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Infrared gas phase intensity measurements. Polar tensors and effective charges of *cis*-dichloroethylene-d_0 and d_2

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The gas phase fundamental intensities of *cis*-dichloroethylene and its dideuterated modification have been measured. Isotopic invariance, the *G* sum rule and the results of molecular orbital calculations have been used to select preferred experimental values for the dipole moment derivatives and polar tensor elements of these molecules. The *F* sum rule has been used to determine individual intensity values of the ν_4, ν_{12} overlapped band system of the dihydrogen molecule. Values of the polar tensor elements for *cis* dichloroethylene are compared with those previously determined for *cis*-difluoroethylene. The hydrogen effective charge values in these molecules are essentially identical (0.17 and 0.18*e*). The polar tensor of *cis*-dichloroethylene is used to predict the vibrational intensities of *trans*-dichloroethylene.

INTRODUCTION

In recent articles our research groups have reported the infrared gas phase intensities, dipole moment derivatives, polar tensors, and effective charges of vinylidene fluoride,[1] *cis*-difluoroethylene[2] and their deuterated analogs. Since these isomers contain the same kind and number of chemical bonds, differences in the vibrational intensities of these molecules can be attributed to the different relative orientations of the chemical bonds within the molecules. Variations in the electronic distortions which accompany analogous molecular displacements of vinylidene fluoride and *cis*-difluoroethylene were documented by a comparison of the values of corresponding polar tensor elements for these molecules. The differences observed reflect different chemical bonding properties when the CF (or CH) bonds have a *geminal* spatial arrangement rather than a *cis* one. It is not surprising that such differences exist since in the one case the molecule contains a CH_2 and a CF_2 moiety whereas in the other, two equivalent CHF moieties.

On the other hand the *cis* and *trans* orientations, which are related by rotation of the CHF moieties by 180° do not provoke different electronic rearrangements for corresponding molecular distortions. Indeed, simple transference of the *cis*-difluoroethylene polar tensor to the *trans* isomer was found to provide excellent estimates of the vibrational intensities of the latter molecule. This is particularly important because the C_{2h} symmetry of the *trans* compound does not allow one to deduce the directional properties of the $\partial p/\partial Q_i$ of this molecule.

The present study of the dichloroethylenes was undertaken to investigate whether the conclusions drawn from the difluoroethylene study are generally applicable. In this paper, experimental infrared gas phase intensities of the vibrational fundamentals of *cis*-dichloroethylene and its dideuterated modification are presented. Comparisons of dipole moment derivative and polar tensor values for the isotopically related molecules,[3] *G* sum rule calculations,[4] and quantum chemical results[5] are used to obtain preferred experimental values of dipole moment derivatives. As in the case of *cis*-difluoroethylene, the spectra of the *cis*-dichloro compounds are complicated by the presence of several overlapping fundamental bands. The *F* sum rule has been used to arrive at estimates of the separate contributions to the total band intensity.[6] The preferred polar tensor of *cis*-dichloroethylene is also transferred to the *trans* isomer to predict its infrared intensities. These theoretical values are compared with experimental values reported in the literature.

EXPERIMENTAL

The integrated intensities were measured with a modified Perkin–Elmer 12C double pass spectrometer. The basic experimental method was that of Wilson, Wells,[7] Penner, and Weber[8] as developed by the Minnesota group.[9] The rotational fine structure of the vibrational fundamentals was broadened by the addition of 200–1000 lb per square inch of high purity argon to the absorbing sample, at a pressure of 5–500 Torr. CaF, NACl, KBr, and CsI prisms were interchanged in the spectrometer to ensure a spectral slit width of less than 2 cm^{-1}. All of the bands measured gave straight Beer's law plots which passed through the origin.

The output of the spectrometer was digitized and recorded onto paper computer tape for input to a digital computer. The digital recording system has been described previously as well as the experimental techniques for using this system.[10,11] Additional experimental details are given in Ref. 12. Standard errors were obtained by a simple least squares treatment of the Beer's law data. The error in the experimental intensities was taken as twice the standard error for all isolated fundamental bands. Larger errors were estimated for those intensities obtained from the graphical separation of overlapped bands.

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TABLE I. Observed fundamental frequencies (cm^{-1}) and intensities (km mol^{-1}) of *cis*-$C_2H_2Cl_2$.

Symm. species	i	ν_i	A_i[a]	A_i[b]
A_1	1	3077	···	···[c]
	2	1587	30.9±1.2	22.0±3.0
	3	1179	···	0.1±0.0
	4	714	21.2±0.8[d] (15.6±0.3)[e]	···[f]
	5	173	···	0.1±0.0
B_1	8	3087	10.3±0.3	11.0±0.5[c]
	9	1303	21.4±0.7	18.0±1.0
	10	857	56.4±2.6	58.0±2.0
	11	571	4.9±0.2	6.0±0.5
B_2	12	697	35.2±0.8[d] (40.8±0.8)[e]	57.0±2.0[a]

[a] This work. The error is twice the least square error, except for overlapped bands.

