QTAIM Charge−Charge Flux−Dipole Flux Models for the Infrared Fundamental Intensities of Difluoro- and Dichloroethylenes

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A quantum theory of atoms in molecules (QTAIM) charge−charge flux−dipole flux (CCFDF) decomposition of the MP2/6-311++G(3d,3p) level molecular dipole moment derivatives is reported for the *cis*-, *trans*-, and 1,1-difluoroethylenes and the *cis*- and *trans*-dichloroethylenes. Although the dipole moment derivatives and infrared fundamental intensities calculated at the MP2 level are overestimated for high-intensity bands corresponding to CF and CC stretching vibrations, the overall agreement is good with a root-mean-square (rms) error of 19.6 km mol^{-1} for intensities ranging from 0 to 217.7 km mol^{-1}. The intensities calculated from the QTAIM/CCFDF model parameters are in excellent agreement with those calculated directly by the MP2/6-311++G(3d,3p) approach with only a 1.8 km mol^{-1} rms error. A high negative correlation ($r = -0.91$) is found between the charge flux and dipole flux contributions to the dipole moment derivatives. Characteristic values of charge, charge flux, and dipole flux contributions are found for CF, CCl, and CH stretching derivatives. The CH stretching derivatives provide especially interesting results with very high charge flux and dipole flux contributions with opposite signs. The charge, charge flux, and dipole flux contributions are found to be transferable from the cis to the trans isomers providing accurate predictions of the theoretical trans intensities with rms errors of 8.6 km mol^{-1} for *trans*-difluoroethylene and 5.9 km mol^{-1} for *trans*-dichloroethylene.

Introduction

Recent studies[1−3] have shown that charge−charge flux−dipole flux (CCFDF) decompositions of molecular dipole moment derivatives are very accurate and provide an attractively simple interpretation of the changes in electronic densities during molecular vibrations. Such CCFDF models can be used to estimate infrared intensities using atomic charges, their fluxes, and fluxes of atomic dipoles. These decompositions have been studied for some diatomic molecules and most linear polyatomic molecules for which experimental infrared gas-phase fundamental intensities are available and for some simple polyatomic molecules, water, formaldehyde, and methane.[1] Most recently the fluorochloromethane family was investigated.[3] Several interesting results were obtained. The most intriguing was a negative correlation between the charge flux and the dipole flux. This was interpreted as a relaxation effect involving the atomic dipoles that accompany the charge flux in a molecule as it vibrates. Electron transfer from one part of the molecule to another during the vibration is compensated by changes in the polarizations of the electron cloud in the opposite direction. For infrared intensity applications the latter are adequately described by changes in the atomic dipoles and their fluxes are seen to be important for determining molecular dipole moment changes during vibrations. Another result found for the fluorochloromethanes and deserving further investigation was the use of charge, charge flux, and dipole flux contributions to discriminate between CH, CF, and CCl characteristic stretching vibrations.

In this paper a detailed CCFDF study of the difluoro- and dichloroethylenes is given. Besides investigating the characteristic values of the charge, charge flux, and dipole flux contributions and the negative correlation between the two fluxes, the transferability of these contributions between the cis and trans isomers is tested for difluoro- and dichloroethylenes. Previous studies[4−6] have demonstrated that the polar tensor elements obtained from the experimental intensities of *cis*-$C_2H_2F_2$ and *cis*-$C_2H_2Cl_2$ can be transferred to their trans isomers permitting relatively accurate estimates of their measured intensities. This is important because the C_{2h} symmetry of the trans isomers does not permit a direct determination of their polar tensor elements. The root-mean-square (rms) error for intensities calculated by the transference procedure in relation to the measured intensities[7] for both *trans*-difluoro- and *trans*-dichloroethylenes is 8.4 km mol^{-1}. Since the cis and trans tensor elements are so transferable, it seems of interest to determine whether the charge, charge flux, and dipole flux contributions are also transferable or if the tensor element values result from fortuitous combinations of these contributions.

