)	55.0	54.9(18)	54.5
∠C ₃ –C ₄ –C ₅ –C ₆	–57.3(23)	–55.8	–56.5(23)	–55.1	–53.9(33)	–54.9	–54.1(33)	–55.0

^a Uncertainties (in parentheses) are 2σ and contain estimates of correlation and systematic errors. Quantities in square brackets were assumed. Experimental values for the aa forms are tied to the ee forms via ab initio differences (B3LYP/6-31G*). ^b Mole fraction. ^c Goodness of fit factor: *R* = [Σ*w_i*Δ_{*i*}²/Σ*w_i*(*s_i*Δ_{*i*}(obsd))²]^{1/2}, where Δ_{*i*} = *s_i*Δ_{*i*}(obsd) – *s_i*Δ_{*i*}(calc.).

TABLE 3: Distances ($r/\text{\AA}$) and rms Amplitudes ($l/\text{\AA}$) for DCCH^a

distance	ee ^b						aa ^b					
	exptl				theor ^c		exptl				theor ^c	
	r_a	r_g	r_a	l	r_e	l	r_a	r_g	r_a	l	r_e	l
C ₁ –H ₉	1.090	1.107(3)	1.101	0.077(4)	1.096	0.077	1.089	1.104(3)	1.099	0.077	1.095	0.077
C ₁ –Cl ₇	1.780	1.787(2)	1.785	0.056(3)	1.825	0.056	1.800	1.806(2)	1.804	0.058	1.845	0.058
C ₁ –C ₂	1.516	1.520(6)	1.517	0.056	1.530	0.053	1.523	1.526(6)	1.524	0.056	1.536	0.053
C ₁ –C ₆	1.522	1.528(6)	1.526	0.056	1.535	0.053	1.516	1.520(6)	1.518	0.056	1.529	0.052
C ₃ –C ₄	1.523	1.531(6)	1.529	0.056	1.537	0.052	1.522	1.528(6)	1.526	0.056	1.536	0.052
C ₄ –C ₅	1.526	1.538(27)	1.536	0.055	1.533	0.052	1.522	1.530(28)	1.528	0.056	1.537	0.052
Cl ₇ –H ₉	2.343	2.36(32)	2.351	0.106	2.363	0.109	2.367	2.38(21)	2.374	0.106	2.363	0.110
C ₁ –H ₁₇	2.152	2.170(13)	2.165	0.103	2.165	0.107	2.142	2.155(13)	2.149	0.105	2.154	0.109
C ₁ –H ₁₀	2.062	2.07(15)	2.067	0.102	2.158	0.106	2.076	2.08(15)	2.079	0.101	2.171	0.105
C ₁ –H ₁₈	2.152	2.170(13)	2.166	0.103	2.165	0.106	2.142	2.155(13)	2.150	0.102	2.154	0.106
C ₄ –H ₁₆	2.152	2.177(27)	2.172	0.104	2.166	0.107	2.145	2.163(29)	2.158	0.103	2.166	0.107
C ₃ –H ₁₄	2.149	2.166(10)	2.161	0.104	2.169	0.107	2.145	2.160(9)	2.155	0.103	2.165	0.107
C ₃ –H ₁₃	2.149	2.171(10)	2.166	0.103	2.169	0.107	2.145	2.161(9)	2.156	0.103	2.165	0.107
C ₄ –H ₁₂	2.153	2.173(13)	2.168	0.104	2.166	0.107	2.147	2.163(13)	2.158	0.104	2.160	0.107
C ₃ –H ₁₀	2.207	2.22(15)	2.215	0.103	2.180	0.107	2.197	2.21(27)	2.202	0.102	2.181	0.105
C ₄ –H ₁₅	2.152	2.175(27)	2.170	0.103	2.166	0.107	2.145	2.162(29)	2.157	0.103	2.166	0.107
C ₄ –H ₁₁	2.153	2.171(13)	2.166	0.103	2.166	0.107	2.147	2.162(13)	2.157	0.103	2.160	0.107
C ₁ –Cl ₈	2.729	2.733(5)	2.731	0.078	2.776	0.076	2.682	2.687(5)	2.684	0.081	2.728	0.079
C ₃ –Cl ₈	2.691	2.699(16)	2.697	0.077	2.738	0.076	2.717	2.723(20)	2.720	0.079	2.777	0.078
C ₁ –C ₃	2.513	2.518(14)	2.516	0.075	2.528	0.073	2.547	2.550(14)	2.548	0.069	2.562	0.067
C ₁ –C ₅	2.492	2.497(14)	2.495	0.074	2.541	0.073	2.508	2.513(13)	2.511	0.069	2.556	0.068
C ₃ –C ₅	2.516	2.525(17)	2.523	0.072	2.527	0.071	2.523	2.529(12)	2.527	0.073	2.538	0.071
Cl ₇ –H ₁₀	2.779	2.790(10)	2.777	0.169	2.904	0.167	2.684	2.69(10)	2.683	0.159	2.807	0.158
Cl ₇ –H ₁₇	2.859	2.875(20)	2.865	0.166	2.883	0.164	3.676	3.687(17)	3.684	0.106	3.737	0.105
Cl ₇ –H ₁₈	2.869	2.888(19)	2.880	0.153	2.911	0.151	2.810	2.821(34)	2.811	0.167	2.865	0.165
Cl ₇ –Cl ₈	3.263	3.269(10)	3.266	0.095(13)	3.355	0.125	4.284	4.286(9)	4.285	0.074	4.365	0.082
C ₃ –C ₆	2.958	2.967(34)	2.965	0.083	2.948	0.076	2.977	2.981(33)	2.978	0.082	2.969	0.075
C ₁ –C ₄	2.920	2.925(14)	2.923	0.082	2.967	0.076	2.933	2.937(14)	2.935	0.081	2.981	0.074
C ₃ –Cl ₇	3.938	3.954(33)	3.951	0.100	4.166	0.075	3.942	3.951(32)	3.949	0.099	3.325	0.129
C ₄ –Cl ₈	3.906	3.918(20)	3.916	0.099	4.147	0.076	3.922	3.932(20)	3.930	0.097	3.332	0.133
C ₄ –Cl ₇	4.565	4.567(15)	4.565	0.094(12)	4.643	0.091	3.842	3.847(22)	3.842	0.138	3.942	0.135