[b] Data from Ref. 15.

[c] ν_1 and ν_8 not separated.

[d] These values were obtained by graphical separation of the over lapped ν_4, ν_{12} band.

[e] These values were obtained by applying the F sum rule to the A_1 symmetry species of *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$.

[f] ν_4 and ν_{12} not separated.

cis-$C_2H_2Cl_2$

A sample of *cis* dichloroethylene was obtained from Columbia Organic Chemicals Co., Inc., Columbia, S.C. It contained 2%–3% of *trans* $C_2H_2Cl_2$ impurity and was purified on a spinning band column. The mixture was refluxed for 2h at 60 °C. The *trans* isomer was distilled off first and discarded and the *cis* isomer was collected at 60 °C at a rate of about ten drops per minute. Infrared analysis showed less than 0.5% *trans* isomer present (using the sharp Q branch of the 898 cm^{-1} *trans* band as a criterion). The infrared spectrum was free from any other impurity bands.

Cis-dichloroethylene has C_{2v} symmetry; $\Gamma_{\text{vib}} = 5A_1 + 2A_2 + 4B_1 + B_2$. In principle, ten of its fundamental vibrations $5A_1 + 4B_1 + B_2$, are infrared active while all 12 are Raman active. The vibrational assignment, due to Bernstein and Ramsey[13] is given in Table I; the frequencies have been slightly revised. Although all five of the A_1 bands are theoretically infrared active, only two of them show up clearly in the vapor phase infrared spectrum, ν_2 at 1587 cm^{-1} and ν_4 at 714 cm^{-1}. A third very weak fundamental at 1183 cm^{-1}, was found in the infrared spectrum of the pure liquid in a 55 μ cell. The far infrared spectrum of a liquid sample of *cis*-$C_2H_2Cl_2$ was scanned several times on a Perkin Elmer 301 spectrometer. No trace could be found of ν_5, which has a polarized band at 173 cm^{-1} in the Raman spectrum. The CH stretching region of the vapor phase infrared spectrum of this molecule showed a medium intensity symmetrical band centered at 3087 cm^{-1} with P, Q, and R branches of roughly equal intensity. This is exactly the band contour predicted qualitatively from the curves of Badger and Zumwalt[14] for the asymmetric CH stretching fundamental ν_8 (type A band). The infrared spectra of the pure liquid and the solid showed no trace of ν_1, the symmetric CH stretching mode.

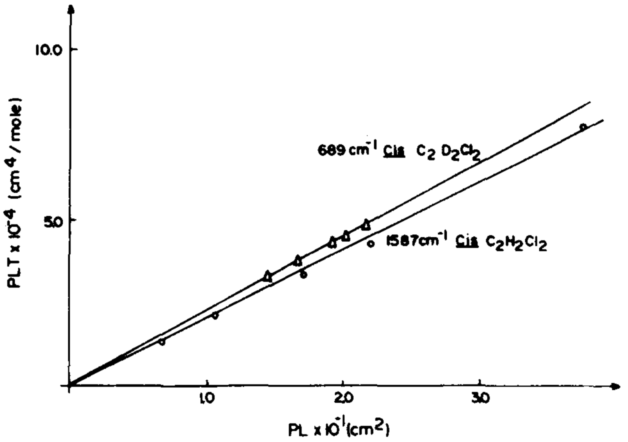

FIG. 1. The Beer's law graphs for the fundamental bands.

In Table I the integrated absorption intensities measured in this work for *cis*-$C_2H_2Cl_2$ are listed along with the measurements of Tanabe and Saeki.[15] The agreement between the two sets of experimental values is excellent with the exception of those values for A_2 which differ by about 30%–40%. It is difficult to explain this difference because our value is obtained from an almost perfectly straight Beer's law graph as shown in Fig. 1.

cis-$C_2D_2Cl_2$

The deuterated sample was prepared by exchanging the hydrogen atoms of the previously purified *cis*-$C_2H_2Cl_2$. After carrying out the deuteration process twice the infrared spectrum showed the sample to be over 99% deuterated.

cis-dichloroethylene-d_2 has the same symmetry as the dihydrogenated modification. Their spectra are similar except for expected frequency shifts and changes in band intensities. The vibrational assignment,[13] fundamental frequencies, and integrated intensities are given in Table II. Note that as in the case of the dihydrogenated molecule, three of the A_1 funda-

TABLE II. Observed fundamental frequencies (cm^{-1}) and intensities (km mol^{-1}) of *cis*-$C_2D_2Cl_2$.