As in our previous studies the quantum theory of atoms in molecules (QTAIM) developed by Bader and collaborators[8,9] has been used to calculate atomic charges and atomic dipoles of the *cis*-, *trans*-, and 1,1-difluoroethylenes and the *cis*- and *trans*-dichloroethylenes. The fundamental intensities of these molecules were measured in the gas phase by Overend's group and were reported in the 1980s.[7,10−12] In addition, Tanabe and Saeki[13] measured the absolute gas phase intensities of the dichloroethylene isomers. The absolute intensity measurements of these two groups are the only gas phase ones that have been

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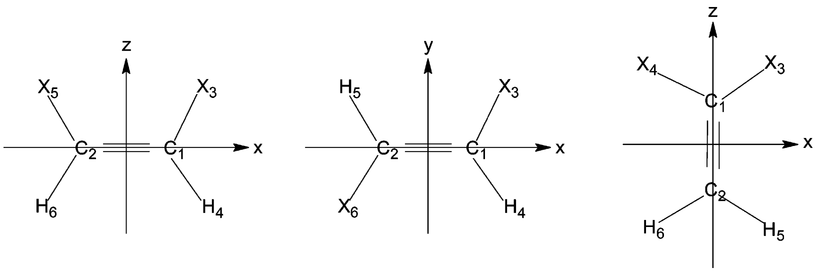

Figure 1. Cartesian coordinate systems and atom numbering schemes for the cis, trans, and 1,1 isomers.

reported for cis and trans isomers and for this reason are especially important for understanding the changes in electronic structures during molecular vibrations.

Calculations

The atomic charges and dipoles and their derivatives are related to the molecular dipole moment and its derivatives by eqs 1−3 of ref 3. The relations between the polar tensor elements,[14,15] dipole derivatives with respect to atomic Cartesian coordinates, and the derivatives with respect to normal coordinates[16] and their respective fundamental intensities[17] are given by eqs 4−10 of this same reference.

Calculations to optimize molecular geometries were executed on a DEC ALPHA workstation using the Gaussian 98 program[18] at the MP2/6-311++G(3d,3p) level. The Cartesian coordinate systems, molecular orientations, and atom numbering schemes of the molecules are shown in Figure 1. Cartesian coordinates of these optimized geometries were used to calculate the vibrational frequencies and the QTAIM atomic charges and dipoles. Average charge and dipole fluxes were calculated from differences in the QTAIM parameters obtained with atoms displaced by ±0.01 Å along each Cartesian axis relative to their positions of the optimized geometry. Normal coordinates from the vibrational frequency calculations of the Gaussian program were used to convert the polar tensors into derivatives with respect to normal coordinates using a FORTRAN program written in our laboratory. The squares of these derivatives were used to obtain the calculated intensities.

Numerical errors in the values of the atomic charges and dipoles and their derivatives can be expected to come from two main sources. The first arises from the numerical integrations within the atomic basins to give the atomic charges and dipoles. To check the numerical precision of the Gaussian results for these quantities, we have compared them with values calculated from a recently acquired MORPHY program.[19] Water was chosen as a test molecule since the Gaussian program calculates atomic charges and dipoles that result in a molecular dipole estimate 0.09 D smaller than the experimental value of 1.91 D. This discrepancy, along with the one found for the HF molecule, is about 10 times larger than those encountered for the dipole moments of other molecules[1−3] including the difluoroethylenes, as will be seen below. Applying the MORPHY program to the same MP2 electronic density information for water provides atomic charges and dipoles that result in a 1.905 D estimate of the molecular dipole moment that is correct within experimental error. Whereas both the Gaussian AIM subroutine and MORPHY furnish atomic charges that are in agreement within 0.00001*e*, there are rather large differences in the atomic dipoles obtained from these programs. The charge fluxes calculated with Gaussian were also found to be in agreement within 0.00001*e* with those obtained from MORPHY. However, the root-mean-square difference in dipole fluxes calculated by these programs for water was found to be ±0.03*e*. One can expect smaller differences in the dipole fluxes calculated by the two programs for the difluoro- and dichloroethylenes. The Gaussian AIM parameters for water provide infrared intensity estimates that have a root-mean-square error of 17.8 km mol^{-1} compared with those calculated directly from the electronic wave function. This is much larger than the error of 2.3 km mol^{-1} found for the water intensities using the MORPHY AIM parameters or the 1.8 km mol^{-1} error found for the dihaloethylene intensities using the Gaussian AIM parameters, as will be discussed later.

A second error source involves using the finite difference formula for nuclear displacements of ±0.01 Å from equilibrium in calculating the charge and dipole fluxes. This amplitude has been long used for calculating dipole moment derivatives for infrared intensities[20] since it is on the same order of magnitude as a molecular vibration. To check this approximation, all the 1,1-$C_2H_2F_2$ derivatives were calculated using alternative displacements of 0.005, 0.001, and 0.0005 Å. Compared with the 0.01 Å results, the largest deviations observed in the charge and dipole fluxes were ±0.02*e*, but most values agreed within ±0.01*e*. For this reason the derivatives reported here are given with two significant digits after the decimal. Indeed the linear approximation appears to work very well for the vibrations of the molecules studied here.

