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QTAIM Charge−Charge Flux−Dipole Flux Models for the Infrared Fundamental Intensities of the Fluorochloromethanes

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The molecular dipole moments, their derivatives, and the fundamental IR intensities of the fluoro-, chloro-, and fluorochloromethanes are determined from QTAIM atomic charges and dipoles and their fluxes at the MP2/6-311++G(3d,3p) level. Root-mean-square (rms) errors of 0.01 D and 5.6 km mol^{-1} are found for the dipole moments and fundamental IR intensities calculated using QTAIM parameters when compared with those obtained directly from the MP2/6-311++(3d,3p) calculations and 0.04 D and 23.1 km mol^{-1} when compared with the experimental values. Charge, charge flux, and dipole flux contributions are calculated for all the normal vibrations of these molecules. A large negative correlation coefficient of −0.92 is calculated between the charge flux and dipole flux contributions and indicates that electron transfer from one side of the molecule to the other during vibrations is accompanied by relaxation with electron density polarization in the opposite direction. The CF, CCl, and CH stretching normal modes of these molecules are shown to have characteristic sets of charge, charge flux, and dipole flux contributions. Although the FCF and ClCCl deformation normal modes can also be discriminated from one another based on the sizes and signs of these contributions, some HCH deformations have contributions that are similar to those for some of the ClCCl deformations.

Introduction

IR vibrational intensities of gas-phase molecules can now be interpreted using a completely classical model.[1−3] The dipole flux contribution, previously treated within a quantum mechanical framework in the charge−charge flux−overlap (CCFO) model[4] of intensities, now combines with the classical charge contributions providing a simple interpretation of electronic density changes for molecular vibrations. This model, the charge−charge flux−dipole flux (CCFDF) model, has been applied recently to most linear molecules for which complete gas-phase IR fundamental intensity data exist as well as to a few small polyatomic molecules.[1−3] One of the most interesting results of these studies was the observation of a high negative correlation coefficient between the charge flux and dipole flux contributions.[2] This result indicates that as the molecule vibrates intramolecular electron transfer in one direction is compensated by electronic density polarizations in the opposite direction.

One of the goals of the work reported here is to determine the accuracy of the charge−charge flux−dipole flux model for a family of polyatomic molecules. One of the few families of molecules for which complete gas-phase fundamental intensities have been measured is the fluorochloromethanes.[5−26] Since experimental intensity data exist for these molecules, the accuracies of CCFDF models for IR intensities as well as expectation values obtained directly from molecular wave functions can be assessed. One other goal is to investigate whether a strong negative correlation between charge flux and dipole flux exists for families of nonlinear polyatomic molecules. The fluorochloromethanes are of special interest in this regard since the movement of highly charged carbon and fluorine atoms are expected to exert large polarization effects on the chlorine atoms. Finally, it is of interest to determine if functional group vibrations, such as the C−H, C−F, and C−Cl stretching and bending modes, are characterized by relatively transferable charge, charge flux, and dipole flux contributions.

The quantum theory of atoms-in-molecules (QTAIM) developed by Bader[27] has been used to calculate atomic charges and atomic dipoles of the CH_xF_y, CH_xCl_y, and CF_xCl_y molecules, where $x = 0, 1, ..., 4$ and $y = 4 - x$. Besides being useful in a wide range of applications,[28] these atomic charges and the changes in both atomic charges and atomic dipoles have already been used to determine dipole moment derivatives.[29] 6-311++G-(3d,3p) basis sets were chosen for these calculations that were carried out at the Møller−Plesset 2 electron correlation treatment level. This kind of calculation has already been shown to be adequate in accurately describing the relationship between IR fundamental intensities of the fluorochloromethanes and their carbon 1s electron ionization energies.[30]

Calculations

The Cartesian components of the molecular dipole moment calculated from QTAIM[27] charges and atomic dipoles can be represented by

$$\mu_r = \sum_a q_\alpha r_\alpha + \sum_\alpha m_{\alpha,r} \qquad (1)$$

where $r = x, y, z$, q_α is the atomic charge on atom α and $m_{\alpha,r}$ is the rth component of dipole moment for atom α. The

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derivatives of these components of the molecular dipole with respect to atomic Cartesian coordinates are given by[29]

$$\frac{\partial p_x}{\partial x_\alpha} = p_{xx}^{(\alpha)} = q_\alpha + \sum_i x_i \frac{\partial q_i}{\partial x_\alpha} + \sum_i \frac{\partial m_{i,x}}{\partial x_\alpha} \tag{2}$$

and

$$\frac{\partial p_x}{\partial x_\alpha} = p_{yx}^{(\alpha)} = \sum_i y_i \frac{\partial q_i}{\partial x_\alpha} + \sum_i \frac{\partial m_{i,y}}{\partial x_\alpha} \tag{3}$$