Symm. species	i	ν_i	A_i
A_1	1	2325	···
	2	1570	27.1±1.4
	3	850	···
	4	689	15.1±0.3
	5	171	···
B_1	8	2280	12.5±0.6
	9	1040	43.1±1.2
	10	761	23.1±1.1
	11	558	16.8±1.3[a] (6.3±0.3)[b]
B_2	12	540	9.7±1.3[a] (20.2±0.4)[b]

[a] These values were obtained by graphical separation of the overlapped ν_{11}, ν_{12} band.

[b] These values were obtained by transferring dipole moment derivatives from the B_2 symmetry species of *cis*-$C_2H_2Cl_2$.

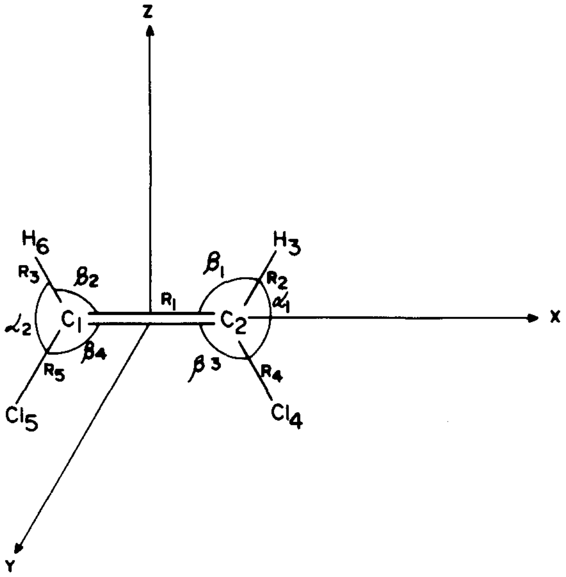

FIG. 2. The Cartesian coordinate system, atom numbering scheme, and internal coordinates of *cis*-dichloroethylene.

mentals ν_1, ν_3, and ν_5, are not found in the vapor phase spectrum of the dideuterated modification.

Band separation problems

cis-dichloroethylene-d_0 and -d_2 each contain a pair of overlapping fundamental bands. In the spectrum of the dihydrogen molecule ν_4 (A_1 symmetry) and ν_{12} (B_2) overlap, whereas in the spectrum of the deuterated species ν_{11} (B_1) and ν_{12} (B_2) overlap. These overlapping bands were initially separated by graphical techniques and the resulting estimates of the individual intensity values are included in Tables I and II. The difficulties involved in obtaining accurate graphical separation values are well known.[16] Indeed the G sum rule analysis for the B_2 symmetry species using the intensity values obtained from the graphical separation leads to imaginary values of the hydrogen effective charge. For this reason theoretical approaches were employed to obtain alternate values for the individual fundamental intensities.

The separation of the ν_4, ν_{12} overlapped band for *cis*-C_2H_2Cl was straightforward. The A_1 symmetry species of the dideuterated molecule contains fundamentals which are free of overlapping problems. Hence the F sum rule[6] applied to the A_1 symmetry species of both isotopic modifications

$$\sum_i (A_i/\nu_i^2)_H = \sum_i (A_i/\nu_i^2)_D$$

allows one to calculate a modified value for A_4 of *cis*-$C_2H_2Cl_2$. The intensity of ν_{12} is obtained by subtracting A_4 from the total intensity of the ν_4, ν_{12} band system. The revised values of A_4 and A_{12} are also listed in Table I.

The separation of ν_{11}, ν_{12} for *cis*-$C_2D_2Cl_2$ is facilitated by our knowledge of the individual value of A_{12} for *cis*-$C_2H_2Cl_2$. Assuming that the sign of $\partial p/\partial Q_{12}$ is positive for the latter molecule and transferring the appropriate polar tensor element to *cis*-$C_2D_2Cl_2$ one obtains a value of 20.2 km mol^{-1} for A_{12} of this molecule. A negative sign for this derivative leads to an alternate value of 28.7 km mol^{-1}. However this latter value is slightly larger than the total experimental intensity $A_{11}+A_{12}=26.5$ km mol^{-1} for the combined band system. Since the graphical band separation suggests that A_{11} is larger than A_{12}, it is difficult to believe that all of the overlapped band intensity is ascribable to A_{12}. Moreover, a zero value for A_{11} results in an unacceptable G sum rule graph for the B_1 symmetry species of the dichloroethylenes. Based on these considerations and on further evidence supporting a positive sign for $\partial p/\partial Q_{12}$ of *cis*-$C_2D_2Cl_2$, which is included in a later section of this paper, $A_{11}=6.3$ and $A_{12}=20.2$ km mol^{-1} are adopted for *cis*-$C_2D_2Cl_2$ in our calculations.

