Quantum Theory of Atoms in Molecules Charge–Charge Flux–Dipole Flux Models for the Infrared Intensities of X_2CY (X = H, F, Cl; Y = O, S) Molecules

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The molecular dipole moments, their derivatives, and the fundamental IR intensities of the X_2CY (X = H, F, Cl; Y = O, S) molecules are determined from QTAIM atomic charges and dipoles and their fluxes at the MP2/6-311++G(3d,3p) level. Root-mean-square errors of ±0.03 D and ±1.4 km mol^{-1} are found for the molecular dipole moments and fundamental IR intensities calculated using quantum theory of atoms in molecules (QTAIM) parameters when compared with those obtained directly from the MP2/6-311++G(3d,3p) calculations and ±0.05 D and 51.2 km mol^{-1} when compared with the experimental values. Charge (C), charge flux (CF), and dipole flux (DF) contributions are reported for all the normal vibrations of these molecules. A large negative correlation coefficient of −0.83 is calculated between the charge flux and dipole flux contributions and indicates that electronic charge transfer from one side of the molecule to the other during vibrations is accompanied by a relaxation effect with electron density polarization in the opposite direction. The characteristic substituent effect that has been observed for experimental infrared intensity parameters and core electron ionization energies has been applied to the CCFDF/QTAIM parameters of F_2CO, Cl_2CO, F_2CS, and Cl_2CS. The individual atomic charge, atomic charge flux, and atomic dipole flux contributions are seen to obey the characteristic substituent effect equation just as accurately as the total dipole moment derivative. The CH, CF, and CCl stretching normal modes of these molecules are shown to have characteristic sets of charge, charge flux, and dipole flux contributions.

Introduction

Gas-phase experimental measurements have been carried out on all the infrared fundamental intensities of only a small number, about 50, of strategically important molecules. Besides diatomic and triatomic molecules, experimental intensities are known for members of the hydrocarbon, fluoromethane, chloromethane, fluorochloromethane, dihaloethylene, and cyanogen families as well as for a few carbonyl and thiocarbonyl compounds. Several intriguing relations involving molecular intensity sums of these molecules have been reported. Person and co-workers reported several relations involving the intensities of the fluorochloromethanes.[1] For example twice the intensity sum for CH_2F_2 (910 km mol^{-1}) is similar to the sum of the CH_4 and CF_4 intensity sums (1054 km mol^{-1}). The difference between these values could be attributed to a rotational contribution for CH_2F_2 and experimental error in the measured intensities. Even more impressive agreement was even found for other sets of molecules. Twice the intensity sum of the CCl_2F_2 molecule of 1615.4 km mol^{-1} is about the same as the sum of all the CCl_3F and CF_3Cl intensities, 1616.0 km mol^{-1}. These observations were later confirmed by simple empirical relations involving the carbon mean dipole moment derivatives determined from the experimental intensities of the halomethanes, some double and triple CC bonded molecules as well as CO_2, OCS and CS_2.[2]

The X_2CY molecules (X = H, F, Cl, Br; Y = O, S) provide an interesting set of molecules to study the effects of substituent changes on intensities. The sum of all the intensities of F_2CO and Cl_2CS of 1241.9 km mol^{-1} is the same within experimental error as the sum for the Cl_2CO and F_2CS intensities, 1250.6 km mol^{-1}.[3] Furthermore, because these molecules all have C_{2v} symmetry, studies need not be restricted to mean dipole moment derivatives and other polar tensor invariant quantities because the X_2CY molecules can be treated using the same relative orientation with respect to a common Cartesian coordinate system. As such, individual polar tensor elements can be compared and related to each other.

In the 1970s it was shown that the atomic polar tensors determined from the experimental fundamental infrared frequencies and intensities of F_2CO, Cl_2CO, F_2CS, and Cl_2CS can be related by[4,5]

$$\mathbf{P}_X^{(\alpha_1)}(Cl_2CO) - \mathbf{P}_X^{(\alpha_2)}(F_2CO) = \mathbf{P}_X^{(\alpha_3)}(Cl_2CS) - \mathbf{P}_X^{(\alpha_4)}(F_2CS)$$

for three cases: (1) $\alpha_1 = \alpha_3 = Cl$; $\alpha_2 = \alpha_4 = F$; (2) $\alpha_1 = \alpha_2 = O$ $\alpha_3 = \alpha_4 = S$; (3) $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = C$. The interpretation of this kind of relation is simple. The effect of substituting F for Cl on the polar tensor elements of the other atoms in the molecule does not depend on whether oxygen or sulfur is the other substituent. This characteristic substituent effect also occurs for oxygen substitution by sulfur when fluorine or chlorine are bonded to carbon. Substituent effects on the carbon atom are quite large because the substituent change involves at least one atom directly bonded to it. The effects on the terminal atoms are much less because the substituent change occurs at a next-nearest neighboring atom. Of course, this sum

