Transferability of the *cis*- and *trans*-Dichloroethylene Atomic Polar Tensors

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The isotopic invariance criterion, *ab initio* molecular orbital results, and principal component analysis are used to resolve the sign ambiguities of the dipole moment derivatives for *cis*-dichloroethylene and the out-of-plane derivatives of *trans*-dichloroethylene. Atomic polar tensors (APTs) for *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ as well as out-of-plane polar tensor elements for *trans*-$C_2H_2Cl_2$ and *trans*-$C_2D_2Cl_2$ are reported. Mean dipole moment derivatives of the difluoro- and dichloroethylenes are compared and interpreted as atomic charges. The APTs of *cis*-dichloroethylene are transferred to *trans*-dichloroethylene to calculate its infrared fundamental vibrational intensities. These intensities are in much better agreement with the experimental intensities than those calculated by a MP2/6-311++G(d,p) wave function. The transferability of mean dipole moment derivatives between the *cis* and *trans*-dichloroethylenes is demonstrated using a simple potential model and carbon and chlorine core electron binding energies obtained by ESCA spectroscopy.

Introduction

The infrared spectra of the difluoro- and dichloroethylenes in the gas phase are particularly intriguing since the fundamental intensity sums of the *cis* and *trans* forms are almost the same.[1−3] Preliminary results[4] based on atomic polar tensors[5] (APTs) determined from measured intensities and normal coordinate transformations obtained from force fields calculated from experimental frequencies indicated that the APTs of the *cis* isomers are transferable to the *trans* forms. Since the isotopic invariance criterion[6] was not sufficient to remove all the sign ambiguities of the dipole moment derivatives with respect to the normal coordinates of these molecules, $\partial\vec{p}/\partial Q_j$, the APTs used in this transference study were determined on the basis of the signs of derivatives calculated using approximate semiempirical CNDO molecular orbital results. Later, the APTs of *cis*- and *trans*-difluoroethylene were studied again[7] using a more secure sign selection procedure involving *ab initio* wave function results displayed on principal component graphs along with the mathematical solutions corresponding to all the possible sign alternatives for the experimental dipole moment derivatives. This analysis for the two in-plane and one out-of-plane symmetry species of *cis*-difluoroethylene showed that, although the in-plane APT elements are transferable between the *cis* and *trans* forms, this is not true for the out-of-plane elements.

Here the transferability of the dichloroethylene APT values is tested. The improved sign selection technique is applied to the APT values of *cis*-dichloroethylene and the out-of-plane values for *trans*-dichloroethylene. The in-plane APT elements of the *trans* isomer cannot be evaluated directly since the $\partial\vec{p}/\partial Q_j$ directions have not been determined. This problem arises owing to the absence of in-plane molecular symmetry axes. For this reason the APT values of the *cis* isomer are transferred to the *trans* form to calculate its fundamental intensities. These results are also compared with the intensities calculated from *ab initio* wave functions. Furthermore information on the validity of this transference procedure for the dichloroethylenes is presented in the form of ESCA core electron energy results. In this way similarities in the electronic structures of these isomers are investigated using both fundamental infrared intensity and 1s electron ionization energy results.

Calculations

The values of the experimental fundamental infrared intensities, vibrational frequencies, molecular geometries, and definitions of the symmetry coordinates of the *cis*-compounds were taken from ref 1. The orientations for *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ in the space-fixed Cartesian coordinate system, the atom numbering scheme, and the internal coordinates are identical to those in Figure 2 of ref 1. The corresponding information for the *trans*- $C_2H_2Cl_2$ and *trans*- $C_2D_2Cl_2$ molecules was taken from ref 2.

The polar tensors of the dichloroethylenes are represented by a juxtaposition of all their atomic polar tensors:[5]

$$P_x = \{P_x^{(C_1)}\, P_x^{(C_2)}\, P_x^{(H_3)}\, P_x^{(Cl_4)}\, P_x^{(Cl_5)}\, P_x^{(H_6)}\}$$

Each atomic polar tensor, $P_x^{(\alpha)}$, is defined by

$$P_x^{(\alpha)} = \begin{pmatrix} \partial p_x/\partial x_\alpha & \partial p_x/\partial y_\alpha & \partial p_x/\partial z_\alpha \\ \partial p_y/\partial x_\alpha & \partial p_y/\partial y_\alpha & \partial p_y/\partial z_\alpha \\ \partial p_z/\partial x_\alpha & \partial p_z/\partial x_\alpha & \partial p_z/\partial z_\alpha \end{pmatrix} = \begin{pmatrix} P_{xx}^{\alpha} & P_{xy}^{\alpha} & P_{xz}^{\alpha} \\ P_{yx}^{\alpha} & P_{yy}^{\alpha} & P_{yz}^{\alpha} \\ P_{zx}^{\alpha} & P_{zy}^{\alpha} & P_{zz}^{\alpha} \end{pmatrix}$$