Results

The MP2/6-311++G(3d,3p) optimized geometries are in excellent agreement with the experimental values. The CC, CH, CF, and CCl calculated bond lengths are within 0.01 Å of the measured values.[21−23] The differences between calculated and experimental angles are about 1°.

Table 1 contains the experimental[21,22,24,25] dipole moments for the cis, trans and 1,1 molecules along with those calculated directly from the MP2/6-311++G(3d,3p) electronic densities and the QTAIM values obtained from these same densities. The agreement is excellent with discrepancies of less than 0.1 D. The atomic charge and dipole contributions to the total calculated QTAIM molecular dipole moments have also been included in this table. The atomic dipole contributions are important especially for the difluoroethylenes with contributions of 4.71 and 5.00 D for the 1,1 and cis isomers, respectively. However, the charge contributions are dominant and of opposite sign for these molecules. The QTAIM atomic charges and atomic dipoles used to calculate the charge and dipole contributions to the QTAIM molecular dipole moments are included in the table.

The experimental IR fundamental intensities[7,10−12] along with those calculated directly at the MP2/6-311++G(3d,3p) level and those calculated from the MP2/6-311++G(3d,3p) QTAIM/CCFDF parameters for the difluoro- and dichloroethylenes are given in graphical form in Figure 2, which allows a comparison of these results. The numerical values are given as Supporting Information. The intensities calculated directly with the MP2/6-311++G(3d,3p) approach have a root-mean-square (rms)

TABLE 1: QTAIM/MP2/6-311++G(3d,3p) Atomic Charges and Atomic Dipoles, QTAIM/MP2/6-311++G(3d,3p), MP2/6-311++G(3d,3p), and Experimental Molecular Dipole Moments of the $C_2H_2X_2$ (X = Cl or F) Molecules

	cis-$C_2H_2Cl_2$	*trans*-$C_2H_2Cl_2$	1,1-$C_2H_2F_2$	*cis*-$C_2H_2F_2$	*trans*-$C_2H_2F_2$
q_C (*e*)	0.11	0.11	1.11, 0.08	0.58	0.58
q_H (*e*)	0.06	0.07	0.05	0.06	0.06
q_F (*e*)			−0.64	−0.64	−0.64
q_{Cl} (*e*)	−0.17	−0.18			
$m_{C,z}$ (D)	0.53	0.00	2.69, 0.81	1.67	0.00
$m_{H,z}$ (D)	0.29	0.00	0.16	0.27	0.00
$m_{F,z}$ (D)			0.44	0.56	0.00
$m_{Cl,z}$ (D)	−0.33	0.00			
p_q(QTAIM) (D)	−2.79	0.00	−6.03	−7.43	0.00
p_m(QTAIM) (D)	0.98	0.00	4.71	5.00	0.00
p(QTAIM) (D)	−1.81	0.00	−1.33	−2.43	0.00
p(MP2) (D)	−1.82	0.00	−1.34	−2.42	0.00
$\|p(\text{exp})\|$ (D)	1.89	0.00	1.37	2.42	0.00

error of 19.6 km mol^{-1} relative to the experimental values that range from 0 to 217.7 km mol^{-1}. Intensities calculated from the QTAIM/CCFDF parameters are in excellent agreement with those calculated directly from the MP2 electronic densities, with only a 1.8 km mol^{-1} rms error. Discrepancies between experimental and theoretical values are notable for the strong bands, especially the 1728 cm^{-1} band of the C═C stretch of 1,1-$C_2H_2F_2$ and the 1160 and 1302 cm^{-1} bands associated with the CF stretches of the trans and 1,1 isomers, respectively. The theoretical values overestimate the experimental values by up to 80 km mol^{-1}. The MP2/6-311++G(3d,3p) results are also systematically larger than the experimental values for bands of intermediate intensities, between 50 and 150 km mol^{-1}. However weak bands, with intensities less than 50 km mol^{-1}, are in good agreement with measured values. These discrepancies are similar to those reported previously for intensity sums of a larger group of molecules where experimental sums were systematically smaller than those calculated at the MP2/6-311++G(3d,3p) level for molecules with large intensity sums (above 200 km mol^{-1}). On the other hand, molecules with smaller intensity sums had theoretical values that were randomly different from the experimental sums.[26]

The largest source of error in the measured intensity value of the 1302 cm^{-1} band for 1,1-$C_2H_2F_2$ is due to the overlapping 1360 cm^{-1} band. The total intensity measured for this band system was 190.1 km mol^{-1}, and all of this was attributed to the 1302 cm^{-1} band. The MP2/6-311++G(3d,3p) result predicts a 235.7 km mol^{-1} total intensity for the band system which is 20% higher than the experimental value. However, the theoretical results confirm the band separation made in the experimental work[21] since the lower frequency band was estimated to be 50 times more intense than the high frequency one.