These derivatives are the elements of the atomic polar tensor (APT) which is represented by

$$\mathbf{P}_{\mathbf{X}}^{(\alpha)} = \begin{pmatrix} \frac{\partial p_x}{\partial x_\alpha} & \frac{\partial p_x}{\partial y_\alpha} & \frac{\partial p_x}{\partial z_\alpha} \\ \frac{\partial p_y}{\partial x_\alpha} & \frac{\partial p_y}{\partial y_\alpha} & \frac{\partial p_y}{\partial z_\alpha} \\ \frac{\partial p_z}{\partial x_\alpha} & \frac{\partial p_z}{\partial y_\alpha} & \frac{\partial p_z}{\partial z_\alpha} \end{pmatrix} = \begin{pmatrix} p_{xx}^{(\alpha)} & p_{xy}^{(\alpha)} & p_{xz}^{(\alpha)} \\ p_{yx}^{(\alpha)} & p_{yy}^{(\alpha)} & p_{yz}^{(\alpha)} \\ p_{zx}^{(\alpha)} & p_{zy}^{(\alpha)} & p_{zz}^{(\alpha)} \end{pmatrix} \tag{4}$$

Using eqs 2 and 3, the APT can be expressed as the sum of three contributions

$$\mathbf{P}_{\mathbf{X}}^{(\alpha)} = \begin{pmatrix} q_a & 0 & 0 \\ 0 & q_a & 0 \\ 0 & 0 & q_a \end{pmatrix} + \begin{pmatrix} \sum x_i \frac{\partial q_i}{\partial x_\alpha} & \sum x_i \frac{\partial q_i}{\partial y_\alpha} & \sum x_i \frac{\partial q_i}{\partial z_\alpha} \\ \sum y_i \frac{\partial q_i}{\partial x_\alpha} & \sum y_i \frac{\partial q_i}{\partial y_\alpha} & \sum y_i \frac{\partial q_i}{\partial z_\alpha} \\ \sum z_i \frac{\partial q_i}{\partial x_\alpha} & \sum z_i \frac{\partial q_i}{\partial y_\alpha} & \sum z_i \frac{\partial q_i}{\partial z_\alpha} \end{pmatrix} + \begin{pmatrix} \sum \frac{\partial m_{i,x}}{\partial x_\alpha} & \sum \frac{\partial m_{i,x}}{\partial y_\alpha} & \sum \frac{\partial m_{i,x}}{\partial z_\alpha} \\ \sum \frac{\partial m_{i,y}}{\partial x_\alpha} & \sum \frac{\partial m_{i,y}}{\partial y_\alpha} & \sum \frac{\partial m_{i,y}}{\partial z_\alpha} \\ \sum \frac{\partial m_{i,z}}{\partial x_\alpha} & \sum \frac{\partial m_{i,z}}{\partial y_\alpha} & \sum \frac{\partial m_{i,z}}{\partial z_\alpha} \end{pmatrix} \tag{5}$$

where the first is the charge contribution, the second is the charge flux, and the last one is the dipole flux.

The molecular polar tensor,[31,32] $\mathbf{P}_{\mathbf{X}}$, is a juxtaposition of APTs

$$\mathbf{P}_{\mathbf{X}} = \{\mathbf{P}_{\mathbf{X}}{}^{(1)}\mathbf{P}_{\mathbf{X}}{}^{(2)},...,\mathbf{P}_{\mathbf{X}}^{(N)}\} \tag{6}$$

with N being the number of atoms in the molecule. Using eq 5, the molecular polar tensor can be represented by

$$\mathbf{P}_{\mathbf{X}} = \{\mathbf{P}_{\mathbf{X}}^{(\mathrm{C})} + \mathbf{P}_{\mathbf{X}}^{(\mathrm{CF})} + \mathbf{P}_{\mathbf{X}}^{(\mathrm{DF})}\} \tag{7}$$

The polar tensor and the individual contributions can be converted to derivatives in normal coordinate space by performing the transformation

$$\mathbf{P}_{\mathbf{Q}} = \mathbf{P}_{\mathbf{X}}\mathbf{AUL}' = (\mathbf{P}_{\mathbf{X}}^{(\mathrm{C})} + \mathbf{P}_{\mathbf{X}}^{(\mathrm{CF})} + \mathbf{P}_{\mathbf{X}}^{(\mathrm{DF})}\mathbf{AUL}' \tag{8}$$

resulting in charge, charge flux, and dipole flux contributions to $\mathbf{P}_{\mathbf{Q}}$, the dipole moment derivatives with respect to normal coordinates

$$\mathbf{P}_{\mathbf{Q}} = \{\mathbf{P}_{\mathbf{Q}}^{(\mathrm{C})} + \mathbf{P}_{\mathbf{Q}}^{(\mathrm{CF})} + \mathbf{P}_{\mathbf{Q}}^{(\mathrm{DF})}\} \tag{9}$$