The polar tensors were calculated from the experimental intensity data for all possible sign alternatives using the TPOLAR program.[8] Molecular orbital calculations were carried out using the Gaussian 92 computer program[9] on a RISC 6000 workstation. All the intensity and APT molecular orbital calculations were carried out using theoretically optimized geometries. The principal components of the dichloroethylene polar tensor data were calculated using a microcomputer version of the ARTHUR program for mainframe computers.[10]

The principal component equation applied to the polar tensor elements can be expressed as[11−13]

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$$p^{(\alpha)}_{i,\sigma\nu} = \overline{p^{(\alpha)}_{\sigma\nu}} + \sum_{a=1}^{A} t_{ia} b^{(\alpha)}_{a,\sigma\nu} + e^{(\alpha)}_{i,\sigma\nu} \tag{1}$$

where $(\sigma,\nu) = (x,y,z)$ and i represents the ith set of signs of the $\partial\vec{p}/\partial Q_j$ and $\overline{p^{(\alpha)}_{\sigma\nu}}$ is the average value of the $\sigma\nu$th polar tensor element of the αth atom over all possible $\partial\vec{p}/\partial Q_j$ sign alternatives. The $b^{(\alpha)}_{a,\sigma\nu}$ elements are called loadings and are the direction cosines relating the rotated principal component space to the original polar tensor space. The t_{ia} values are the scores giving the transformed coordinate values of the ith set of signs for the ath principal component. These values are used to construct low-dimensional projections of the information contained in higher order polar tensor space. The $e^{(\alpha)}_{i,\sigma\nu}$ are residual values expressing the differences between the experimental values of $p^{(\alpha)}_{i,\sigma\nu}$ and those predicted by the principal component model. These residuals contain contributions from both experimental and modeling errors. If the $e^{(\alpha)}_{i,\sigma\nu}$ values for a two principal component representation are larger than the experimental errors and a bidimensional projection is not sufficient to give an accurate representation of the $\partial\vec{p}/\partial Q_j$ sign dependence of the polar tensor element values, additional projections involving the third, fourth, etc., principal components can be employed.

In practice, the loadings and scores in eq.1 are obtained by diagonalizing the covariance matrix, $\mathbf{X}^t\mathbf{X}$, where $\mathbf{X}$ is a data matrix containing the nonzero polar tensor element values calculated using the experimental intensities for all possible sign set alternatives of the $\partial\vec{p}/\partial Q_j$ for both the hydrogen and deuterium analogues. The resulting eigenvectors contain the loadings and define the directions of the new axes, called principal components, relative to the original coordinate system. The associated eigenvalues are equivalent to the variances described by the principal components.

The principal component scores, which are graphed to determine preferred $\partial\vec{p}/\partial Q_j$ sign sets, are obtained from the loadings and the original data matrix, $\mathbf{X}$. For the ith sign combination and the ath principal component, PC$_a$, the score is given by

$$t_{ia} = \sum_{\sigma\nu} p^{(\alpha)}_{i,\sigma\nu} b^{(\alpha)}_{\sigma\nu,i} \tag{2}$$

where the sum is taken over all nonzero and nonequivalent polar tensor elements in the symmetry species being treated and contains contributions from all the atoms in the molecule. In this equation the modeling error is assumed to be zero, that is, all the $e^{(\alpha)}_{i,\sigma\nu}$ elements are zero.

The principal component loadings, $b^{(\alpha)}_{a,\sigma\nu}$, in eq 1 are determined using only the polar tensor element values, $p^{(\alpha)}_{i,\sigma\nu}$, for all the possible sign combinations, i, of the $\partial\vec{p}/\partial Q_j$ for the symmetry species being treated. Theoretical values of the principal component scores, t_{ia}, in eq 2 are calculated by substituting the theoretical values of the polar tensor elements into this equation, whereas the loading values, $b^{(\alpha)}_{a,\sigma\nu}$, are those obtained from eq 1. Individual calculations of the principal component equations for each symmetry species of *cis*-$C_2H_2Cl_2$ and the A_u symmetry species of *trans*-$C_2H_2Cl_2$ are discussed below.