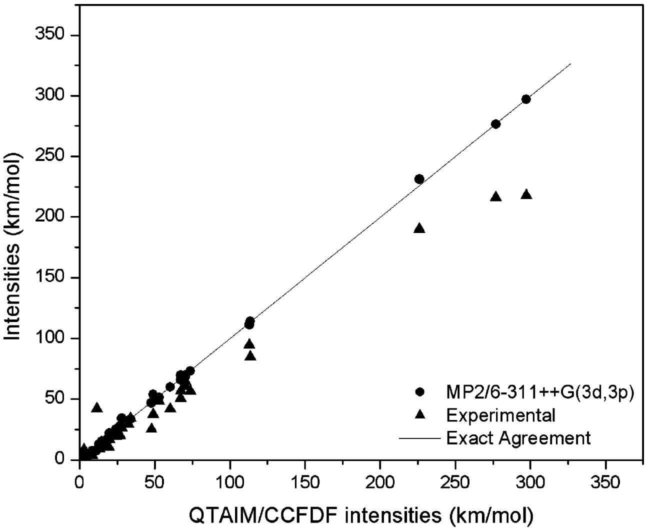

Figure 2. Comparison of infrared fundamental intensities obtained from QTAIM/CCFDF/MP2/6-311++G(3d,3p) with those calculated directly from the electronic density at the MP2/6-311++G(3d,3p) level and experimental ones.

Discrepancies between experimental and theoretical intensity values, 79.2 km mol^{-1} for the $\nu = 1160$ cm^{-1} band of *trans*-$C_2H_2F_2$ and 60.5 km mol^{-1} for the $\nu = 1728$ cm^{-1} band of 1,1-$C_2H_2F_2$, are much larger than the reported experimental errors of 4.4 and 4.3 km mol^{-1}. There are no neighboring bands overlapping these, so the differences are not easily explained.

Table 2 contains the charge, charge flux, and dipole flux contributions to the total dipole moment derivatives with respect to the normal coordinates of all five molecules. Any one of the three derivative contributions can be predominant depending on the molecule and the form of the normal coordinate. Large charge flux contributions are often accompanied by large dipole flux contributions of opposite sign. Figure 3 contains a graph of the charge flux contributions vs the dipole flux contributions for all normal modes. The correlation coefficient for these two contributions is −0.91, indicating a highly negative linear relation between the fluxes. On the other hand, the correlations between the charge and these two fluxes are small, 0.14 and −0.16.

The CH stretching vibrations have large flux contributions with charge flux values between 0.4*e* and 0.5*e* being canceled by dipole fluxes of the same size but of opposite signs. Large charge contributions are found for some of the CF stretches and bends with values up to 0.2*e*.

Discussion

A negative correlation of −0.97 between the charge flux and dipole flux values has already been observed for diatomic and polyatomic linear molecules plus methane, water, and formaldehyde.[1] In another study a −0.92 coefficient was observed for the fluorochloromethanes.[3] The correlation coefficient calculated here is very similar, −0.91. These correlations can be interpreted as a relaxation effect of the atomic dipoles provoked by intramolecular charge transfer. Electron transfer from one side of the molecule to the other during molecular vibrations is accompanied by electron density polarization in the opposite direction.

A detailed examination of the charge, charge flux, and dipole flux contributions for the fluorochloromethane vibrations showed that the CF, CCl, and CH stretching vibrations are characterized by distinct ranges of values. Here these contributions to the dipole moment derivatives of the difluoro- and dichloroethylenes are examined.