Here, the **A**, **U**, and **L** matrixes are well-known transformation matrixes relating atomic Cartesian, internal, symmetry, and normal coordinates.[33]

Within the harmonic oscillator−linear dipole moment approximations, fundamental IR intensities, A_i, are directly related to the squares of the elements of the $\mathbf{P}_{\mathbf{Q}}$ matrix, $\partial p_r/\partial Q_i$ ($r = x, y, z$)

$$A_i = \frac{N_{\mathrm{A}}\pi}{3c^2}\left(\frac{\partial \vec{p}}{\partial Q_i}\right)^2 \quad i = 1,2,...,3N - 6 \tag{10}$$

where N_{A} and c are Avogradro's number and the velocity of light, respectively.[34]

Theoretical calculations of the polar tensors, $\mathbf{P}_{\mathbf{X}}$, and the normal coordinate transformation matrixes (**AUL′**) were performed using the Gaussian 98 program[35] on a DEC ALPHA workstation. MP2 (Møller−Plesset) frozen-core perturbation theory was used with a 6-311++G(3d,3p) basis set. All calculations were made relative to theoretical equilibrium geometries. Atomic charges and atomic dipoles were obtained directly from the relaxed densities of the frozen-core MP2 energies of the Gaussian program using the DENSITY = CURRENT option. The fluxes were calculated numerically from 0.01 Å geometrical distortions. Charge, charge flux, and dipole flux contributions to the dipole moment derivatives were calculated using a FORTRAN 77 program written in our laboratory.

Results

MP2/6-311++G(3d,3p) level wave functions have already been used to calculate the fundamental IR intensities of the fluorochloromethanes.[30] They provide estimates with root-mean-square (rms) errors within 0.01 Å for the C−F, C−Cl, and C−H bond lengths and within 0.91°, 0.21°, and 1.6° for the FCF, HCH, and ClCCl angles, respectively. Excellent agreement between dipole moments calculated from these wave functions and the experimental values can be seen upon comparing the last two columns of Table 1. The calculated absolute values have a rms error of 0.05 D relative to the experimental ones. In all cases, the absolute value of the calculated dipole is larger than the experimental one. The QTAIM atomic charges and atomic dipoles can also be used to calculate these dipole moments and their values are given in Table 2. The third from last column of Table 1 contains the dipole moments calculated from these MP2/6-311++G(3d,3p) QTAIM parameters. They result in dipole moment estimates having less than a 0.01 D rms error relative to the dipole moments calculated directly from the MP2 relaxed densities and a 0.04 D error when compared with the experimental values. The atomic dipole contributions are just as important as those of the atomic charges for accurately calculating the molecular dipole moments. This can be seen by comparing the values in the first two columns of Table 1. Although the magnitudes of the charge contributions are larger than the dipole ones, the latter are sometimes almost as large.

The experimental IR fundamental intensities along with those calculated directly at the MP2/6-311++G(3d,3p) level and those obtained from the corresponding QTAIM parameters are presented in Table 3 for the fluoro-, chloro-, and fluorochloromethanes. The intensities calculated directly with the MP2/6-311++G(3d,3p) approach have a rms error of 23.1 km mol^{-1} relative to the experimental values that range from 0.0 to 1259.9 km mol^{-1}. The intensities calculated from the QTAIM/MP2/6-311++G(3d,3p) parameters are in excellent agreement with only a 5.6 km mol^{-1} rms error relative to those determined

TABLE 1: MP2/6-311++G(3d,3p), QTAIM/MP2/6-311++G(3d,3p), and Experimental Dipole Moments for the Fluoro-, Chloro-, and Fluorochloromethanes in Units of Debye (D)

molecule	μ_q(QTAIM)[a]	μ_m(QTAIM)[b]	μ(QTAIM)	μ (MP2/6-311++G(3p,3d)	$\lvert\mu$ (exp)$\rvert$
CH_4	0.00	0.00	0.00	0.00	0.00
CH_3F	−4.31	2.39	−1.92	−1.93	1.86
CH_2F_2	−5.11	3.07	−2.04	−2.04	1.98
CHF_3	4.72	−3.04	1.68	1.68	1.65
CF_4	0.00	0.00	0.00	0.00	0.00
CH_3Cl	−2.27	0.34	−1.93	−1.93	1.89
CH_2Cl_2	−2.20	0.57	−1.63	−1.63	1.60
$CHCl_3$	1.62	−0.57	1.05	1.05	1.04
CCl_4	0.00	0.00	0.00	0.00	0.00
$CClF_3$	3.43	−2.87	0.56	0.56	0.50
CCl_2F_2	−3.80	3.20	−0.60	−0.60	0.51
CCl_3F	−3.15	2.65	−0.50	−0.50	0.46

[a] Atomic charge contribution for the molecular dipole moment. [b] Atomic dipole contribution for the molecular dipole moment.