The A_1 symmetry species has five infrared active bands, although only two of these are strong enough to be observed. Since there exist six nonzero and distinct polar tensor elements, the principal component transformation is capable of exactly projecting the six-dimensional polar tensor space onto a bidimensional principal component space. There are only four distinct sign combinations for each of the *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ dipole moment derivatives. As such the data matrix is 8 × 6 for the A_1 species, where each row corresponds to a different sign set alternative for *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$ and the columns correspond to six polar tensor elements. The B_1 symmetry species has four nonzero intensities for both *cis*-$C_2H_2Cl_2$ and $C_2D_2Cl_2$ and six nonequivalent and nonzero polar tensor elements. As such its $\mathbf{X}$ data matrix has dimensions of 32 × 6. The B_2 symmetry species has only one infrared active mode but has three nonzero polar tensor elements. The $\mathbf{X}$ data matrix is 4 × 3, and one principal component exactly represents the polar tensor data of the *cis* isomers of this symmetry species. For the A_u symmetry species of the *trans* isomer there are two active fundamentals and three polar tensor elements. Hence its data matrix, including the *trans*-$C_2D_2Cl_2$ values, is 8 × 3.

TABLE 1: Principal Component Equations for Polar Tensor Elements of *cis*- and *trans*-Dichloroethylene

A_1 Symmetry Species	
$PC_1 \approx -0.81p_{zx}^{(C_1)} - 0.39p_{zz}^{(C_1)} - 0.26p_{zx}^{(Cl_4)} + 0.34p_{zz}^{(Cl_4)}$	53.5%
$PC_2 \approx 0.57p_{zx}^{(C_1)} - 0.47p_{zz}^{(C_1)} - 0.10p_{zz}^{(H_3)} - 0.36p_{zx}^{(Cl_4)} + 0.57p_{zz}^{(Cl_4)}$	46.4%
B_1 Symmetry Species	
$PC_1 \approx -0.30p_{xx}^{(C_1)} + 0.76p_{xz}^{(C_1)} - 0.21p_{xx}^{(Cl_4)} + 0.54p_{xz}^{(Cl_4)}$	70.9%
$PC_2 \approx -0.81p_{xx}^{(C_1)} + 0.31p_{xz}^{(C_1)} + 0.32p_{xx}^{(H_3)} - 0.15p_{xz}^{(H_3)} + 0.33p_{xx}^{(Cl_4)} + 0.13p_{xz}^{(Cl_4)}$	17.3%
$PC_3 \approx -0.51p_{xz}^{(C_1)} + 0.36p_{xx}^{(H_3)} - 0.25p_{xz}^{(H_3)} - 0.42p_{xx}^{(Cl_4)} + 0.60p_{xz}^{(Cl_4)}$	8.4%
B_2 Symmetry Species	
$PC_1 = 0.57p_{yy}^{(C_1)} - 0.79p_{yy}^{(H_3)} + 0.22p_{yy}^{(Cl_4)}$	100%
A_u Symmetry Species	
$PC_1 \approx -0.73p_{yy}^{(C_1)} - 0.69p_{yy}^{(H_4)}$	97.5%
$PC_2 \approx -0.37p_{yy}^{(C_1)} - 0.44p_{yy}^{(H_4)}$	2.5%

Results

***cis*-Dichloroethylene: A_1 Symmetry Species.** The first two principal components are capable of exactly projecting the six dimensional polar tensor space onto two dimensions. These components describe 53.6% and 46.4% of the total APT data variance due to the sign ambiguities in the $\partial\vec{p}/\partial Q_j$ and their equations are given in Table 1. The score graph for these components is shown in Figure 1. The sizes of the symbols in the graph indicate one standard deviation uncertainties in the scores due to estimated errors in the measured intensities. These errors were propagated into the polar tensor values and then into the score values as described previously.[12,13]

No pair of polar tensor score points, one for $C_2H_2Cl_2$ and one for $C_2D_2Cl_2$, overlap each other. At least one overlapping pair of points is expected if the isotopic invariance criterion is obeyed and if the experimental errors are properly estimated. However all pairs of points are in close proximity. If the estimated propagated errors were twice as large (or alternatively if 95% confidence intervals for these errors were used), all isotopic pairs would overlap in Figure 1. For these reasons the isotopic invariance criterion is not helpful in selecting the correct set of signs for the A_1 symmetry $\partial\vec{p}/\ \partial Q_j$. On the other hand, all the *ab initio* results for the scores of the APT elements cluster close to the pair of points corresponding to the (0−0−0) sign set; that is, $\partial\vec{p}/\partial Q_2$ and $\partial\vec{p}/\partial Q_4$ are both negative. The APT element values for *cis*- $C_2H_2Cl_2$ and $C_2D_2Cl_2$ for this sign selection are presented in Table 2. Averages of these values are the best estimates of the A_1 APT elements, and their errors are taken to be the larger of either the standard deviation of the isotopomer results or the propagated errors obtained from the errors in the measured intensities. Along with these values, the theoretical results for the APT element values are included