TABLE 2: QTAIM Charge (*C*), Charge Flux (CF), and Dipole Flux (DF) Contributions to Dipole Moment Derivatives for Normal Modes of $C_2H_2X_2$ (X = F or Cl) Molecules in Units of Electrons (*e*)

		$\partial p/\partial Q_i$			
Q_i	vibration	C	CF	DF	total
		cis-$C_2H_2Cl_2$			
Q_1	ν(C−H)	0.03	0.40	−0.44	−0.01
Q_2	ν(C=C)	0.01	−0.11	0.00	−0.10
Q_3	δ(C−H)	0.03	−0.09	0.08	0.02
Q_4	ν(C−Cl)	−0.04	−0.06	0.02	−0.08
Q_5	δ(C−Cl)	−0.01	0.00	0.00	−0.01
Q_8	ν(C−H)	0.02	0.26	−0.19	0.09
Q_9	δ(C−H)	0.03	−0.26	0.14	−0.09
Q_{10}	ν(C−Cl)	−0.02	−0.11	−0.02	−0.15
Q_{11}	δ(C−Cl)	−0.04	−0.04	0.04	−0.04
Q_{12}	δ(C−H)	0.03	0.00	0.10	0.13
		trans-$C_2H_2Cl_2$			
Q_6	δ(C−Cl)	0.04	0.00	0.09	0.13
Q_7	δ(C−Cl)	−0.05	0.00	0.04	−0.01
Q_9	ν(C−H)	0.04	0.47	−0.49	0.08
Q_{10}	δ(C−H)	0.04	−0.26	0.18	−0.08
Q_{11}	ν(C−Cl)	−0.05	−0.16	0.01	−0.20
Q_{12}	δ(C−H)	−0.05	0.02	0.02	−0.03
		1,1-$C_2H_2F_2$			
Q_1	ν(C−H)	0.02	0.29	−0.25	0.06
Q_2	ν(C=C)	−0.15	−0.25	0.10	−0.30
Q_3	δ(C−H)	−0.04	−0.20	0.20	−0.04
Q_4	ν(C−F)	−0.11	0.06	−0.10	−0.15
Q_5	δ(C−F)	−0.11	−0.03	0.10	−0.04
Q_7	ν(C−H)	0.02	0.48	−0.47	0.03
Q_8	ν(C−F)	−0.20	0.21	−0.29	−0.28
Q_9	δ(C−H)	−0.06	0.01	−0.04	−0.09
Q_{10}	δ(C−F)	−0.02	−0.01	0.01	−0.02
Q_{11}	δ(C−H)	0.05	0.00	0.11	0.16
Q_{12}	δ(C−F)	−0.19	0.00	0.18	−0.01
		cis-$C_2H_2F_2$			
Q_1	ν(C−H)	0.00	0.20	−0.15	0.05
Q_2	ν(C=C)	−0.03	0.11	−0.23	−0.15
Q_3	δ(C−H)	0.10	−0.08	0.09	0.11
Q_4	ν(C−F)	−0.14	0.06	−0.07	−0.15
Q_5	δ(C−F)	−0.07	0.00	0.04	−0.03
Q_8	ν(C−H)	0.00	0.47	−0.50	−0.03
Q_9	δ(C−H)	−0.03	−0.12	0.05	−0.10
Q_{10}	ν(C−F)	−0.06	0.04	−0.17	−0.19
Q_{11}	δ(C−H)	−0.04	0.00	0.17	0.13
Q_{12}	δ(C−F)	−0.15	−0.05	0.09	−0.11
		trans-$C_2H_2F_2$			
Q_6	δ(C−H)	0.01	0.00	0.15	0.16
Q_7	δ(C−F)	−0.19	0.01	0.12	−0.06
Q_9	ν(C−H)	0.01	0.51	−0.53	0.07
Q_{10}	δ(C−H)	−0.04	−0.16	0.16	−0.07
Q_{11}	ν(C−F)	−0.19	0.14	−0.23	0.32
Q_{12}	δ(C−F)	−0.19	0.00	0.15	−0.04

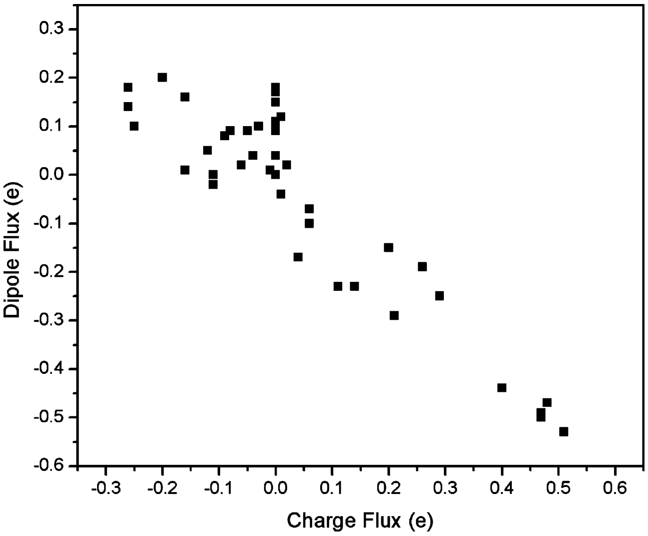

Figure 3. Charge flux vs dipole flux contributions to dipole moment derivatives for normal coordinates of $C_2H_2X_2$ (X = Cl or F) molecules.