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QTAIM Charge−Charge Flux−Dipole Flux Models

J. Phys. Chem. A, Vol. 111, No. 32, 2007 **7871**

rule would be valid if the polar tensor elements of terminal atoms of these molecules were transferable from molecule to molecule.

The polar tensor elements are molecular dipole moment derivatives with respect to atomic Cartesian displacement coordinates that have been used to estimate atomic charges identified by the acronym GAPT (generalized atomic polar tensor).[6] Within the quantum theory of atoms in molecules[7,8] (QTAIM) their interpretation is more complex. Besides having a charge component, the dipole moment derivatives also have charge flux and dipole flux contributions. These fluxes have been shown to be negatively correlated and tend to cancel one another in simple diatomic and triatomic molecules and in the molecules of the fluorochloromethane and difluoro- and dichloroethylene families.[9,10]

Because characteristic substituent shifts are of fundamental interest in chemistry, the QTAIM charge−charge flux−dipole flux (CCFDF) model has been applied to the theoretical analysis of the polar tensor elements of the X_2CY molecules. The principal objective is to determine if the characteristic substituent effect relation above applies to the individual atomic charge, atomic charge flux, and atomic dipole flux contributions as well as it does for the total polar tensor elements. Furthermore, the existence of a negative correlation between the atomic charge and atomic dipole flux contributions of these molecules is investigated and compared with those found for other families of molecules. If these flux contributions indeed cancel the interpretation of mean dipole moment derivatives as atomic charges would be valid. Finally, the values of the CCFDF contributions obtained in this work for the CH, CF, and CCl stretching and HCH, FCF, and ClCCl bending vibrations are compared with those found previously for the fluorochloromethanes and the difluoro- and dichloroethylenes. One might expect these contributions to be more similar to the difluoro- and dichloroethylenes owing to the presence of a common double bond.

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 10. The relations between the polar tensor elements,[11,12] dipole moment derivatives with respect to atomic Cartesian coordinates, and their derivatives with respect to normal coordinates[13] and their respective fundamental intensities[14] are given by eqs 4−10 of this same reference.

The geometry optimization, vibrational frequency, and QTAIM atomic charges and dipoles calculations were executed on a DEC ALPHA workstation using the Gaussian 98 program[15] at the MP2/6-311G++(3d,3p) level. These QTAIM parameters were calculated for the equilibrium geometry and for those geometries obtained with atoms displaced by ±0.01 Å along each Cartesian axis relative to their positions in the optimized geometry. After that, these values were used to calculate the dipole moment derivatives with respect to Cartesian coordinates that were converted to normal coordinates and then the squares of these were used to obtain the calculated intensities. The calculations described above were executed by FORTRAN programs written in our laboratory using the normal coordinate matrices obtained from the vibrational frequency calculation executed by the Gaussian program.

Numerical calculation of charges and dipoles fluxes requires using differences in QTAIM atomic charge and dipole values that are normally much smaller than the charges and dipoles themselves. During the course of our investigation we acquired
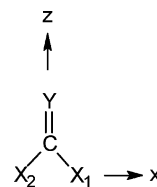

Figure 1. Cartesian coordinate system and atom numbering scheme for the X_2CY molecules.

the MORPHY program[16] so it was decided to check the numerical accuracies of the Gaussian CCFDF results. The MP2/6-311G++(3d,3p) results for H_2CO and F_2CO that had been treated with the Gaussian QTAIM subroutine were then subjected to analysis using the QTAIM algorithm of the MORPHY program.

The QTAIM parameters obtained by Morphy were calculated using a wave function generated with Gaussian. The calculation of dipole moment derivatives in Cartesian coordinates using these parameters was executed by the Placzek program,[17,18] which uses the Hessian matrix obtained from the vibrational frequency calculation of the Gaussian program to convert these derivatives to normal coordinates. After that, the squares of these latter derivatives were used to obtain the calculated intensities.