RESULTS

Dipole moment derivatives and polar tensor elements were calculated using the usual equations.[17] The orientation of the Cartesian coordinate system and the atom numbering scheme are shown in Fig. 2. This figure also includes the definitions of the in-plane internal displacement coordinates. Table III contains the definitions of the symmetry coordinates and of the out-of-plane internal coordinates. Values of the rotational corrections for the symmetry coordinates and the corresponding reference molecule distortions in Cartesian coordinate space are shown in Fig. 3. A permanent dipole moment value[18] of +0.394 e Å and the equilibrium geometry of Ref. 19 were employed in our calculations. The $\mathbf{L}^{-1}$ matrices used are given in Table IV and were calculated from the force field given in Ref. 20.

As in our previous papers,[1,2] the isotopic invariance criterion and G sum rule restrictions are used to determine the preferred sign choices of the $\partial p/\partial Q_i$'s. The G sum rule equation for the dichloroethylenes is given by

$$K^{-1}\sum A_i + \Omega = 2(\xi_C^2/m_C + \xi_{Cl}^2/m_{Cl}) + (1 + x/2)\xi_H^2/m_H ,$$

where x represents the number of hydrogen atoms in

TABLE III. Symmetry coordinates for *cis*-dichloroethylene.

	In-plane
A_1	$S_1 = R_1$
	$S_2 = 1/\sqrt{2}\,(R_2 + R_3)$
	$S_3 = 1/\sqrt{2}\,(R_4 + R_5)$
	$S_4 = 1/2\sqrt{3}\,(2\alpha_1 - \beta_1 - \beta_3 + 2\alpha_2 - \beta_4 - \beta_2)$
	$S_5 = 1/2\,(\beta_1 - \beta_3 + \beta_2 - \beta_4)$
B_1	$S_8 = 1/\sqrt{2}\,(R_2 - R_3)$
	$S_9 = 1/\sqrt{2}\,(R_4 - R_5)$
	$S_{10} = 1/2\sqrt{3}\,(2\alpha_1 - \beta_1 - \beta_3 - 2\alpha_2 + \beta_4 + \beta_2)$
	$S_{11} = 1/2\,(\beta_1 - \beta_3 - \beta_2 + \beta_4)$
	Out-of-plane
B_2	$S_{12} = 1/\sqrt{2}\,(\eta_1 + \eta_2)$[a]

[a] $\eta_1 = \Delta$ angle between bond C_1–H_6 and plane (C_2–C_1–Cl_5), $\eta_2 = \Delta$ angle between bond C_2–H_3 and plane (C_1–C_2–Cl_4).

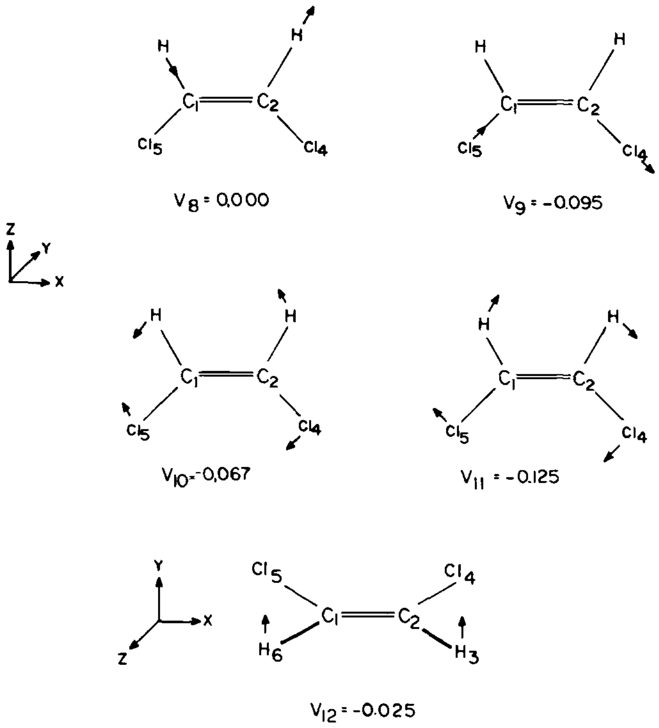

FIG. 3. Symmetry coordinate distortions and rotational correction values for the B_1 and B_2 symmetry coordinates.

the molecule. We have also made use of CNDO molecular orbital calculations, which have been quite successful in predicting algebraic *signs* of dipole moment derivatives, in our attempts to resolve the sign ambiguity problem. For these calculations atomic displacements resulting in changes in the internal coordinates of ±0.02 Å and ±2° were used.