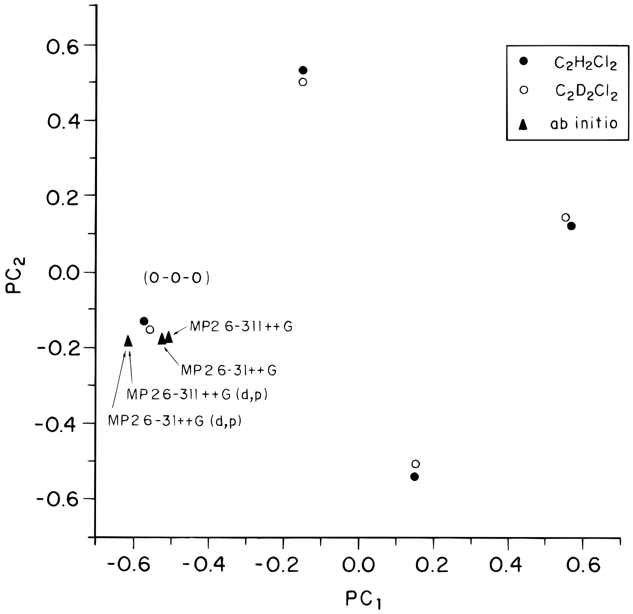

Figure 1. Principal component score graph of the A_1 symmetry species polar tensor element values as a function of the signs of the $\partial\vec{p}/\partial Q_j$ for *cis*-dichloroethylene. This graph contains 100% of the total data variance.

TABLE 2: Experimental and Theoretical APT Values for the A_1 Species of *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ (*e*)[a]

	$P_{ZX}^{(C_1)}$	$P_{ZZ}^{(C_1)}$	$P_{ZX}^{(H_3)}$	$P_{ZZ}^{(H_3)}$	$P_{ZX}^{(Cl_4)}$	$P_{ZZ}^{(Cl_4)}$
signs						
$(0-0-0)^H$	0.392	0.283	0.033	−0.017	0.196	−0.265
$(0-0-0)^D$	0.366	0.290	0.019	−0.017	0.196	−0.273
average	0.379	0.287	0.026	−0.017	0.196	−0.269
standard deviation	0.018	0.004	0.010	0.0	0.0	0.006
propagated error	0.010	0.004	0.001	0.002	0.003	0.003
MP2/6-31++G(d,p)	0.394	0.362	0.013	−0.040	0.166	−0.322
MP2/6-311++G(d,p)	0.394	0.362	0.011	−0.039	0.166	−0.323
MP2/6-31++G	0.323	0.322	0.010	−0.027	0.135	−0.295
MP2/6-311++G	0.311	0.316	−0.002	−0.030	0.127	−0.286

[a] Units of electrons.

in the above table. They are in good agreement with the values of the (0−0−0) set obtained from the measured intensities.

***cis*-Dichloroethylene: B_1 Symmetry Species.** The first two principal components of this symmetry species explain 88.2% of the total polar tensor data variance. The score graph using these components to define the coordinate axes is presented in Figure 2. Two pairs of points overlap, indicating isotopically invariant polar tensor elements, one on the extreme right of the figure, the other on the extreme left. However the molecular orbital results cluster close to the pair on the right, the (+--+) sign combination for both $C_2H_2Cl_2$ and $C_2D_2Cl_2$. The APT values for these isotopomers are listed in Table 3 along with the corresponding values for the (---+) sign combination for the pair of points just below the (+--+) pair. Note that the larger distance between the points of the (---+) pair compared with the one for the (+--+) pair is consistent with the larger differences between the APT values in Table 3 for the H and D isotopomers of the (---+) sign set. Preferred APT element values for this symmetry species are taken to be the averages of the values for the (+--+) pair. These values, the standard deviations and propagated errors as well as the theoretical estimates are included in Table 3. Note how the (+--+) element values in this table are in much better agreement with the theoretical ones than are the values for the (---+) set. For this reason the theoretical principal component points cluster around the (+--+) solutions in Figure 2. Although about 12% of the data variance has been lost in projecting the six dimensional polar tensor space onto the two dimensional principal component space, graphical analysis of the latter space permits a secure sign selection for the $\partial\vec{p}/\partial Q_j$ of this symmetry species for *cis*-dichloroethylene.