The charge and dipole flux values calculated from the Gaussian and Morphy programs agree within ±0.01 *e* for the normal coordinates. The agreement between polar tensor element values was not quite as good but was within ±0.05 *e* except in one case, which has a difference of 0.08 *e*.

The Cartesian coordinate system, molecular orientation, and atom-numbering scheme of the molecules are shown in Figure 1.

Results

Compared with the experimental geometries the MP2/6-311++G(3d,3p) calculations provide estimates with root-mean-square (rms) errors within ±0.04 Å for the bond lengths and 1° for the bond angles. Table 1 contains the atomic charges and dipoles of the X_2CY molecules determined from QTAIM. The charges on the fluorines (ranging from −0.61 to −0.63 *e*), chlorines (−0.10 to −0.11 *e*), oxygens (−1.03 to −1.09 *e*), sulfurs (0.42 to 0.45 *e*) and hydrogens (0.00 to 0.08 *e*) are approximately transferable among these molecules. The charges on the carbons are the negatives of the sum of the substituent atoms so the difference between the carbon charges in F_2CO and Cl_2CO (1.07 *e*) is about the same as the difference in F_2CS and Cl_2CS (0.99 *e*). The molecular dipole moments calculated at the MP2/6-311++G(3d,3p) level have a rms error of ±0.05 D in relation to the experimental values.[19−24] The dipole moments calculated from the QTAIM parameters agree within 0.01 D with these theoretical values except for HFCO and F_2CS where the differences are 0.07 D for both molecules.

Note that for HFCO and all the X_2CY molecules large charge contributions to the dipole moment tend to cancel large dipole contributions with opposite signs. The most efficient cancellation occurs for F_2CS where a +8.08 D charge contribution almost exactly cancels a −8.07 D dipole contribution. The value determined by observing the Stark effect of two lines in the microwave spectrum was 0.08 D[21]. Although a very large dipole moment would be predicted owing to the large electronegativity difference between the F and S atoms, as is indeed predicted by the charge contribution to the F_2CS dipole moment, the small 0.01 D calculated value is explained by its cancellation with the atomic dipole contribution.

Figure 2 shows a graph of the theoretical MP2/6-311++ G(3d,3p) and the experimental intensities plotted against the

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 X_2CY (X = Cl, F, H; Y = O, S) Molecules

	H$_2$CO	HFCO	F$_2$CO	Cl$_2$CO	F$_2$CS	Cl$_2$CS
q_C (e)	1.05	1.64	2.33	1.26	0.77	−0.22
q_H (e)	0.00	0.08				
q_F (e)		−0.63	−0.62		−0.61	
q_{Cl} (e)				−0.11		−0.10
q_O (e)	−1.04	−1.09	−1.09	−1.03		
q_S (e)					0.45	0.42
$m_{C,z}$ (D)	2.08	1.33	0.13	1.85	−4.27	−2.30
$m_{H,z}$ (D)	0.22	0.17				
$m_{F,z}$ (D)		−0.34	−0.47		−0.47	
$m_{Cl,z}$ (D)				0.23		0.31
$m_{O,z}$ (D)	1.11	1.37	1.42	1.30		
$m_{S,z}$ (D)					−2.85	−2.83
p_q(QTAIM) (D)	−6.04	−2.88	−1.53	−4.79	8.08	4.19
p_m(QTAIM) (D)	3.64	5.03	0.62	3.61	−8.07	−4.52
p(QTAIM) (D)	−2.40	2.15	−0.91	−1.18	0.01	−0.33
p(MP2) (D)	−2.40	2.09	−0.91	−1.19	0.01	−0.32
$|p$(exp)$|$ (D)	2.33 ± 0.02	2.02 ± 0.02	0.95 ± 0.01	1.18 ± 0.01	0.08 ± 0.001	0.28 ± 0.02

[a] Reference 19. [b] Reference 20. [c] Reference 21. [d] Reference 22. [e] Reference 23. [f] Reference 24.
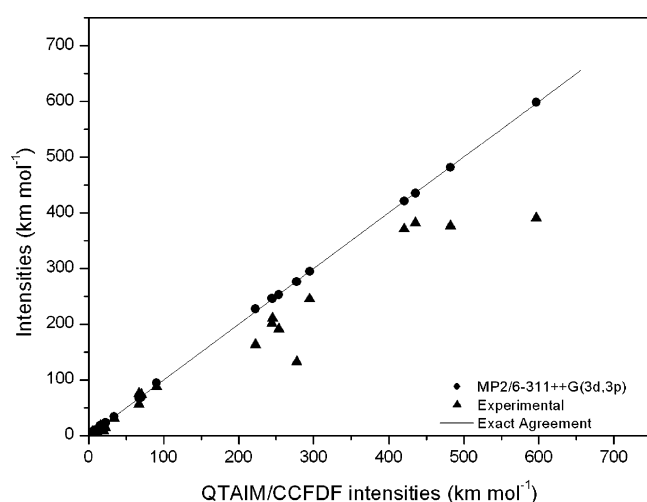