^a Amplitudes in curly brackets were refined as a group. ^b Structure of the aa form tied to the ee via ab initio differences (B3LYP/6-31G*). ^c Values of r_e are from B3LYP/6-31G* calculation; values of l are from normal coordinate calculations at the temperature of the experiment based on the B3LYP/6-31G* force field. l values of the aa form were tied to those of the ee by the theoretical (B3LYP/6-31G*) and ASYM40) differences; uncertainties for the two forms are identical.

restraint,¹³ which was assigned the value 109.1°. The vibrational amplitude parameters were handled in the usual way by refining them in groups. The differences between group members were taken from the theoretical amplitude values obtained from the normal coordinate calculations. Under the conditions specified above the final refinements led to the geometries summarized in Table 2. Tables 3 and 4 contain all of the important interatomic distances and the vibrational amplitudes for both systems. The correlation matrixes for the refined parameters of the ee forms of both molecules are found in the Supplementary Information.

Discussion

The agreement between the final models for each molecular system and the experimental data is good. This is most easily seen in the difference curves found in Figures 2–4 and S1, and in the small differences between the observed rotational constants (B_z) and those calculated for the ee form of the difluoride found in Table 5. The quality of the agreement with experiment inspires confidence in the values of the parameters listed in Table 2, most of which were obtained without structural constraints. In particular, the experimental values listed as *averages* in this table should be accurate because average parameters are not strongly correlated with small differences between their components. However, the values of the individual distances listed in Tables 3 and 4 must be looked at with a bit more caution; since the values that make up each average have been constrained to the differences calculated from theory, their

reliability hinges on the accuracy of these theoretical differences. We find these differences calculated with use of the basis sets 6-31G* and the much larger cc-aug-pVTZ differ by only 0.001–0.002 Å; thus we believe their reliability is better than the uncertainties given for the individual distances in Tables 3 and 4.

With these matters in mind, several points may be made. First, for each of the two systems most of the experimental bond lengths (r_g , for example, Tables 3 and 4) appear to be a few thousandths of an angstrom shorter than predicted by B3LYP/6-31G* theory (r_e). This is contrary to expectation since the experimental values reflect the thermal effects of vibrational averaging and the theoretical ones do not. We have carried out a few tests which show that the phenomenon is in good part due to the size of the basis set: for example, the experiment minus theory differences are only about one-third as large for calculations carried out at the B3LYP/cc-aug-pVTZ level as for the B3LYP/6-31G*.¹⁴ Second, the structures of the carbon skeletons of the ee forms of DCCH and DFCH are quite similar, as are those of the aa forms (Table 2). There are significant differences, however, in the values of the bond angles C₂–C₁–X, which are larger for the ee form than the aa of each substance. Further, this angle in both the ee and aa forms of DCCH is larger than its counterparts in DFCH. There are also significant differences in the torsion angles X–C–C–X: they are 6–8° larger in both forms of DFCH than in their DCCH counterparts. All of these observations are consistent with the relative bond polarity C–F > C–Cl that tends to push the fluorine atoms