***cis*-Dichloroethylene: B_2 Symmetry Species.** This symmetry species has only one IR active normal mode, although it contains three unique nonzero APT elements, one for each type of atom in the molecule. These elements are dipole moment derivatives with respect to the *y* Cartesian coordinate that is perpendicular to the molecular plane. The *y* atomic Cartesian coordinates are used to describe the out-of-plane normal coordinate associated with the A_{12} intensity value, and one need only determine the sign of $\partial\vec{p}/\partial Q_{12}$ to determine the three polar tensor element values. One principal component, given in Table 1, is sufficient to describe all of the variance in the APT values. For this reason a principal component graph for this symmetry species is not shown here. Both sets of APT solutions are isotopically invariant within the estimated experimental error. However only the APT solution for $\partial\vec{p}/\partial Q_{12} > 0$ provides results in good agreement with the theoretical APT results as can be seen in Table 4. The APT values for $\partial\vec{p}/\partial Q_{12} < 0$ have magnitudes very similar to the ones in Table 4 but have opposite signs. Since these values are much different than the theoretical values, the negative sign solution for this symmetry species is securely discarded as the incorrect one. Furthermore the principal component score values confirm this conclusion.

***trans*-Dichloroethylene: A_u Symmetry Species.** Since only two IR active bands have A_u symmetry for *trans*-dichloroethylene, two principal components (See Table 1) are sufficient to describe all the data variance in the corresponding APT element values. The first principal component describes 97.5% of the variance, reflecting the large intensity of the ν_6 mode. The second component explains only 2.5% of the total variance since the $\partial\vec{p}/\partial Q_7$ absolute magnitude is much smaller than the $\partial\vec{p}/\partial Q_6$ one and data variations owing to sign changes in the latter value are much larger than those for the former. The two-dimensional PC graph for this symmetry species is shown in Figure 3. Two pairs of points, one for $C_2H_2Cl_2$ and the other for $C_2D_2Cl_2$, overlap. However only the pair corresponding to the (++) sign combination is close to the theoretical score points. As such the average of the (++) results is chosen to provide the preferred out-of-plane APT elements for *trans*-dichloroethylene. These values, along with the estimated errors and theoretical values have been included in Table 5.

Discussion

The preferred polar tensor element values in Tables 2−5 are similar to those determined some years ago based on the isotopic invariance criterion and semi-empirical CNDO estimates.[1] All the signs of the $\partial\vec{p}/\partial Q_j$ for the A_1 and B_2 symmetry species of *cis*-dichloroethylene are identical to those chosen previously using CNDO results. The only difference in sign attribution between the previous and present work involves the $\partial\vec{p}/\partial Q_8$ derivative of the B_1 symmetry species. Here our analysis clearly indicates the (+--+) sign attributions to be the correct ones, whereas previously the (---+) set was chosen. As such, the largest differences for the polar tensor element values chosen here from the ones reported earlier[1] occur for the B_1 symmetry elements occupying the first row of the polar tensor corresponding to changes in the *x*-component of the dipole moment.

The values of the polar tensor invariants,[14] atomic mean dipole moment derivatives (p_α), anisotropies (β_α^2), and effective charges (χ_α) for the new set of preferred signs are shown in Table 6. These values are similar to the invariant values determined previously.[1] For example, the 0.160*e*, 0.047*e*, and

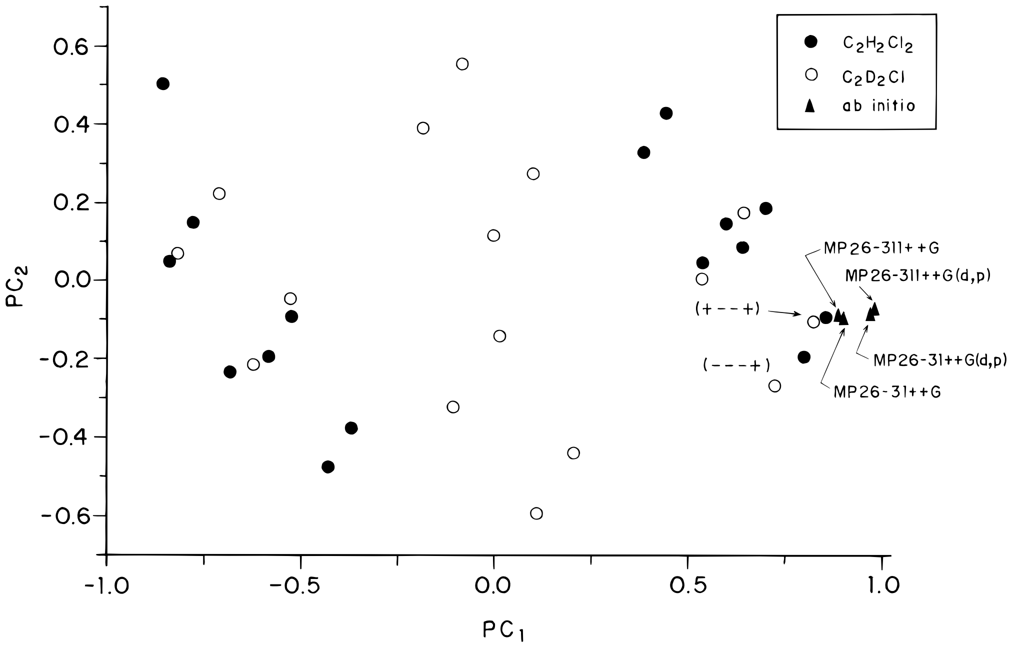

Figure 2. Principal component score graph of the B_1 symmetry species polar tensor element values as a function of the signs of the $\partial\bar{p}/\partial Q_j$ for *cis*-dichloroethylene. This graph contains 88% of the total data variance.