TABLE 2: QTAIM/MP2/6-311++G(3d,3p) Equilibrium Atomic Charges and Atomic Dipoles for the Fluoro-, Chloro-, and Fluorochloromethanes in Units of Electron (e) and Debye (D), Respectively

molecule	q_C	q_H	q_F	q_{Cl}	$m_{C,z}$	$m_{Ha,z}$	$m_{Hb,z}$	$m_{Fa,z}$	$m_{Fb,z}$	$m_{Cla,z}$	$m_{Clb,z}$
CH_4	0.09	−0.02			0.00	−0.35	0.12				
CH_3F	0.64	0.00	−0.65		1.52	0.15		0.43			
CH_2F_2	1.22	0.03	−0.64		1.93	0.20		0.37			
CHF_3	1.85	0.08	−0.64		−1.89	−0.28		−0.28			
CF_4	2.51		−0.63		0.00			0.76	−0.25		
CH_3Cl	0.19	0.02		−0.25	0.42	0.16				−0.54	
CH_2Cl_2	0.27	0.06		−0.20	0.48	0.22				−0.17	
$CHCl_3$	0.34	0.10		−0.14	−0.41	0.05				−0.31	
CCl_4	0.40			−0.10	0.00					−0.56	0.19
$CClF_3$	1.96		−0.62	−0.09	−1.54			−0.29		−0.45	
CCl_2F_2	1.42		−0.62	−0.10	1.77			0.43		0.28	
CCl_3F	0.90		−0.61	−0.10	1.51			0.61		0.18	

directly from the MP2 calculations. Figure 1 shows a graph of QTAIM intensities plotted against the experimental intensities and those calculated directly with the MP2/6-311++G(3d,3p) approach. The excellent agreement shows that the MP2/6-311++G(3d,3p) calculations adequately describe the experimental intensities and that the QTAIM parameters provide an accurate description of the MP2/6-311++G(3d,3p) electron densities.

A study of the charge−charge flux−dipole flux contributions to the dipole moment derivatives can be carried out in terms of normal coordinates or Cartesian displacement coordinates. Although the polar tensors in terms of the Cartesian coordinates are very useful in many applications, they do not have one-to-one relationships with the experimental intensities as do the normal coordinates. Furthermore, owing to their symmetry properties, the latter provide a more compact description of the dipole moment derivatives. Unfortunately, uncertainties in the normal coordinates are confounded with those in the QTAIM parameter approximations of the molecular electronic densities. Despite this problem, interpretation using derivatives with respect to normal coordinates is much more appealing since each derivative corresponds to only one experimentally measured intensity.

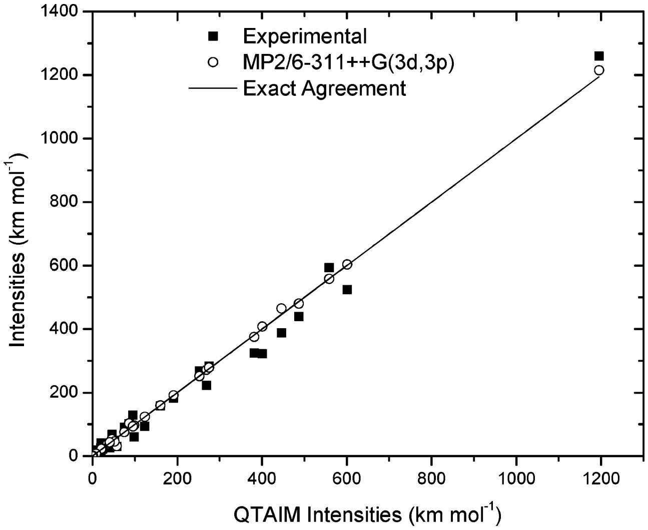

Figure 1. Comparison of IR fundamental intensities obtained from AIM-CCFDF-MP2/6-311++G(3d,3p) with those calculated directly from the wave function at the MP2/6-311++G(3d,3p) level and experimental ones.

Table 4 lists the QTAIM charge (C), charge flux (CF), and dipole flux (DF) contributions to the dipole moment derivatives for the normal coordinates of the fluoro-, chloro-, and fluorochloromethanes along with their total values. Any one of the three derivative contributions can be predominant depending on the molecule and form of the normal vibration. Perhaps the most interesting aspect of these values is that for almost all vibrations the signs of the charge flux and dipole flux are opposite. Figure 2 contains a graph of the charge flux contributions against the dipole flux ones for all the $\partial p/\partial Q_i$ of these molecules. The correlation coefficient for these two contributions is −0.92 indicating a highly negative linear correlation between the fluxes.