Figure 2. Comparison of experimental infrared fundamental intensities with those obtained from QTAIM/CCFDF/MP2/6-311++G(3d,3p) and those calculated directly from the electronic density at the MP2/6-311++G(3d,3p) level for the X_2CY (X = H, F, Cl; Y = O, S) and HFCO molecules.

intensities calculated from the QTAIM parameters. The corresponding intensity values are given in Table A1 as Supporting Information. The QTAIM values are in almost exact agreement with the theoretical MP2/6-311++G(3d,3p) values having a rms error of ±1.4 km mol^{-1}. Although these theoretical results are in good agreement with the experimental values for the weaker bands, below 100 km mol^{-1}, they overestimate the experimental values above 200 km mol^{-1}. Without exception, all the experimental CF, CO, and CS stretching intensities are lower than the theoretical values with differences ranging from about 35 to 200 km mol^{-1}. The biggest discrepancy occurs for the CS stretch of F$_2$CS where the experimental value of 390.4 km mol^{-1} is about 200 km mol^{-1} smaller than the theoretical 598.3 km mol^{-1} estimate. Theoretical MP2/6-311++G(3d,3p) estimates of the C=C and C−F bond stretching intensities of the difluoroethylenes have also been found to overestimate the experimental values by 45−80 km mol^{-1}.[25]

Another big discrepancy between calculated and experimental values occurs for the ν_4 CF stretching intensity of HFCO. Mizuno and Saëki[26] measured the HFCO intensities. The infrared G sum intensity rule[27] would predict that HFCO would have a slightly larger or equivalent intensity sum compared with the sum for DFCO. This is contrary to the results for the

TABLE 2: QTAIM Charge (C), Charge Flux (CF), and Dipole Flux (DF) Contributions to Dipole Moment Derivatives for the Normal Modes of the X_2CY (X = Cl, F, H; Y = O, S) Molecules in Units of Electrons (e)

			$\partial p/\partial Q_i$			
molecule	Q_i	vibration	C	CF	DF	total
H$_2$CO	Q_1	ν(C−H)	−0.03	0.30	−0.42	−0.15
	Q_2	ν(C=O)	−0.22	0.25	−0.19	−0.16
	Q_3	δ(H-C−H)	0.07	−0.18	0.17	0.06
	Q_4	ν(C−H)	−0.06	0.22	−0.34	−0.18
	Q_5	δ(O=C−H)[a]	−0.12	−0.08	0.14	−0.06
	Q_6	δ(O=C−H)[b]	−0.11	0.00	0.16	0.05
HFCO	Q_1	ν(C−H)	−0.04	0.37	−0.40	−0.07
	Q_2	ν(C=O)	−0.31	0.32	−0.33	−0.32
	Q_3	δ(H−C−F)	0.04	−0.03	−0.03	−0.02
	Q_4	ν(C−F)	−0.29	0.09	−0.19	−0.39
	Q_5	δ(O=C−F)[a]	0.16	0.05	−0.17	0.04
	Q_6	δ(H−C−F)[b]	−0.17	0.00	0.18	0.01
F$_2$CO	Q_1	ν(C=O)	−0.41	0.42	−0.39	−0.38
	Q_2	ν(C−F)	−0.09	0.02	−0.08	−0.15
	Q_3	δ(O=C−F)	0.17	0.05	−0.17	0.05
	Q_4	ν(C−F)	−0.40	0.17	−0.15	−0.38
	Q_5	δ(F−C−F)	−0.10	−0.03	0.09	−0.04
	Q_6	δ(O=C−F)[b]	−0.43	0.00	0.33	−0.10
Cl$_2$CO	Q_1	ν(C=O)	−0.26	0.22	−0.28	−0.32
	Q_2	ν(C−Cl)	−0.02	−0.06	0.00	−0.08
	Q_3	δ(Cl−C−Cl)	−0.01	−0.01	0.03	0.01
	Q_4	ν(C−Cl)	−0.23	−0.35	0.18	−0.40
	Q_5	δ(O=C−Cl)[a]	0.10	−0.04	−0.08	−0.02
	Q_6	δ(O=C−Cl)[b]	−0.25	0.00	0.21	−0.04
F$_2$CS	Q_1	ν(C=S)	−0.13	−0.62	0.30	−0.45
	Q_2	ν(C−F)	−0.05	0.23	−0.26	−0.08
	Q_3	δ(F−C−F)	−0.11	0.07	−0.02	−0.06
	Q_4	ν(C−F)	−0.16	0.18	−0.31	−0.29
	Q_5	δ(S=C−F)[a]	0.01	0.02	−0.03	0.00
	Q_6	δ(S=C−F)[b]	−0.15	0.00	0.13	−0.02
Cl$_2$CS	Q_1	ν(C=S)	0.05	−0.90	0.56	−0.29
	Q_2	ν(C−Cl)	−0.02	0.02	−0.08	−0.08
	Q_3	δ(Cl−C−Cl)	−0.02	0.01	0.00	−0.01
	Q_4	ν(C−Cl)	0.03	−0.28	−0.03	−0.28
	Q_5	δ(S=C−Cl)[a]	0.04	0.00	−0.01	0.03
	Q_6	δ(S=C−Cl)[b]	−0.04	0.00	0.01	−0.03