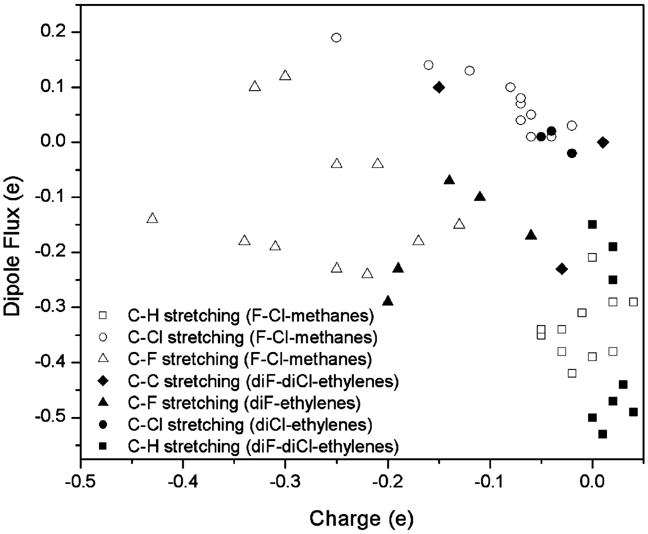

Figure 4. Charge plotted against dipole flux contribution for the stretching modes of $C_2H_2X_2$ (X = Cl or F) molecules and fluorochloromethanes.

Figure 4 shows a graph of the charge vs the dipole flux contributions for the CC, CF, CH, and CCl stretching derivatives. Besides showing points representing the difluoro- and dichloroethylene derivatives, points for the fluorochloromethanes have been included. Since the charge flux and dipole flux values are negatively correlated for both these methanes and ethylenes, a charge vs charge flux graph would be essentially the same as the one in Figure 4 except that the ordinate values would be inverted.

Three clusters of points can be observed in Figure 4. The CF stretching normal coordinates of the difluoroethylenes have relatively large negative charge contributions ranging between −0.06*e* and −0.22*e*. This interval overlaps the one for the CF stretches of the fluorochloromethanes that range between −0.13 and −0.43*e*. The corresponding dipole fluxes for the ethylenes are between −0.07*e* and −0.29*e*, and the charge fluxes are between +0.04*e* and +0.21*e*.

The CCl stretching derivative cluster of points for the methanes and ethylenes are located in the upper-right-hand corner of the graph in Figure 4. These points overlap two of those for the C=C stretching derivatives. Note that the charge contributions of the CCl stretching derivatives for the dichloroethylenes, like those for the CF stretching derivatives for the difluoroethylenes, are mostly smaller than those of the fluorochloromethanes. The CCl stretching charge contributions range from −0.05*e* to −0.02*e*, the charge flux ones range from −0.06*e* to −0.16*e*, and the dipole flux contributions range from −0.02*e* to +0.02*e*.

The CH stretching derivative contributions form a well-defined group of points in the lower-right-hand corner. For both the fluorochloromethanes and the difluoro- and dichloroethylenes the CH contributions have small charge contributions, from 0.00*e* to 0.04*e*, and very large negative dipole flux contributions, from −0.19*e* to −0.53*e*. Since the dipole flux is negatively correlated with the charge flux, the latter values are large and positive, ranging from +0.20*e* to +0.47*e*. However, it is not clear why some CH stretches of the difluoro- and dichloro-

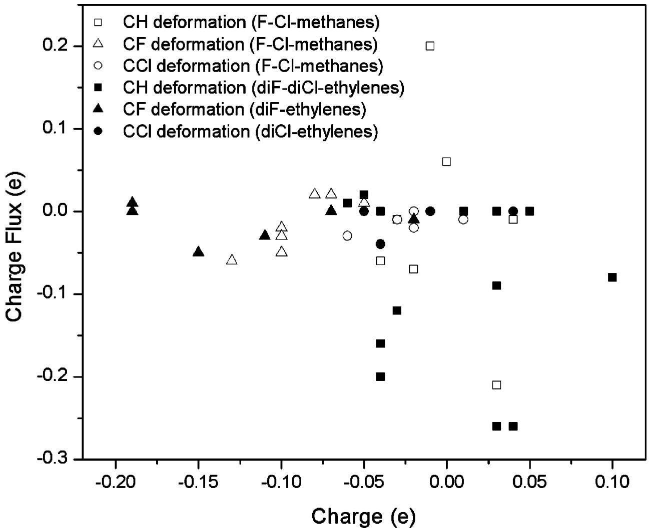

Figure 5. Charge plotted against charge flux contribution for the bending modes of $C_2H_2X_2$ (X = Cl or F) molecules and fluorochloromethanes.