A_1 symmetry species

Since *cis*-dichloroethylene-d_0 and $-d_2$ each have only two effectively nonzero intensities in the A_1 symmetry species there are only four possible sign combinations for each molecule. All possible sign choices lead to isotopically invariant pairs of dipole moment derivatives as shown in Table V. All these sign choices also lead to atomic effective charge values which are in agreement with those calculated from the A_1 fundamental intensity sums using the G sum rule. For these reasons the preferred sign choice cannot be made on the basis of the experimental evidence presented here; one must resort to quantum chemical calculations or other theoretical considerations to determine the correct set of signs for the dipole moment derivatives.

Unfortunately the values of the dipole moment derivatives determined from CNDO calculations, also included in Table V are not helpful in determining the preferred signs of the $\partial p/\partial Q_i$. The quality of these theoretical values for molecules containing second row atoms, such as chlorine, are known to be inferior to those calculated for simpler molecules.[21] Part of this problem stems from the uncertainty of how to incorporate the 3*d* orbitals into the calculation. The large change in the CNDO value for $\partial p_z/\partial S_3$ resulting from a change from *sp* to *spd* basis sets provides one manifestation of this difficulty. On the other hand, if the substitution of fluorine by chlorine does not cause radical changes in the electronic structure of the dihaloethylenes one might expect that the signs of the $\partial p/\partial S_j$ values for *cis*-$C_2H_2Cl_2$ could be determined from those previously determined for *cis*-$C_2H_2F_2$.[2] Since the Cartesian coordinate system, atom numbering scheme, and symmetry coordinate definitions of both molecules are identical one expects to find that those dipole moment derivatives with relatively large values, i.e., $\partial p_z/\partial S_1$ and $\partial p_z/\partial S_3$, have the same sign in both the chloro and fluoro compounds. Since for *cis*-$C_2H_2F_2$ the values of $\partial p_z/\partial S_1$ and $\partial p_z/\partial S_3$ are negative and positive, respectively, the (0-0-0) set of signs for the $\partial p/\partial Q_i$ is taken as the preferred choice for both *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$. This notation indicates that

TABLE IV. L^{-1} matrix of *cis*-dichloroethylene (amu)$^{1/2}$.

			$C_2H_2Cl_2$		
A_1 species					
	S_1	S_2	S_3	S_4	S_5
Q_1	−0.0363	0.9628	0.0087	0.0039	0.0204
Q_2	2.0460	0.1330	−0.1463	0.2227	−0.0512
Q_3	−1.4311	−0.0367	0.2950	0.6977	−0.2401
Q_4	−1.5876	−0.2024	−3.4671	0.0977	0.1622
Q_5	−3.9504	0.0644	−2.1062	3.7337	6.5319
B_1 species					
	S_8	S_9	S_{10}	S_{11}	
Q_8	0.9646	0.0296	−0.0021	−0.0014	
Q_9	0.0125	0.2820	−0.6491	0.2241	
Q_{10}	0.1896	2.1043	0.5856	0.5258	
Q_{11}	0.1876	−3.2401	0.7191	1.5713	
B_2 species					
	S_{12}				
Q_{12}	0.9666				
			$C_2D_2Cl_2$		
A_1 species					
	S_1	S_2	S_3	S_4	S_5
Q_1	−0.2482	1.2812	−0.0224	−0.0030	0.0293
Q_2	2.1950	0.3523	−0.2106	0.1503	−0.0200
Q_3	−1.3818	−0.0332	0.4239	1.0240	−0.3394
Q_4	−1.7241	−0.4114	−3.5232	0.1217	0.1592
Q_5	−3.8834	0.1279	−2.0747	3.7084	6.5557
B_1 species					
	S_8	S_9	S_{10}	S_{11}	
Q_8	1.3051	0.0223	−0.0170	−0.0253	
Q_9	0.1241	1.0571	−0.6288	0.3375	
Q_{10}	0.3880	1.8346	1.0012	0.4973	
Q_{11}	0.3523	−3.4257	0.5395	1.6472	
B_2 species					
	S_{12}				
Q_{12}	1.2534				

TABLE V. Experimental and CNDO calculated derivatives of the A_1 symmetry species of *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$.[a]