[a] In-plane. [b] Out-of-plane.

experimental intensity sums, 360.7 and 400.5 km mol^{-1}, respectively, for the HFCO and DFCO molecules. However, this difference is not large enough to explain all of the discrepancy between theoretical and experimental values. On the other hand, changing the basis set and electron correlation treatment level has been shown to have a small effect on the
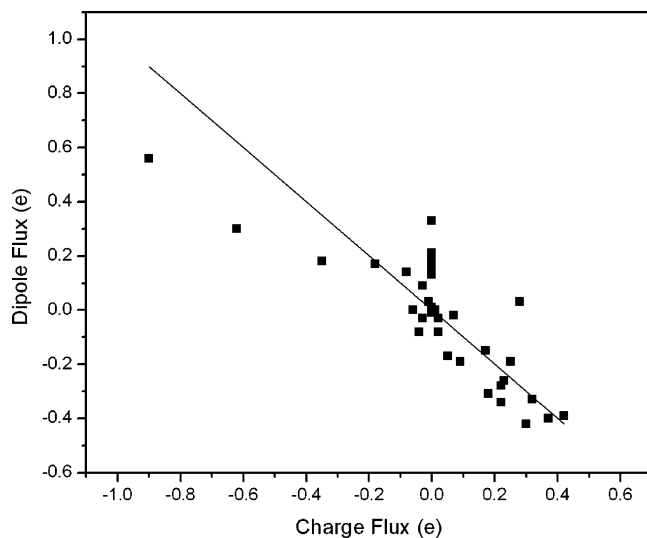
QTAIM Charge−Charge Flux−Dipole Flux Models

J. Phys. Chem. A, Vol. 111, No. 32, 2007 **7873**

Figure 3. Charge flux vs dipole flux contributions to dipole moment derivatives for normal coordinates of the X_2CY (X = H, F, Cl; Y = O, S) molecules.

Figure 4. Cl_2CS dipole moment derivatives calculated from F_2CO, Cl_2CO, and F_2CS derivatives using the characteristic substituent effect equation vs Cl_2CS derivatives calculated directly from the electronic density of Cl_2CS and from experimental Cl_2CS spectroscopic data. Units of electrons, *e*.

HFCO intensity values. Almost equivalent theoretical intensity sums of 577.0, 567.9, and 580.5 km mol⁻¹ were obtained for B3LYP/cc-pVTZ, MP2(FC)/6-311++G(3d,3p), and QCISD/aug-cc-pVTZ calculations.[28]

Table 2 contains the charge, charge flux, and dipole flux contributions to the total dipole moment derivatives with respect to the normal coordinates of H_2CO, HFCO, F_2CO, Cl_2CO, F_2CS, and Cl_2CS. Any one of the three derivative contributions can be predominant depending on the molecule and the form of the normal coordinate. The CO stretching vibrations are characterized by large negative charge, positive charge flux and negative dipole flux contributions. The CS stretching vibrations have substantial negative charge flux and positive dipole flux terms. The CH stretches have small charge contributions, as would be expected owing to the large displacements of the slightly charged hydrogen atoms but high positive charge fluxes and negative dipole fluxes. Large flux contributions of opposite sign and small charge contributions, were also found for the CH stretching modes of the fluorochloromethanes and difluoro- and dichloroethylenes. The CF stretching modes all have negative charge, positive charge flux and negative dipole flux contributions. The CCl stretching modes, like those for the CF ones, have contributions whose values depend heavily on whether the vibration is symmetric or asymmetric. The polar tensor element values for these molecules have been included in Table A2 of Supporting Information.