TABLE 3: Experimental and Theoretical APT Values for the B_1 Species of *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ (*e*)[a]

	$P_{XX}^{(C_1)}$	$P_{XZ}^{(C_1)}$	$P_{XX}^{(H_3)}$	$P_{XZ}^{(H_3)}$	$P_{XX}^{(Cl_4)}$	$P_{XZ}^{(Cl_4)}$
signs						
$(+--+)^H$	0.298	0.614	0.003	0.052	−0.300	0.380
$(+--+)^D$	0.299	0.575	0.017	0.064	−0.316	0.378
$(---+)^H$	0.371	0.496	−0.068	−0.070	−0.303	0.383
$(---+)^D$	0.409	0.386	−0.088	−0.117	−0.321	0.378
average[b]	0.299	0.595	0.010	0.058	−0.308	0.379
standard deviation	0.001	0.028	0.010	0.008	0.011	0.001
propagated error	0.009	0.015	0.005	0.005	0.006	0.012
MP2/631++G(d,p)	0.329	0.719	0.006	0.056	−0.335	0.415
MP2/6-311++G(d,p)	0.321	0.722	0.013	0.055	−0.334	0.429
MP2/6-31++G	0.322	0.689	−0.013	0.059	−0.309	0.330
MP2/6-311+G	0.312	0.685	−0.012	0.055	−0.300	0.327

[a] Units of electrons. [b] Average and standard deviations of the (+--+) results.

TABLE 4: Experimental and Theoretical APT Values for the B_2 Species of *cis*-$C_2H_2Cl_2$ and *cis*-$C_2D_2Cl_2$ (*e*)[a]

	$P_{YY}^{(C_1)}$	$P_{YY}^{(H_3)}$	$P_{YY}^{(Cl_4)}$
signs			
$(+)^{H,b}$	−0.106	0.147	−0.041
$(+)^D$	−0.106	0.147	−0.041
average	−0.106	0.147	−0.041
standard deviation	0.0	0.0	0.0
propagated error	0.003	0.001	0.002
MP2/6-31++G(d,p)	−0.168	0.188	−0.019
MP2/6-311++G(d,p)	−0.172	0.185	−0.013
MP2/6-31++G	−0.174	0.218	−0.045
MP2/6-311++G	−0.171	0.215	−0.044

[a] Units of electrons. [b] The polar tensor elements of both sets of values, $(+)^H$ and $(+)^D$, are identical since band separation for *cis*-$C_2D_2Cl_2$ was performed by transference of polar tensor elements from its H-isotopomer.

−0.206*e* values found here for $\bar{p}_C$, $\bar{p}_H$, and $\bar{p}_{Cl}$, respectively, can be compared with 0.182*e*, 0.021*e*, and −0.203*e* values obtained previously. These atomic mean dipole moment derivatives sum to zero, as required owing to the electrical neutrality of the molecule.

It is of interest to compare the invariant values obtained for *cis*-$C_2H_2Cl_2$ to those for *cis*-$C_2H_2F_2$, also presented in Table 6. Recently it has been suggested that the atomic mean dipole moment derivatives can be interpreted as atomic charges.[15,16] The values for the $\bar{p}_\alpha$ values in Table 6 support this argument. The $\bar{p}_{Cl}$ value for *cis*-$C_2H_2Cl_2$, −0.206*e*, is less negative than the $\bar{p}_F$ value of −0.372*e* for *cis*-$C_2H_2F_2$. This ordering can be expected since fluorine is much more electronegative than chlorine. For this same reason one expects the $\bar{p}_H$ and $\bar{p}_C$ values for *cis*-$C_2H_2F_2$, +0.059 and +0.313*e*, respectively, to be more positive than the analogous values for *cis*-$C_2H_2Cl_2$, +0.047*e* and +0.160*e*. The absolute values of the effective charge invariant, $|\chi_\alpha|$, present the same ordering as found for the mean dipole moment derivatives. However these values are not convenient to interpret as atomic charges since there exists a sign ambiguity problem in their determination. Even if electronegativity arguments are used to attribute signs to these quantities (for example, use of the sign of the $\bar{p}_\alpha$ values as the signs of χ_α), the atomic effective charge values of the *cis*-$C_2H_2Cl_2$ or *cis*-$C_2H_2F_2$ molecules do not sum to zero. The atomic anisotropy values are more difficult to interpret. It is interesting though that the β_C^2 and β_H^2 values are almost identical for these fluorine- and chlorine-containing molecules. Of course, the β_F^2 and β_{Cl}^2 values are quite different, as expected.