On the other hand, the atomic charge contribution to the dipole moment derivative is not correlated with either of the flux quantities. This observation is confirmed by principal component calculations showing that 94% of the data variance in Table 4 can be described in two dimensions, one specified by the charges and the other by the differences between the charge and dipole fluxes.

TABLE 3: Experimental, MP2/6-311++G(3d,3p), and QTAIM/MP2/6-311++G(3d,3p) IR Fundamental Intensities of the Fluoro-, Chloro-, and Fluorochloromethanes

	experimental		MP2/6-311++G(3d,3p)	QTAIM			experimental		MP2/6-311++G(3d,3p)	QTAIM	
i	υ_i (cm^{-1})	A_i (km/mol)[a]	A_i (km/mol)	A_i (km/mol)	refs	i	υ_i (cm^{-1})	A_i (km/mol)[a]	A_i (km/mol)	A_i (km/mol)	refs
CH_4											
3	3019	68.8	54.4	45.9	5, 6, 7	4	1311	34.2	30.8	28.8	5, 6, 7
CH_3F											
1	2910	31.1	32.0	57.0	8, 9	4	3006	49.2	46.2	51.6	8, 9
2	1460	2.2	1.6	0.0	8, 9	5	1468	7.4	9.0	8.5	8, 9
3	1049	101.7	103.7	86.7	8, 9	6	1182	2.2	2.7	4.2	8, 9
CH_2F_2											
1	2948	26.7	37.7	34.8	10, 11	6	3014	41.6	23.7	20.6	10, 11
2	1508	0.0	0.4	0.4	10, 11	7	1178	4.5	15.9	16.3	10, 11
3	1113	60.7	96.7	98.4	10, 11	8	1435	10.5	12.8	12.6	10, 11
4	529	4.9	4.8	4.6	10, 11	9	1090	269.1	252.4	252.4	10, 11
CHF_3											
1	3036	27.4	22.2	20.3	6, 12, 13, 14	4	1372	90	75.2	75.0	6, 12, 13, 14
2	1117	129	93.9	95.6	12	5	1152	525.0	603.5	601.0	12,13
3	700	14.0	12.1	11.9	6, 12, 13, 14	6	507	4.9	4.2	4.1	6, 12, 13, 14
CF_4											
3	1283	1259.9	1215.2	1194.9	6, 15	4	632	13.7	10.5	10.5	6, 15
CH_3Cl											
1	2930	18.9	22.4	20.4	9, 14, 16	4	3006	9.7	5.5	3.8	9, 14, 16
2	1355	7.9	12.4	11.7	9, 14, 16	5	1452	11.0	10.0	8.9	9, 14, 16
3	732	22.1	23.7	24.1	9, 14, 16	6	1017	4.1	4.5	4.0	9, 14, 16
CH_2Cl_2											
1	2997	6.9	4.9	3.6	17	6	3055	0.0	0.6	1.2	17
2	1467	0.6	0.0	0.2	17	7	898	1.2	1.4	1.0	17
3	717	8.0	10.1	10.6	17	8	1268	26.6	41.0	40.5	17
4	282	0.6	0.4	0.4	17	9	758	95.0	123.9	123.6	17
$CHCl_3$											
1	3034	0.3	1.6	2.0	18	4	1221	30.8	44.0	40.6	18, 19
2	681	4.4	3.0	3.3	18, 19	5	769	222.4	272.0	268.6	18, 19
3	366	0.5	0.1	0.1	18	6	258	0.1	0.0	0.0	18
CCl_4											
3	793	322.0	408.2	400.4	18	4	310	20.0	0.4	0.4	18
$CClF_3$											
1	1102	439.9	480.7	486.9	20, 21	4	1210	593.5	558.2	558.4	20, 21
2	783	31.5	23.2	20.6	20, 21	5	560	3.3	2.1	2.4	20, 21
3	470	0.0	0.0	0.0	20, 21	6	350	0.0	0.0	0.1	20, 21
CCl_2F_2											
1	1095	284.3	279.5	274.9	11, 22, 23	6	1152	183.3	192.0	191.5	11, 22, 23
2	665	12.3	7.7	8.2	11	7	475	0.1	0.0	0.1	13
3	442	0.2	0.0	0.0	11	8	915	324.8	375.3	381.7	11, 22, 23
4	261	2.6	0.2	0.1	11	9	432	0.1	0.0	0.0	11
CCl_3F											
1	1085	158.0	159.8	160.1	22, 24, 25, 26	4	846	388.3	465.1	445.6	22, 24, 25, 26
2	539	1.1	0.9	1.2	24	5	384	0.1	0.0	0.1	24
3	347	0.3	0.4	0.8	24	6	243	0.0	0.2	0.1	24

[a] These values are the mean of experimental IR fundamental intensities obtained from the references shown in the last column of the table.