Charge flux contributions are often accompanied by dipole flux contributions of opposite sign. Figure 3 contains a graph of the dipole flux contributions against the charge flux contributions for all the normal modes. Except for points on a vertical line at zero charge flux a very clear negative correlation is seen. The correlation coefficient for these two contributions for all the points on the graph is −0.83. The dipole moment derivative contributions with zero charge fluxes, as required by planar symmetry, correspond to the six out-of-plane deformations. As expected, the correlation coefficient becomes even more negative, −0.91, if the data for these deformations are removed from the calculation.

Discussion

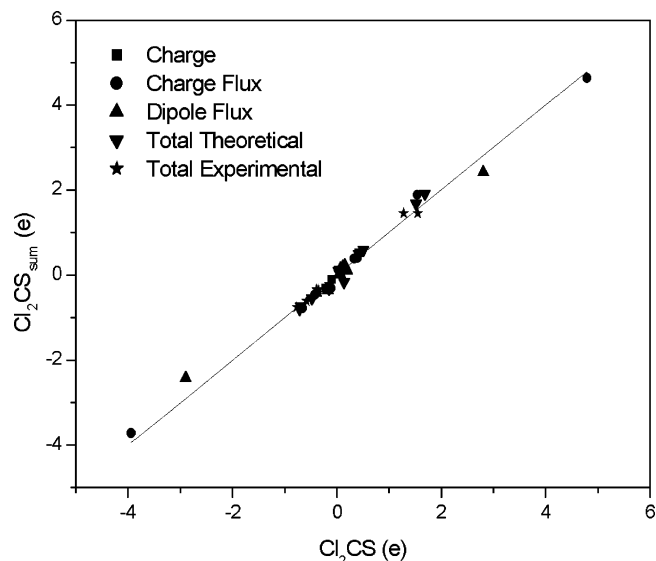It is now well-established that the QTAIM charge flux and dipole flux contributions are negatively correlated for most vibrations. Correlation coefficients of −0.97, −0.92, and −0.91 have been observed for diatomic and linear polyatomic molecules,[9] the fluorochloromethanes,[10] and the difluoro- and dichloroethylenes.[29] These correlations have been interpreted in terms of a relaxation effect of the atomic dipoles provoked by intramolecular charge transfer during the vibrations. Electronic charge transfer from one side of the molecule to the other is accompanied by electron density polarization in the opposite direction.

The characteristic substituent effect equation was tested using charge, charge flux, and dipole flux contributions of the F_2CO, Cl_2CO, F_2CS, and Cl_2CS polar tensors. These molecules have C_{2v} symmetry, and all values were calculated using the same molecular orientation relative to the Cartesian coordinate system shown in Figure 1. The individual contributions and the total polar tensor elements of Cl_2CS were calculated using their corresponding values from F_2CO, Cl_2CO, and F_2CS. These Cl_2CS values have been included in Table A2 in the Supporting Information and can be compared with Cl_2CS values calculated directly at the MP2/6-311++G(3d,3p) level for Cl_2CS. An indication of the accuracy of the characteristic substituent effect equation can be seen in Figure 4 where values calculated from the F_2CO, Cl_2CO and F_2CS results are plotted against those obtained for Cl_2CS. The agreement is very good with a root-mean-square difference of 0.17 *e* for values that range from −3.9 to +4.8 *e*. The large positive and negative values in the figure correspond to the charge flux and dipole flux contributions to the p_{zz} tensor element for the carbon and sulfur atoms of Cl_2CS.