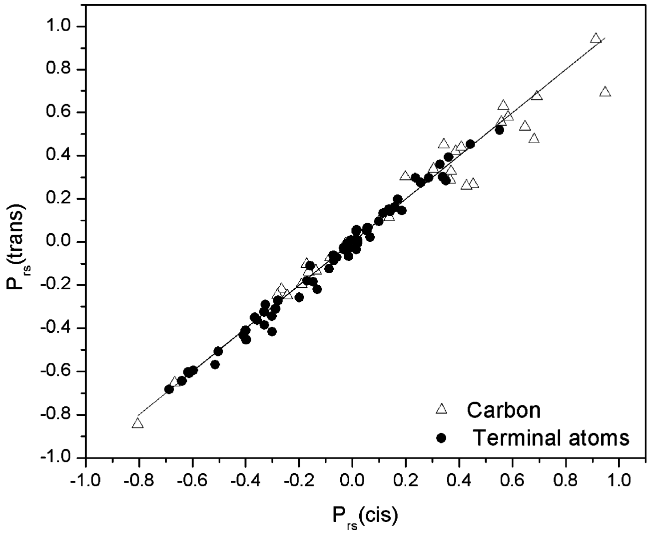

Figure 6. Graph of MP2/6-311++G(3d,3p) charge, charge flux, and dipole flux contributions to dipole moment derivatives of *trans*-dihaloethylenes vs transferred values from their cis isomers.

ethylenes have larger flux contributions than the fluorochloromethanes whereas others have smaller ones.

Figure 5 contains a graph of the CH, CF, and CCl deformations of these molecules. The CF deformation cluster of points with larger negative charge contributions is positioned mostly to the left of the CCl deformation group of points. On the other hand, points for the CH deformations are highly dispersed, overlapping the CCl deformation group and part of the CF deformation cluster.

It has been noted previously that the *cis*-difluoro- and *cis*-dicloroethylene polar tensors obtained from measured fundamental infrared intensities can be transferred to their respective trans isomers and used to obtain accurate estimates of the trans intensities.[4−6] Here transference of the charge, charge flux, and dipole flux derivatives between cis and trans isomers is investigated. The polar tensor elements of the difluoro- and dichloroethylenes used in the transference calculations are provided as Supporting Information. Assuming that electronic density only changes for nearest neighbors and the displaced atom, one can expect these polar tensor contributions to be transferable from one isomer to another. Terminal atoms are expected to have even more transferable polar tensor element contributions than those for carbon since even next-nearest-neighboring atoms to the displaced atom are the same for both isomers. For the molecular orientations and coordinate systems employed here, this means that one can transfer atomic polar tensor element contributions from the cis isomer to the trans one by simply changing the *z*-axis to the *y*-axis and making appropriate sign changes for the off-diagonal tensor elements of the fluorine, carbon, and hydrogen atoms with negative *x*-coordinates. This is necessary since the orientations of their HCF angles are reversed in these two molecules.

The trans tensor element contributions for both difluoro- and dichloroethylenes are plotted against the transferred values from their cis isomers in the graph in Figure 6. Indeed the charge, charge flux, and dipole flux contributions are close to the line, indicating exact agreement as are the total tensor values. Furthermore, the tensor elements for the terminal atoms show significantly better agreement than those for the carbon atoms. The rms errors are 0.088*e* for the carbons and 0.034*e* for the hydrogen, fluorine, and chlorine atoms. The ratio of the squares of these errors, $(0.088/0.034)^2 = 6.7$, is significantly larger than the tabulated $F_{30,60,95\%}$ value of 1.5 at the 95% confidence level. This result is expected if our argument about electronic density changes on nearest- and next-nearest-neighboring atoms as well as on displaced atoms is correct.

The QTAIM/CCFDF tensor element contributions transferred from the cis isomer were used to calculate the intensities of the trans isomers. These estimated intensities are included in the Supporting Information. As can be seen, the agreement is excellent with rms errors of 8.6 km mol^{-1} for the difluoroethylenes and 5.9 km mol^{-1} for the dichloroethylenes relative to the intensities calculated directly from the QTAIM/CCFDF polar tensor contributions of the trans isomers.