TABLE 4: Distances ($r/\text{\AA}$) and rms Amplitudes ($l/\text{\AA}$) for DFCH^a

distance	ee ^b						aa ^b					
	exptl				theor ^c		exptl				theor ^c	
	r_α	r_g	r_a	l	r_c	l	r_α	r_g	r_a	l	r_c	l
C ₁ –H ₉	1.106	1.114(3)	1.108	0.083(4)	1.098	0.077	1.10 5	1.113(3)	1.107	0.083	1.097	0.077
C ₁ –F ₇	1.386	1.390(2)	1.388	0.055	1.396	0.047	1.39 5	1.398(2)	1.396	0.055	1.405	0.047
C ₁ –C ₂	1.512	1.513(6)	1.511	0.058	1.520	0.051	1.52 3	1.525(6)	1.522	0.058	1.532	0.051
C ₁ –C ₆	1.518	1.521(6)	1.519	0.058	1.527	0.051	1.51 5	1.517(6)	1.515	0.058	1.523	0.051
C ₃ –C ₄	1.528	1.531(6)	1.529	0.058	1.536	0.052	1.52 9	1.531(6)	1.529	0.058	1.537	0.052
C ₄ –C ₅	1.531	1.535(32)	1.533	0.058	1.537	0.052	1.532	1.535(32)	1.533	0.058	1.537	0.052
F ₇ –H ₉	2.092	2.100(17)	2.094	0.104	2.016	0.100	1.942	1.949(81)	1.943	0.105	2.025	0.100
C ₁ –H ₁₇	2.157	2.165(18)	2.159	0.112	2.159	0.107	2.152	2.159(18)	2.153	0.113	2.154	0.109
C ₁ –H ₁₀	2.130	2.140(23)	2.129	0.111	2.141	0.107	2.155	2.160(22)	2.154	0.110	2.165	0.106
C ₁ –H ₁₈	2.157	2.165(18)	2.159	0.111	2.159	0.106	2.152	2.159(18)	2.153	0.111	2.154	0.107
C ₄ –H ₁₆	2.178	2.187(24)	2.182	0.111	2.170	0.107	2.176	2.184(24)	2.179	0.111	2.167	0.107
C ₃ –H ₁₄	2.175	2.183(14)	2.178	0.111	2.170	0.106	2.173	2.180(14)	2.175	0.111	2.167	0.106
C ₃ –H ₁₃	2.175	2.184(14)	2.178	0.111	2.170	0.107	2.173	2.181(14)	2.175	0.111	2.167	0.107
C ₄ –H ₁₂	2.165	2.174(18)	2.168	0.112	2.168	0.107	2.164	2.172(18)	2.166	0.111	2.166	0.107
C ₃ –H ₁₀	2.121	2.127(94)	2.121	0.110	2.178	0.106	2.243	2.25(18)	2.244	0.109	2.177	0.104
C ₄ –H ₁₅	2.178	2.187(24)	2.181	0.111	2.170	0.107	2.176	2.184(24)	2.178	0.111	2.167	0.107
C ₄ –H ₁₁	2.165	2.174(18)	2.168	0.111	2.168	0.107	2.164	2.172(18)	2.166	0.110	2.166	0.106
C ₁ –F ₈	2.363	2.365(5)	2.363	0.070	2.376	0.069	2.340	2.343(6)	2.340	0.072	2.353	0.071
C ₃ –F ₈	2.357	2.361(15)	2.359	0.070	2.381	0.069	2.393	2.397(38)	2.395	0.070	2.391	0.069
C ₁ –C ₃	2.496	2.498(14)	2.496	0.071	2.522	0.070	2.510	2.511(14)	2.510	0.068	2.536	0.067
C ₁ –C ₅	2.542	2.544(19)	2.542	0.073	2.534	0.072	2.539	2.541(19)	2.539	0.069	2.531	0.068
C ₃ –C ₅	2.510	2.513(13)	2.511	0.070	2.533	0.070	2.515	2.518(12)	2.516	0.070	2.538	0.070
F ₇ –H ₁₀	2.575	2.58(25)	2.571	0.157	2.560	0.157	2.607	2.61(24)	2.602	0.155	2.588	0.155
F ₇ –H ₁₇	2.562	2.570(31)	2.560	0.160	2.592	0.160	3.336	3.342(30)	3.339	0.100	3.332	0.100
F ₇ –H ₁₈	2.637	2.646(21)	2.638	0.146	2.664	0.146	2.644	2.650(64)	2.640	0.160	2.624	0.160
F ₇ –F ₈	2.822	2.826(29)	2.815	0.183(46)	2.809	0.119	3.532	3.534(12)	3.534	0.056	3.558	0.066
C ₃ –C ₆	2.897	2.899(26)	2.897	0.080	2.951	0.076	2.912	2.913(26)	2.911	0.076	2.966	0.073
C ₁ –C ₄	2.962	2.964(14)	2.962	0.078	2.959	0.074	2.963	2.965(14)	2.963	0.076	2.960	0.073
C ₃ –F ₇	3.702	3.704(11)	3.702	0.074	3.940	0.110	2.914	2.917(27)	2.911	0.134	3.949	0.109
C ₄ –F ₈	3.731	3.733(6)	3.732	0.074	3.949	0.108	2.979	2.982(63)	2.976	0.134	3.949	0.107
C ₄ –F ₇	4.197	4.198(14)	4.196	0.100(12)	4.213	0.083	3.536	3.539(36)	3.532	0.150	3.516	0.133