Mean dipole moment derivatives, one-third of the sum of the diagonal polar tensor elements, are attractive as possible measures of atomic charge because they can be determined from experimental measurements, namely infrared fundamental intensities and frequencies, dipole moments, and molecular geometries. Table 3 contains the mean dipole moment derivatives of all the atoms of the molecules studied here. The theoretical charge, charge flux, and dipole flux values are given in the second to fourth columns. The last column contains the theoretical total values that can be compared with the corresponding experimental values[5,24] given in parentheses. The

TABLE 3: QTAIM Charge (C), Charge Flux (CF) and Dipole Flux (DF) Contributions to the Mean Dipole Moment Derivatives of the X$_2$CY Molecules in Units of Electrons (e)

	C	CF	DF	total
		H$_2$CO		
$\bar{p}_C$	+1.05	−0.60	0.15	0.60 (0.59)[a]
$\bar{p}_O$	−1.04	+0.44	+0.09	−0.51 (−0.51)
$\bar{p}_H$	0.00	+0.08	−0.12	−0.04 (−0.04)
		HFCO		
$\bar{p}_C$	1.64	−0.73	0.21	1.12
$\bar{p}_O$	−1.09	0.44	0.09	−0.56
$\bar{p}_F$	−0.63	0.12	−0.08	−0.59
$\bar{p}_H$	0.08	0.17	−0.22	0.03
		F$_2$CO		
$\bar{p}_C$	2.33	−0.93	+0.22	1.62 (1.51)[b]
$\bar{p}_O$	−1.09	+0.53	−0.02	−0.58 (−0.58)
$\bar{p}_F$	−0.62	+0.20	−0.10	−0.52 (−0.48)
		Cl$_2$CO		
$\bar{p}_C$	1.26	0.37	−0.26	1.37 (1.24)[b]
$\bar{p}_O$	−1.03	0.30	0.11	−0.62 (−0.58)
$\bar{p}_{Cl}$	−0.11	−0.33	0.08	−0.36 (−0.33)
		F$_2$CS		
$\bar{p}_C$	0.77	0.87	−0.30	1.34 (1.16)[b]
$\bar{p}_S$	0.45	−1.11	0.42	−0.24 (−0.26)
$\bar{p}_F$	−0.61	0.12	−0.06	−0.55 (−0.45)
		Cl$_2$CS		
$\bar{p}_C$	−0.22	2.11	−0.88	1.01 (0.89)[b]
$\bar{p}_S$	0.42	−1.35	0.75	−0.18 (−0.28)
$\bar{p}_{Cl}$	−0.10	−0.36	0.09	−0.37 (−0.30)
		Cl$_2$CS[c]		
$\bar{p}_C$	−0.30	2.17	−0.78	1.09
$\bar{p}_S$	0.51	−1.34	0.54	−0.29
$\bar{p}_{Cl}$	−0.10	-.41	0.12	−0.39
		HFCO[d]		
$\bar{p}_C$	1.69	−0.77	0.18	1.10
$\bar{p}_O$	−1.06	0.49	0.04	−0.53
$(\bar{p}_H + \bar{p}_F)/2$	−0.31	0.14	−0.11	−0.28

[a] From ref 21. [b] From ref 5. [c] Determined from F$_2$CO, Cl$_2$CO, and F$_2$CS results. [d] Determined from H$_2$CO and F$_2$CO results.

theoretical values have a 0.08 *e* rms error relative to the experimental values. Although the charge contribution is often the largest one, there are quite substantial flux contributions as well. Table 3 also contains mean dipole moment derivative values calculated for Cl$_2$CS that were estimated using the F$_2$CO, Cl$_2$CO, and F$_2$CS mean derivatives in the characteristic shift equation. The agreement of these values with those calculated using only the Cl$_2$CS results is very good. Most values, except one, agree within 0.1 *e*, and the rms difference is 0.09 *e*.

The characteristic shift equation can also be used to estimate HFCO dipole moment derivatives from the H$_2$CO and F$_2$CO derivatives. The $\bar{p}_C$ and $\bar{p}_O$ derivatives in HFCO are within 0.05 *e* of the averages of these derivatives for the H$_2$CO and F$_2$CO molecules. Furthermore, the averages of the hydrogen and fluorine mean derivatives in HFCO are almost the same as the averages of these derivatives in H$_2$CO and F$_2$CO.

It is also of interest to determine if different stretching normal modes have characteristic values of the charge, charge flux, and dipole flux contributions. Because there exists a strong correlation between the fluxes, a two-dimensional graph of charge against either one of the fluxes gives almost as much information as the three-dimensional graph.