Discussion

The negative correlation of the charge and dipole fluxes can be interpreted as follows. Electron transfer from one side of the molecule to the other during the vibration is accompanied by relaxation with electronic density polarization in the opposite direction. This compensation may be compared to the charge donation−back-donation effects often invoked to explain complex formation. The back-donation in the complex involves out-lying orbitals relative to the inner ones involved in the charge donation.[36] For vibrations, the analogy would be the dipole flux contributions involving the more polarizable outer portions of the electronic density whereas electron transfer would occur through the inner portions of the valence orbitals.

A more detailed examination of the charge, charge flux, and dipole flux contributions can be made as a function of the type of molecule and/or vibration involved. It is interesting to determine if functional group vibrations can be characterized by specific ranges of values for the derivative contributions at least for families of molecules. These contributions have signs that depend on both the alignment of the molecule along the fixed Cartesian coordinate axes and the phase of the normal coordinate. Figure 3 shows this alignment and the normal coordinate phases for the C_{3v} symmetry molecules. Normal coordinate phases are always positive for bond extension or an opening of the angle of the functional group involved. Furthermore, the terminal atom of the functional group is always displaced in the positive Cartesian coordinate direction.

TABLE 4: QTAIM Charge (C), Charge Flux (CF), and Dipole Flux (DF) Contributions to Dipole Moment Derivatives for the Normal Modes of the Fluoro-, Chloro-, and Fluorochloromethanes in Units of Electrons (e)[a]

			$\partial p/\partial Q_i$			
molecule	Q_i	vibration	C	CF	DF	TOTAL
CH_4	Q_3	ν_{CH}	−0.02	0.36	−0.42	−0.08
	Q_4	δ_{HCH}	−0.02	−0.07	0.15	0.06
CH_3F	Q_1	ν_{CH}	−0.01	0.19	−0.31	−0.13
	Q_2	δ_{HCH}	−0.03	−0.01	0.03	−0.01
	Q_3	ν_{CF}	−0.13	0.11	−0.15	−0.17
	Q_4	ν_{CH}	−0.03	0.33	−0.38	−0.08
	Q_5	δ_{HCH}	−0.02	−0.07	0.13	0.04
	Q_6		0.06	0.04	−0.07	0.03
CH_2F_2	Q_1	ν_{CH}	−0.03	0.26	−0.34	−0.11
	Q_2	δ_{HCH}	−0.04	−0.06	0.09	−0.01
	Q_3	ν_{CF}	−0.21	0.06	−0.04	−0.19
	Q_4	δ_{FCF}	−0.10	−0.02	0.09	−0.03
	Q_6	ν_{CH}	−0.05	0.31	−0.35	−0.09
	Q_7		0.13	0.06	−0.12	0.07
	Q_8	δ_{HCH}	0.04	−0.01	0.04	0.07
	Q_9	ν_{CF}	−0.22	0.16	−0.24	−0.30
CHF_3	Q_1	ν_{CH}	−0.05	0.30	−0.34	−0.09
	Q_2	ν_{CF}	−0.30	0.00	0.12	−0.18
	Q_3	δ_{FCF}	−0.16	−0.05	0.15	−0.06
	Q_4	δ_{HCF}	−0.09	0.03	−0.05	−0.11
	Q_5	ν_{CF}	−0.31	0.18	−0.19	−0.32
	Q_6	δ_{FCF}	−0.10	−0.03	0.10	−0.03
CF_4	Q_3	ν_{CF}	−0.43	0.20	−0.14	−0.37
	Q_4	δ_{FCF}	−0.13	−0.06	0.16	−0.03
CH_3Cl	Q_1	ν_{CH}	0.00	0.13	−0.21	−0.08
	Q_2	δ_{HCH}	−0.01	0.2	−0.12	0.07
	Q_3	ν_{CCl}	−0.04	−0.06	0.01	−0.09
	Q_4	ν_{CH}	0.00	0.37	−0.39	−0.02
	Q_5	δ_{HCH}	0.00	0.06	−0.10	−0.04
	Q_6		0.01	0.03	−0.06	−0.02
CH_2Cl_2	Q_1	ν_{CH}	0.02	0.24	−0.29	−0.03
	Q_2	δ_{HCH}	0.03	−0.09	0.07	0.01
	Q_3	ν_{CCl}	−0.06	−0.06	0.05	−0.07
	Q_4	δ_{ClCCl}	−0.03	−0.01	0.02	−0.02
	Q_6	ν_{CH}	0.02	0.37	−0.38	0.01
	Q_7		0.01	0.06	−0.08	−0.01
	Q_8	δ_{HCH}	0.03	−0.21	0.06	−0.12
	Q_9	ν_{CCl}	−0.06	−0.16	0.01	−0.21
$CHCl_3$	Q_1	ν_{CH}	0.04	0.28	−0.29	0.03
	Q_2	ν_{CCl}	−0.07	−0.03	0.07	−0.03
	Q_3	δ_{ClCCl}	−0.03	−0.01	0.03	−0.01
	Q_4	δ_{HCCl}	−0.04	0.18	−0.05	0.09
	Q_5	ν_{CCl}	−0.07	−0.19	0.04	−0.22
	Q_6		0.02	0.00	−0.01	0.01
						0.00
CCl_4	Q_3	ν_{CCl}	−0.07	−0.22	0.08	−0.21
	Q_4	δ_{ClCCl}	−0.02	0.00	0.02	0.00
$CClF_3$	Q_1	ν_{CF}	−0.33	−0.18	0.10	−0.41
	Q_2	ν_{CCl}	−0.12	−0.10	0.13	−0.09
	Q_3	δ_{FCF}	−0.07	0.02	0.05	0.00
	Q_4	ν_{CF}	−0.34	0.21	−0.18	−0.31
	Q_5	δ_{FCF}	−0.10	−0.05	0.13	−0.02
	Q_6	δ_{ClCF}	−0.02	−0.01	0.03	0.00
CCl_2F_2	Q_1	ν_{CF}	−0.25	−0.02	−0.04	−0.31
	Q_2	ν_{CCl}	−0.08	−0.07	0.10	−0.05
	Q_3	δ_{ClCCl}	−0.06	−0.03	0.09	0.00
	Q_4	δ_{ClCCl}	0.01	−0.01	0.01	0.01
	Q_6	ν_{CF}	−0.25	0.22	−0.23	−0.26
	Q_7	δ_{FCF}	−0.05	0.01	0.05	0.01
	Q_8	ν_{CCl}	−0.25	−0.30	0.19	−0.36
	Q_9	δ_{FCF}	−0.08	0.02	0.05	−0.01
CCl_3F	Q_1	ν_{CF}	−0.17	0.11	−0.18	−0.24
	Q_2	ν_{CCl}	−0.02	−0.04	0.03	−0.03
	Q_3	δ_{ClCCl}	−0.02	−0.02	0.05	0.01
	Q_4	ν_{CCl}	−0.16	−0.26	0.14	−0.28
	Q_5	δ_{FCCl}	−0.06	0.01	0.04	−0.01
	Q_6	δ_{ClCCl}	0.01	−0.01	0.00	0.00