^a Amplitudes in curly brackets were refined as a group. ^b Structure of the aa form tied to the ee via ab initio differences (B3LYP/6-31G*). ^c Values of r_c are from B3LYP/6-31G* calculation; values of l are from normal coordinate calculations at the temperature of the experiment based on the B3LYP/6-31G* force field. l values of the aa form were tied to those of the ee by the theoretical (B3LYP/6-31G* and ASYM40) differences; uncertainties for the two forms are identical.

TABLE 5: Rotational Constants/MHz for ee Form of DFCH

obsd		calcd ^a	difference
B_0	B_z	B_z	$B_z^{\text{obsd}} - B_z^{\text{calcd}}$
1215.506	1215.536	1216.388	−0.852
1929.876	1929.806	1930.548	−0.742
2701.281	2701.401	2701.687	−0.286

^a From parameters of ee form (Table 2).

further apart. The bond angles and torsion angles in the fragments X–C–C–X suggest comparisons with 1,2-dichloroethane and 1,2-difluoroethane, each of which exists as a mixture of gauche and anti forms. The dominant species in 1,2-dichloroethane is the anti (about 70% at 100 °C — the temperature of our DCCH experiments),¹⁵ similar to the aa form

in our systems, and in 1,2-difluoroethane it is the gauche (90% at 70 °C),¹⁶ similar to the ee form. In 1,2-dichloroethane, the average anti-gauche C–C–Cl angle at 100 °C was found to be 108.8(2)°, which is in good agreement with the corresponding average of 109.4(3)° in DCCH. However, the C–C–Cl angles of the anti and gauche forms were assumed to be the same in the dichloroethane work so that anti-aa and gauche-ee comparisons are not possible. A similar assumption was made in the 1,2-difluoroethane investigation, but because the sample consists almost entirely of the gauche form the average angle of about 110.3(1)° is actually a good estimate of the gauche value itself. It is in good agreement with the value (109.2(6)°) in DFCH. The torsion angles X–C–C–X are about 15° larger in the dihaloethanes than in the corresponding dihalocyclohexanes, probably as a result of ring constraints in the latter.

TABLE 6: Theoretical Compositions Predicted for DCCH and DCFH^a

	B3LYP/6-31G(d)		B3LYP/aug-cc-pVTZ		MP2/6-31G(d)	
	aa	ee	aa	ee	aa	ee
DCCH						
$E/h + 1153.0$	−2.075352	−2.074538	−2.235467	−2.234800	−0.061333	−0.060404
thermal corrections to $\Delta G/h^a$	0.105437	0.104722	0.103777	0.103165	0.109616	0.108744
$\Delta G_{\text{rel}}/\text{kcal}\cdot\text{mol}^b$	0.000	0.062	0.000	0.034	0.000	0.036
mol fraction	0.521	0.479	0.512	0.488	0.512	0.488
DFCH						
$E/h + 433.0$	−1.347208	−1.345937	−1.525195	−1.525678	−0.036022	−0.033042
thermal corrections to $\Delta G/h^a$	0.115014	0.114656	0.113085	0.113126	0.118684	0.118044
$\Delta G_{\text{rel}}/\text{kcal}\cdot\text{mol}^b$	0.000	0.573	0.000	−0.277	0.000	1.468
mol fraction	0.684	0.316	0.408	0.592	0.879	0.104

^a At the temperature and pressure of the electron-diffraction experiment: 343 K and estimated 0.02 atm. Frequencies were not scaled. ^b Relative to the aa form.