	$\partial P_z/\partial S_1$	$\partial p_z/\partial S_2$	$\partial p_z/\partial S_3$	$\partial p_z/\partial S_4$	$\partial p_z/\partial S_5$
h_2 (0 − 0 − 0)[b]	−0.163 ± 0.012	+0.002 ± 0.001	+0.465 ± 0.011	−0.052 ± 0.001	−0.011 ± 0.001
d_2 (0 − 0 − 0)	−0.151 ± 0.012	−0.007 ± 0.002	+0.474 ± 0.005	−0.040 ± 0.001	−0.016 ± 0.001
h_2 (0 + 0 − 0)[b]	+0.565	+0.049	+0.413	+0.027	−0.030
d_2 (0 + 0 − 0)	+0.580	+0.110	+0.404	+0.010	−0.023
CNDO (*spd*)	−0.281	−0.254	−0.050	+0.104	+0.155
CNDO (*sp*)	−0.233	−0.235	+0.248	+0.152	+0.173

[a] Units of electrons e, $1\ e = 4.803$ DÅ^{-1}. Besides the pairs listed here the (0 + 0 + 0) and (0 − 0 + 0) pairs are also isotopically invariant. These sign choices lead to $\partial p/\partial S_j$ values which are identical in magnitude but opposite in sign to the ones listed above.

[b] The relative signs are expressed in the usual notation. However, since A_1, A_3, and A_5 have zero intensity, their signs are indicated by zeroes.

$\partial p_z/\partial Q_2$ and $\partial p_z/\partial Q_4$ have negative signs and that $\partial p_z/\partial Q_1$, $\partial p_z/\partial Q_3$, and $\partial p_z/\partial Q_5$ are zero.

For this sign choice the absolute magnitude of the experimental value of $\partial p_z/\partial S_2$ is very small. This means that as the CH bond is stretched, there is a negligible change in the molecular dipole moment. For most molecules, it has been deduced that the CH stretching motions cause small but significant dipole moment changes which have a polarity equivalent to an increase in electron density in the direction of the stretched hydrogen atoms. Acetylene and hydrogen cyanide are the only well established exceptions to this behavior. In spite of the fact that CH stretching motions can normally be expected to result in a more negative polarity in the direction of the stretched hydrogen atoms, one must use caution in applying this criterion in the selection of preferred signs of dipole moment derivatives. For stretching motions involving terminal atoms which are more electronegative than hydrogen, this criterion is much more secure.

B_1 symmetry species

There are 16 possible sign choices for the $\partial p/\partial Q_1$ of each isotopic modification of *cis*-dichloroethylene in this symmetry species. The four most isotopically invariant pairs of the $\partial p/\partial S_j$ are given in Table VI. It should be noted that our error estimates for $\partial p_x/\partial S_8$ and $\partial p_x/\partial S_{10}$ for these molecules appears to be too low because strict isotopic invariance for these two derivatives is not observed for any of the possible pairs of values. Of the sign alternatives listed in Table VI the (− + + −) and the (+ + + −) sets are easily eliminated from consideration as the correct one based on G sum rule calculations using the B_1 symmetry intensity sums. The remaining sets have almost identical $\partial p_x/\partial S_j$ values for $j = 9, 10$, and 11. Of the alternate pairs the (− − − +) set of signs for the $\partial p_x/\partial Q_i$ is preferred for the following reasons. First, it is the only set with signs of the $\partial p_x/\partial S_j$ which are in complete agreement with the CNDO calculated signs (for both the *sp* and *spd* basis set calculations). Second, its values of $\partial p/\partial S_8$ has a negative sign implying a polarity of the dipole moment change which is in agreement with those found for most CH stretching motions. Of course, one can not definitively rule out the (+ − − +) set as the correct one, but one finds very similar values of $\partial p_x/\partial S_j$ for either of these alternative sign choices and the selection of either set of signs does not lead to polar tensor values which are very different.

B_2 symmetry species

The sign selection for $\partial p_y/\partial Q_{12}$ depends on the band separation used to assign individual intensity values to

TABLE VI. Experimental and CNDO calculated derivatives of the B_1 symmetry species of *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$.[a]

	$\partial p_x/\partial S_8$	$\partial p_x/\partial S_9$	$\partial p_x/\partial S_{10}$	$\partial p_x/\partial S_{10}$
h_2 (− + + −)	−0.065 ± 0.004	+0.869 ± 0.025	+0.061 ± 0.009	+0.173 ± 0.011
d_2 (− + + −)	−0.091 ± 0.005	+0.867 ± 0.014	+0.044 ± 0.007	+0.145 ± 0.006
h_2 (+ − − +)	+0.065	−0.680	+0.073	+0.077
d_2 (+ − − +)	+0.090	−0.689	+0.084	+0.109
h_2 (+ + + −)	+0.133	+0.875	+0.061	+0.173
d_2 (+ + + −)	+0.205	+0.872	+0.041	+0.139
h_2 (− − − +)	−0.133	−0.686	+0.074	+0.077
d_2 (− − − +)	−0.206	−0.694	+0.087	+0.115
CNDO (*spd*)	−0.056	−0.295	+0.149	+0.105
CNDO (*sp*)	−0.066	−0.547	+0.291	+0.308

[a] Units of electrons e. $1\ e = 4.803$ DA^{-1} $= 1.60 \times 10^{-19}$ C.