[a] ν_{CH}, ν_{CF}, and ν_{CCl} are symbols for the CH, CF, and CCl stretching modes. δ_{HCH}, δ_{FCF}, and δ_{ClCCl} are symbols for the HCH, FCF, and ClCCl deformations modes. Unmarked lines correspond to modes that are mixed and hence not characteristic of functional groups. The form of the theoretical molecular vibration and its frequency value were used to classify the vibrations, ν_{CH} ranged from 2910 to 3055 cm^{-1}, ν_{CF} from 1049 to 1283 cm^{-1}, ν_{CCl} from 539 to 915 cm^{-1}, δ_{HCH} from 1221 to 1508 cm^{-1}, δ_{FCF} from 442 to 632 cm^{-1}, and δ_{ClCCl} from 243 to 432 cm^{-1}.

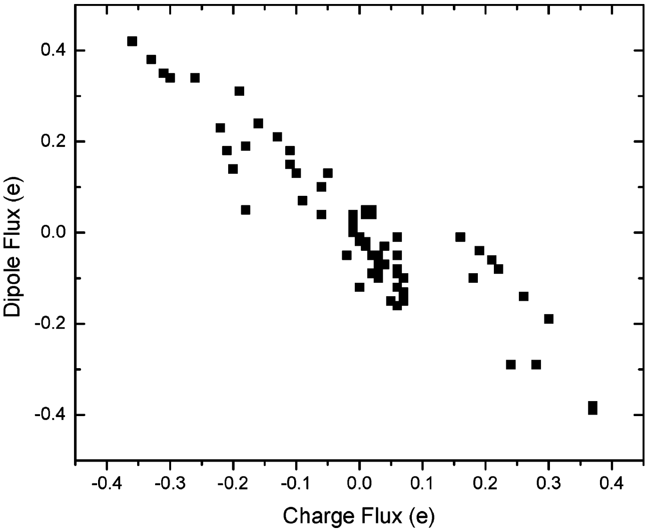

Figure 2. Charge flux vs dipole flux contributions to dipole moment derivatives for the normal coordinates of the fluoro-, chloro-, and fluorochloromethanes.

Three-dimensional (3D) graphs with charge, charge flux, and dipole flux axes could be drawn to describe the functional group vibrations. However, since the charge flux and dipole flux have such a high negative correlation, they both provide essentially the same information and bidimensional graphs involving the charge on one axis and either of the fluxes on the other results in a very accurate representation of the 3D space.