The most interesting feature of the dihalocyclohexane systems is their composition. Wiberg (hereafter KW) has described the results of extensive *ab initio* and DFT calculations at different levels of theory with several basis sets on this subject for the monofluoro, monochloro, and monobromo compounds and for the corresponding *trans*-1,2-dihalocyclohexanes. He concluded that the best agreement with experiment, where it existed, was provided by the QCISD/6-311+G(2df,p) model. With this model the theoretical compositions for our systems are predicted to be 40% ee (DCCH) and 46% ee (DFCH). Our corresponding experimental value for the former is in perfect agreement, but for DFCH it is 12% larger. We carried out some similar calculations (B3LYP/6-31G(d), B3LYP/aug-cc-pVTZ, and MP2/6-31G(d)) for DCCH and DFCH that do not duplicate KW's results. The results are found in Table 6. It is seen that, in agreement with the GED experimental result for DCCH, the predicted composition in each case is slightly in favor of the aa form, as KW also found with his extensive list of calculations. The situation is much less clear for DFCH where the GED experimental result indicates the ee form as the more stable, whereas the predicted compositions are vary over the large range $41 \leq aa \leq 88\%$.

So what may one conclude about the composition of these two systems? First it is quite likely that the aa form of DCCH is the more stable because the experimental and theoretical results agree very well and because the theoretical results do not seem to be strongly dependent on either theoretical level or basis-set size. However, the best numerical estimate of the composition of DCCH is not so clear. Although the theoretical results lie within a narrow range averaging 51.5% aa, there is some concern that the reliability of some of the assumptions built into the theoretical estimates, such as the unscaled (harmonic) wavenumbers and the E to G conversion, could influence these values. For these reasons we believe the best estimate of the DCCH composition is the experimental one, i.e., 60(2σ = 4)% aa. In the case of DFCH, a decision about the relative stability of the two forms is more difficult. Here the experimental result taking into account the compositional uncertainty barely favors the ee form, and the theoretical results — obviously much more sensitive to theoretical level and basis-set size than in DCCH — are inconsistent in their predictions of composition. We believe the best numerical estimate of the composition of DFCH is 42(2σ = 7)% aa, again the experimental value, but this conclusion is less firm than that for DCCH.

During the course of our work we were aware of a concurrent, and now recently published, experimental (NMR) and theoretical study of the DFCH conformational problem by Wiberg et al.¹⁷

They conclude that the aa form is the main component in the gas phase by a small, but undefined, amount. Although this result differs from our 58(7)% ee, we do not view the difference as a major problem.

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Supporting Information Available: Figure of the intensity curves for DCCH, tables of the intensity data for both DCCH and DFCH, and the correlation matrixes for the ee forms of each. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) $sI_M(s) = k \sum A_i A_j (Z_i Z_j)^{-1} \exp[-s^2/(2\langle l_{ij}^2 \rangle)] \cos(\eta_i - \eta_j) \sin[s(r_{ij} - \kappa_{ij}s^2)]$; where A is an electron-scattering amplitude multiplied by s^2 , l is a root-mean-square amplitude of vibration, η is a phase shift, and κ is an anharmonicity constant. The A and η values were obtained from the tables of ref 4.
- (12) The distance relations used for GED are $r_a^T = r_g^T - (l^2)^T/r = r_a^\circ + (3a/2)[(l^2)^T - (l^2)^\circ] + \delta r^T + K^\circ - (l^2)^T/r$. The GED MW connection is through $r_a^\circ = r_z$, where $B_z(r_z) = B_0(r_0) + \sum \alpha_i^T d_i/2$. In these formulas a is an anharmonicity constant assumed equal to 2.0 \AA^{-1} , l^2 is a mean-square amplitude of vibration, r is a centrifugal distortion, K is the perpendicular amplitude correction, α is a harmonic vibration correction for a mode of degeneracy d , and the superscripts refer to temperature.
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