TABLE VII. Experimental and CNDO calculated derivatives of the B_2 symmetry species of *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$.[a]

	$\partial p_y/\partial S_{12}$
h_2 (+)	+0.223
d_2 (+)	+0.223
CNDO (*spd*)	+0.138
CNDO (*sp*)	+0.140

[a] Units of electrons *e*.

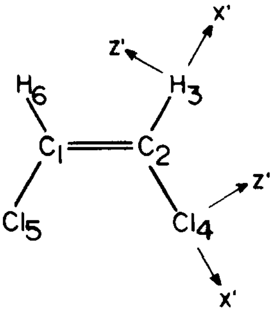

FIG. 4. The localized Cartesian coordinate systems used to calculate the hydrogen and chlorine polar tensors of *cis*-dichloroethylene.

A_{11} and A_{12} of *cis*-$C_2D_2Cl_2$. Because the most reasonable band separation was obtained by assigning a positive sign to $\partial p_y/\partial Q_{12}$ of *cis*-$C_2H_2Cl_2$ its corresponding $\partial p_y/\partial S_{12}$ value of +0.223 *e* was transferred to the deuterated species. This value also leads to a positive sign for $\partial p_y/\partial Q_{12}$ of *cis*-$C_2D_2Cl_2$. The positive sign of $\partial p_y/\partial S_{12}$ is in agreement with the CNDO calculated sign (both *sp* and *spd* basis set calculations) and with the sign of $\partial p_y/\partial S_{12}$ previously determined for *cis*-difluoroethylene.[2]

DISCUSSION

The values of $\partial p/\partial Q_i$ of *cis*-$C_2H_2Cl_2$ with the signs chosen in the previous section were transformed into polar tensor values. This representation has been shown to be useful in predicting infrared intensities of structurally similar molecules. For the hydrogen and chlorine atoms, polar tensor values referring to the localized Cartesian coordinate systems of Fig. 4 were used whereas the coordinate system of Fig. 2 was used for the carbon atom polar tensors. The atomic polar tensor and effective charge values for *cis*-$C_2H_2Cl_2$ are given in Table VIII.

The hydrogen effective charge value of 0.180 *e* calculated from the polar tensor ($\xi_H = 0.202 \pm 0.031$ *e* from the *G* sum rule) is very similar to the value calculated for *cis*-$C_2H_2F_2$ ($\xi_H = 0.173$ *e*) and to the values calculated for the hydrogen atom in a reasonably large number of molecules.[2] The absolute values of the hydrogen polar tensor elements are all less than 0.1 *e* with the exception of $\partial p'_y/2y'_H$ (0.147 *e*). Similar values have been reported for $\mathbf{P}_{X'}^{(H)}$ of *cis*-difluoroethlyene.[2] The carbon effective charge in *cis*-$C_2H_2Cl_2$ is significantly smaller than the one in *cis*-$C_2H_2F_2$; this results mainly because the individual polar tensor elements are generally somewhat smaller than those observed for *cis*-$C_2H_2F_2$ rather than due to a large change in the value of any one specific polar tensor element. With the exception of $\partial p_z/\partial z_{C_1}$ the polar tensor elements of *cis*-$C_2H_2Cl_2$ may be rather well estimated using the elements from $\mathbf{P}_X^{(C1)}$ of the fluorine compound multiplied by a common scale factor.

The chlorine effective charge is much smaller than the value observed for ξ_F in *cis*-$C_2H_2F_2$. This is mainly due to the differing values of $\partial p_x/\partial x'$, −0.533 and −0.867 *e* for *cis*-$C_2H_2Cl_2$ and *cis*-$C_2H_2F_2$, respectively. Each of these values indicates the extent of the change in the dipole moment component along the carbon–halogen bonds due to stretching motions of these bonds. ξ_{Cl} in *cis*-dichloroethylene is also substantially smaller than the values found in Cl_2CO and Cl_2CS (0.86 and 0.87 *e*, respectively). For this reason it does not appear advisible to transfer the chlorine

TABLE VIII. Polar tensors and effective charges for *cis*-$C_2H_2Cl_2$.[a]

(C_1)
P_X

$$\begin{pmatrix} 0.371 \pm 0.012 & 0.000 & 0.496 \pm 0.018 \\ 0.000 & -0.106 \pm 0.003 & 0.000 \\ 0.392 \pm 0.008 & 0.000 & 0.282 \pm 0.007 \end{pmatrix} \qquad \xi_{C_1} = 0.792$$