Conclusions

The QTAIM/CCFDF model evaluated at the MP2/6-311++G(3d,3p) level indicates that the large negative correlation between the charge and dipole fluxes found for the fluorochloromethanes is also important for the difluoro- and dichloroethylene vibrations. Characteristic values of the charge, charge flux, and dipole flux contributions to the CF, CCl, and CH stretching dipole moment derivatives are similar for these molecules. Furthermore, charge, charge flux, and dipole flux contributions to the polar tensor elements are found to be transferable between the cis and trans isomers of difluoro- and dichloroethylenes.

Both atomic charges and atomic dipoles are found to be important for modeling electronic structures of these methane and ethylene molecules. As such one should consider their use in models for electronic structure changes occurring for the even larger molecular distortions involved in complex chemical phenomena.

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Supporting Information Available: Tables of infrared intensities, QTAIM charge, charge flux, and dipole flux contributions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Haiduke, R. L. A.; Bruns, R. E. *J. Phys. Chem. A* **2005**, *109*, 2680.

(2) César, P. H.; Faria, S. H. D. M.; Viçozo, J. S., Jr.; Haiduke, R. L. A.; Bruns, R. E. *Chem. Phys.* **2005**, *317*, 35.

(3) Viçozo, J. S., Jr.; Haiduke, R. L. A.; Bruns, R. E. *J. Phys. Chem. A* **2006**, *110*, 4839.

(4) Ramos, M. N.; Neto, B. B.; Bruns, R. E. *J. Phys. Chem.* **1985**, *89*, 4979.

(5) Suto, E.; Ramos, M. N.; Bruns, R. E. *J. Phys. Chem.* **1993**, *97*, 6161.

(6) Silva, J. B. P.; Ramos, M. N.; Suto, E.; Bruns, R. E. *J. Phys. Chem. A* **1997**, *101*, 6243.

(7) Kagel, R. O.; Powell, D. L.; Hopper, M. J; Overend, J.; Ramos, M. N.; Bassi, A. B. M. S.; Bruns, R. E. *J. Phys. Chem.* **1984**, *88*, 521.

(8) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(9) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; Macdougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142.

(10) Kagel, R. O.; Powell, D. L.; Overend, J.; Ramos, M. N.; Bassi, A. B. M. S.; Bruns, R. E. *J. Chem. Phys.* **1982**, *77*, 1099.

(11) Kagel, R. O.; Powell, D. L.; Overend, J.; Ramos, M. N.; Bassi, A. B. M. S.; Bruns, R. E. *J. Chem. Phys.* **1983**, *78*, 7029.

(12) Hopper, M. J; Overend, J.; Ramos, M. N.; Bassi, A. B. M. S.; Bruns, R. E. *J. Chem. Phys.* **1983**, *79*, 19.

(13) Tanabe, K.; Saëki, S. *Bull. Chem. Soc. Jpn.* **1974**, 2545.

(14) Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.

(15) Biarge, J. F.; Herranz, J.; Morcillo, J. *An. R. Soc. Esp. Fis. Quim., Ser. A* **1961**, *57*, 81.

(16) Wilson, E. B.; Decius J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.

(17) Overend, J. In *Infrared Spectroscopy and Molecular Structure*; Davis, M., Ed.; Elsevier: New York, 1963; Chapter 10, p 354.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewsk, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liaskenko, A.; Piskorz, P.; Komaroni, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chem, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian Inc.: Pittsburgh, PA, 1998.

(19) MORPHY 98, a program written by P. L. A. Popelier with contributions from R. G. A. Bone, UMIST, Manchester, England, EU, 1998.

(20) Bruns, R. E. Approximate quantum mechanical calculations of infrared and Raman vibrational intensities. In *Vibrational Intensities in Infrared and Raman Spectroscopy*; Person, W. B., Zerbi, G., Eds.; Elsevier: Amsterdam, 1982; Chapter 7.

(21) Roberts, A.; Edgell, W. F. *J. Chem. Phys.* **1949**, *17*, 742.

(22) Laurie, V. W. *J. Chem. Phys.* **1956**, *24*, 635.

(23) *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Sutton, L. E., Ed.; Special Publication 11; Chemical Society: London, 1958.

(24) Margott, A. A.; Hobbs, M. E.; Cross, P. M. *J. Am. Chem. Soc.* **1941**, *63*, 659.

(25) McClellan, A. L. *Table of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963.

(26) Oliveira, A. E.; Haiduke, R. L. A.; Bruns, R. E. *J. Phys. Chem.* **2000**, *104*, 5320.