Figure 5 shows a graph of the dipole vs charge flux contributions of the CH, CF, and CCl stretches of the carbonyl halides, thiocarbonyl halides, fluorochloromethanes, and the difluoro- and dichloroethylenes. Three separate clusters of points can be seen, each one corresponding to the stretching modes of
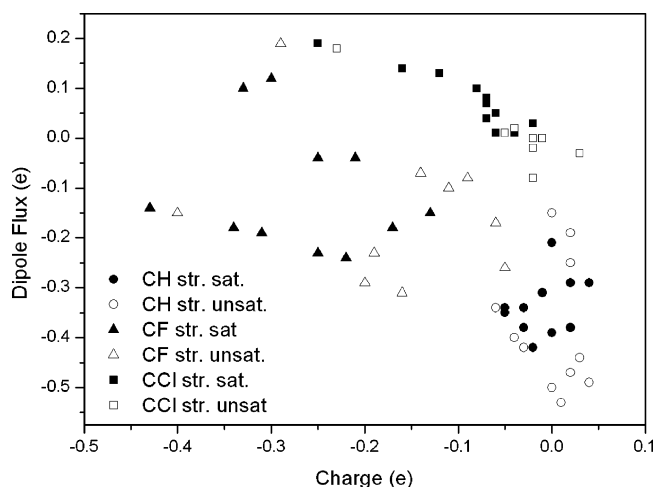

Figure 5. Charge plotted against the dipole flux contribution for the stretching modes of the X$_2$CY (X = H, F, Cl; Y = O, S) molecules.

one of the bonds. The tighter cluster in the lower right-hand corner of the graph contains points for the CH stretches. The charge contributions are very small for these stretches ranging from −0.06 to +0.04 *e*. On the other hand the dipole flux contributions are very large, varying from −0.19 to −0.53 *e*. Charge flux contributions are large and positive, from 0.13 to 0.51 *e*. CH stretches are thus seen to be characterized by very small charge contributions but having large flux contributions of opposite sign.

The largest cluster, in the center of Figure 5, has points identified by CF stretches. The charge contributions have a large range of values, −0.06 to −0.43 *e*, and dipole flux contributions varying from −0.29 to +0.19 *e*. Note that we have distinguished between CF stretches in the fluorochloromethanes from those in molecules with a double bond adjacent to the CF bond. Except for the asymmetric CF stretch in F$_2$CO and the CF stretch in HFCO, most of the saturated methanes have larger fluorine charges than do the difluoroethylenes and carbonyl and thiocarbonyl fluoride. The CF stretches have charge fluxes ranging from −0.18 to +0.23 *e*.

The elongated cluster in the upper right-hand corner corresponds to points for the CCl stretching modes. Their charge contributions are smaller than those of the CF stretches, as expected, ranging from +0.03 to −0.25 *e*. The dipole fluxes vary from −0.08 to +0.19 *e* whereas the charge fluxes have values from zero to −0.35 *e*. As in the case of the CF stretches, the unsaturated molecules tend to have lower charge contributions than the saturated ones.

The analogous graph for the HCH, FCF, and ClCCl bends does not show the formation of three distinct clusters. The charge vs charge flux graph is given in the Supporting Information.

Conclusions

Characteristic substituent effects for the polar tensor element values of molecules are probably more common than one might suspect. Characteristic substituent effects have been observed for the carbon mean dipole moment derivatives of the fluorochloromethanes, although direct comparison of the individual polar tensor element values is not meaningful because of their different point group symmetries. Several research groups in the 1970s showed that the shifts in atomic core electron-binding energies can be expressed as the sum of characteristic shifts of substituent atoms or chemical groups bonded to the ionizing atom.[30−35] More than a dozen ionizing atoms and substituents groups were included in these studies. Furthermore, Siegbahn's

QTAIM Charge−Charge Flux−Dipole Flux Models

J. Phys. Chem. A, Vol. 111, No. 32, 2007 **7875**

simple potential models[36] have been found that linearly relate experimental ionization energies and mean dipole moment derivatives for sp, sp[2], and sp[3] hybridized carbon atoms, sp and sp[3] hybridized nitrogen atoms, and Si, Ge, O, F, B, P and Cl atoms, i.e., for all kinds of atoms existing in molecules for which both core ionization energies and infrared intensities have been measured.[37−39] Substitution of these Siegbahn simple potential models into the characteristic substituent equation used here results in an analogous equation for the core electron ionization energies. Here it has been demonstrated that the atomic charge and its flux as well as the dipole flux also have behaviors described by the characteristic substituent effect equations. Because these quantities, especially the atomic charge and atomic dipole, are easier to apply in physical models than dipole moment derivatives and ionization energies, this could help us understand molecular electronic properties in a more profound way.

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

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