(H_3)
$P_{X'}$

$$\begin{pmatrix} -0.046 \pm 0.002 & 0.000 & -0.019 \pm 0.003 \\ 0.000 & 0.147 \pm 0.001 & 0.000 \\ 0.082 \pm 0.003 & 0.000 & -0.039 \pm 0.004 \end{pmatrix} \qquad \begin{array}{l} \xi_{H_3} = 0.180^{b} \\ (0.202 \pm 0.031)^{c} \end{array}$$

(Cl_4)
$P_{X'}$

$$\begin{pmatrix} -0.533 \pm 0.016 & 0.000 & -0.056 \pm 0.004 \\ 0.000 & -0.041 \pm 0.002 & 0.000 \\ -0.243 \pm 0.019 & 0.000 & -0.035 \pm 0.006 \end{pmatrix} \qquad \xi_{Cl_4} = 0.591$$

[a] Units of electrons *e*.
[b] Calculated using the hydrogen polar tensor.
[c] Calculated using the *G* sum rule.

TABLE IX. Comparison of experimental intensities of *trans*-dichloroethylene with theoretical values calculated using the polar tensors of *cis*-dichloroethylene.[a]

Sym. Species	i	ν_i (cm^{-1})	$(A_i)_{\rm expt}$	$(A_i)_{\rm calc}$
A_u	6	898	48.0 ± 0.5[b] (49.0 ± 1.0)[c]	45.0 ± 0.2
	7	227	0.2 ± 0.0 (0.1 ± 0.0)	0.3 ± 0.1
B_u	9	3097	10.5 ± 0.2 (12.0 ± 0.5)	13.4 ± 0.2
	10	1201	16.7 ± 0.6 (17.0 ± 0.5)	21.3 ± 0.3
	11	826	93.3 ± 3.0 (96.0 ± 2.0)	78.0 ± 0.4
	12	250	0.1 ± 0.0 (0.1 ± 0.0)	1.9 ± 0.3

[a] Units of km mol^{-1}.

[b] Reference 12.

[c] Reference 15.

polar tensor from the *cis* isomer to 1,1-dichloroethylene to predict the fundamental vibrational intensities of the latter compound. Rather, it seems more reasonable to take the chlorine polar tensors from Cl_2CO and Cl_2CS for this calculation since the fluorine polar tensors and effective charges of F_2CO, F_2CS, and 1,1-$C_2H_2F_2$ have very similar values.

The polarities of the dipole moment changes for simple stretching and bending motions can be determined using the values of the polar tensor elements in Table VIII. Both $\partial p_{x'}/\partial x'_{\rm Cl}$ and $\partial p_{x'}/\partial x'_{\rm H}$ are negative indicating that as the CCl and CH bonds are stretched negative polarity is increased in the direction of the stretched terminal atoms. As stated earlier, identical behavior has been observed for the sense of the dipole moment changes occurring for almost all stretching motions investigated thus far. The diagonal elements of the polar tensor for the y' and z' chlorine atomic coordinates are negative, indicating a polarity equivalent to C^+Cl^- for the CCl bending deformations. This is identical to the polarity found for the fluorine bending motions in the difluoroethylenes. On the other hand $\partial p_{z'}/\partial z'_{\rm H}$ is negative whereas $\partial p_{y'}/\partial y'_{\rm H}$ is positive. This situation reminds us of the behavior of the CH bends in formaldehyde[22]; the in-plane bend presents a polarity equivalent to C^+-H^- although the out-of-plane bend exhibits the opposite polarity.

The senses of the dipole moment changes indicated by the $\partial p/\partial S_j$ values of *cis*-dichloroethylene are identical to those of the corresponding *cis*-difluoroethylene derivatives except for those derivatives having very small values ($\partial p_z/\partial S_2$, $\partial p_z/\partial S_4$ and $\partial p_z/\partial S_5$). Because these derivatives are almost zero, a change in sign is not surprising.

The transference of the *cis*-$C_2H_2Cl_2$ polar tensor to *trans*-$C_2H_2Cl_2$ in order to calculate the fundamental intensities of the latter compound is a useful test of the transferability of the newly derived intensity parameters. The intensities in Table IX were calculated from the transferred polar tensors and the values of the normal coordinate coefficients calculated from the force field given in Ref. 12. The experimental values listed in the table were taken from Refs. 12 and 15 and will be the subject of a future paper on the *trans*-dihaloethylenes. The calculated and experimental values agree exceptionally well. Considering that transference of the *cis* polar tensors of both difluoro and dichloroethylene to their respective *trans* isomers results in excellent predictions of the infrared intensities of the *trans* forms, one might expect that simple transference of polar tensors from one form of a rotational isomer to another will result in accurate calculated intensity values.

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