The *cis*-$C_2H_2Cl_2$ polar tensor determined previously based on the CNDO APT results was shown to be transferable to the *trans* isomer for the purpose of predicting its intensities. In our study this transference procedure has been repeated using the APT elements preferred in this study. In Table 7 the measured fundamental intensity values of *trans*-dichloroethylene are compared with those obtained by transference of the preferred *cis* isomer atomic polar tensors determined here. With the exception of the ν_{11} intensity, the calculated intensities are in excellent agreement with the experimental values. Included in Table 7 are fundamental intensity values calculated using a MP2/6-311++G(d,p) wave function. These results are not in as good agreement with the experimental values as are those obtained by the transference procedure.

The success of this transference procedure is consistent with the results of several direct experimental measurements. The fundamental intensity sums for the *cis*- and *trans*-$C_2H_2Cl_2$ isomers are very similar, 180.3 and 168.6 km mol^{-1}, respec-

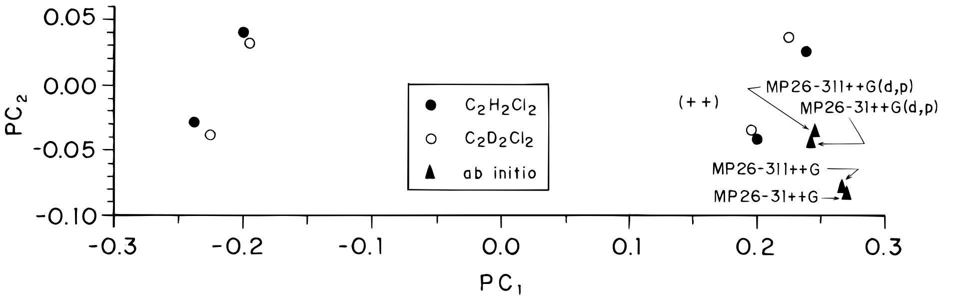

Figure 3. Principal component score graph of the A_u symmetry species polar tensor element values as a function of the signs of the $\partial\bar{p}/\partial Q_j$ for *trans*-dichloroethylene. This graph contains 100% of the total data variance.

TABLE 5: Experimental and Theoretical APT Values for the A_u Species of *trans*-$C_2H_2Cl_2$ and *trans*-$C_2D_2Cl_2$ (*e*)[a]

	$p_{zz}^{(C_1)}$	$p_{zz}^{(H_4)}$	$p_{zz}^{(Cl_3)}$
signs			
$(+\,+)^H$	−0.183	0.150	0.033
$(+\,+)^D$	−0.177	0.138	0.039
average	−0.180	0.144	0.036
standard deviation	0.004	0.008	0.004
propagated error	0.006	0.004	0.004
MP2/6-31++G(d,p)	−0.161	0.185	−0.024
MP2/6-311++G(d,p)	−0.165	0.183	−0.018
MP2/6-31++G	−0.165	0.221	−0.055
MP2/6-311++G	−0.165	0.217	−0.053

[a] Units of electrons.

TABLE 6: Atomic Mean Dipole Moment Derivatives, Anisotropies, and Effective Charges of *cis*-Dichloro- and *cis*-Difluoroethylene (*e*)

	cis-dichloroethylene	*cis*-difluoroethylene
$\bar{p}_C$	0.160	0.313
$\lvert\chi_C\rvert$	0.476	0.551
β_C^2	0.906	0.927
$\bar{p}_H$	0.047	0.059
$\lvert\chi_H\rvert$	0.095	0.104
β_H^2	0.031	0.034
$\bar{p}_X$	−0.206	−0.372
$\lvert\chi_X\rvert$	0.342	0.548
β_X^2	0.336	0.727

[a] Units of electrons. X = F or Cl.

TABLE 7: Experimental and Calculated Fundamental Intensities of *trans*-$C_2H_2Cl_2$ (km mol^{-1})

sym. species	i	ν_i (cm^{-1})	A_i (expt)	A_i (transfer)	A_i (MO)[a]
B_u	9	3090	10.5	10.1	15.8
	10	1200	16.7	14.7	19.6
	11	817	93.3	69.7	117.1
	12	245	0.1	0.2	3.0
A_u	6	895	48.0	44.7	69.1
	7	226	0.2	0.4	0.1

[a] MP2/6-311++G(d,p) molecular orbital calculation.

tively. The $C_2D_2Cl_2$ isomers also have similar fundamental sums, 147.4 and 129.5 km mol^{-1}. Similar intensity sums are expected for these isomers if their effective charges, χ_α, are the same[17] since the rotational corrections to the intensity sums for these isomers are very similar. Identical effective charge values result when the sums of the squares of the APT elements are equal. Transferable APTs will have equal tensor elements and hence equivalent effective charges.

Recently our group has shown that the carbon 1s electron ionization energies are related to the carbon mean dipole moment derivatives[18] by the simple potential model proposed by Siegbahn and co-workers.[19] In terms of mean dipole moment derivatives, $\bar{p}_\alpha$, the carbon 1s electron binding energy, $E_{1s,C}$ can be expressed as

$$E_{1s,C} = k_C\,\bar{p}_c + \sum \bar{p}_A/r_{AC}$$

where r_{AC} represents the internuclear distance between atoms A and C and k_C is a proportionality constant identified with the average Coulombic interaction between an electron in the 1s core orbital and another in a valence orbital of the carbon atom. The sum is taken over all the atoms in the molecule except for the atom from which the electron has been removed during the ionization process. If the mean dipole moment derivatives are the same for both isomers, which would be the case for transferable tensors, and if the *cis* and *trans* internuclear distances and bond angles are about the same, as is probably correct considering the available structural data, the above equation leads to the conclusion that the carbon 1s ionization energies in the *cis* and *trans* isomers should be the same. This is indeed true; the *cis* and *trans* 1s carbon electron binding energies determined by ESCA are 292.31 and 292.41 eV, respectively, both values with estimated experimental errors of 0.1 eV. This contrasts with the carbon 1s ionization energies observed for the 1,1-$C_2H_2Cl_2$, 290.93 and 293.62 eV. It is interesting that the average of the 1s ionization energies of the carbon atoms in the vicinyl isomer, 292.28 eV, is almost identical to the *cis* and *trans* carbon ionization energies.

The 2s electron binding energies observed by ESCA for the chlorine atoms in the *cis*, *trans*, and *vicinyl* isomers are also about the same, 277.76, 277.77, and 277.90 eV, respectively. Small differences could be expected for these values since the neighboring atom electrostatic potentials for the molecules, $\Sigma\bar{p}_A/r_{AC}$, would be slightly different even if these molecules had identical chlorine atom mean dipole moment derivatives. Further evidence that these mean dipole moment derivatives are the same come from the chlorine $2p_{3/2}$ electron binding energies also measured by X-ray photoelectron spectroscopy. Values of 206.80, 206.82, and 206.84 are reported for the dichloroethylenes.

On the other hand, small differences in the values of the *cis*- and *trans*-dichloroethylene polar tensor elements can be observed in Tables 4 and 5 for the carbon and chlorine out-of-plane APT values. In our recent study[7] of the APTs of *cis* and *trans* difluoroethylene it was shown that although their in-plane elements are transferable, this is not the case for the out-of-plane elements. The out-of-plane intensity sum for *trans*-$C_2H_2F_2$ of 69.4 km mol^{-1} is almost twice the *cis*-$C_2H_2F_2$ out-of-plane sum of 39.0 km mol^{-1}. The similar in-plane APT values of these difluoroethylene isomers was attributed to similar charge flux contributions, whereas the different out-of-plane APT values were related to slightly different fluorine (and carbon) atomic charge values that are very dominant over the charge flux contributions for the out-of-plane vibrations. These differing charge values were found to be consistent with the small differences in the CF bond distances and CCF angles in these isomers. The CF bond distance in the *trans* isomer is 0.015 Å longer and the CCF angle 2.9° smaller than the values found in the *cis* isomer.[20] An increase in p character can be expected to result in a larger negative charge on the fluorine atoms in the *trans*-$C_2H_2F_2$ isomer, which can be expected to contribute to the higher out-of-plane intensity sum of this isomer. Similar geometrical differences are found for the *cis*- and *trans*-dichloroethylenes.[21] The *trans*-dichloroethylene C−Cl bond is 0.008 Å longer and the Cl−C−C angle 3.1° smaller than the corresponding values in the *cis* isomer. Although the *cis*- and *trans*-$C_2H_2Cl_2$ and -$C_2D_2Cl_2$ out-of-plane intensity values seem to be consistent with this interpretation, uncertainties in band separations to obtain these values do not permit its confirmation. On the other hand, molecular orbital calculations performed in this work predict larger out-of-plane intensity sums for the *trans* isomers. Furthermore they are also consistent with the above argument since they predict more negative chlorine (Mulliken) charges for the *trans* form.

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