Figure 4 shows a graph of charge vs dipole flux values for the stretching modes of all the molecules studied here. The use of charge flux instead of dipole flux in this graph would amount essentially to changing the sign of the ordinate values but would have little effect on the relative positions of the points. Three distinct groups can be identified, one for each characteristic stretching vibration.

The large negative fluorine charges and positive carbon ones in the fluoromethanes and fluorochloromethanes result in large charge contributions to the C−F stretching dipole moment derivatives ranging from −0.13 to −0.43 e. The right-most point in this group corresponds to the CF stretch in CH_3F and the one on the extreme left to the CF_4 stretch. The sum of the electronegativities of the terminal atoms gradually increases as one moves from right to left in this group.

The C−F stretches have charge fluxes varying between −0.02 to 0.22 e whereas their dipole fluxes are mostly negative ranging from +0.12 to −0.22 e. Figure 3 shows the relative sizes of

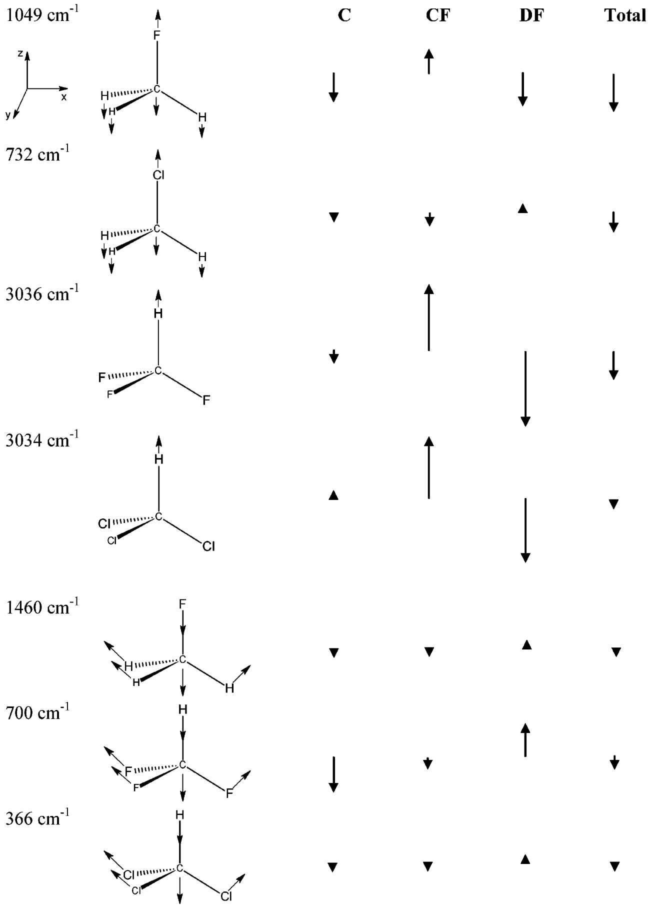

Figure 3. Functional group stretching and deformation vibrations and their corresponding charge, charge flux, and dipole flux contributions. The arrows represent − → + polarity.

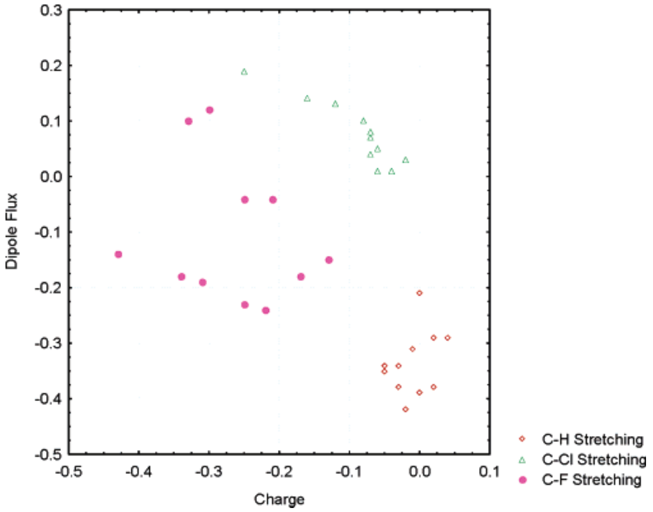

Figure 4. Charge plotted against dipole flux contribution for the stretching modes of the fluoro-, chloro-, and fluorochloromethanes.

the charge, charge flux, and dipole flux contributions for the CF stretch of CH_3F. The charge contribution is of about the same size as both flux contributions. Since the charge and dipole fluxes partially cancel one another, the total dipole moment derivative has a value close to the one for charge contribution. As more fluorines (and/or chlorines) are substituted for hydrogen, the charge contribution increases in importance while the two flux contributions still cancel one another. As such, the charge contributions dominate the C−F stretching derivatives of the fluoromethanes. For the same reason, charge contributions are also important for determining the values of the C−F stretching derivatives in the fluorochloromethanes.

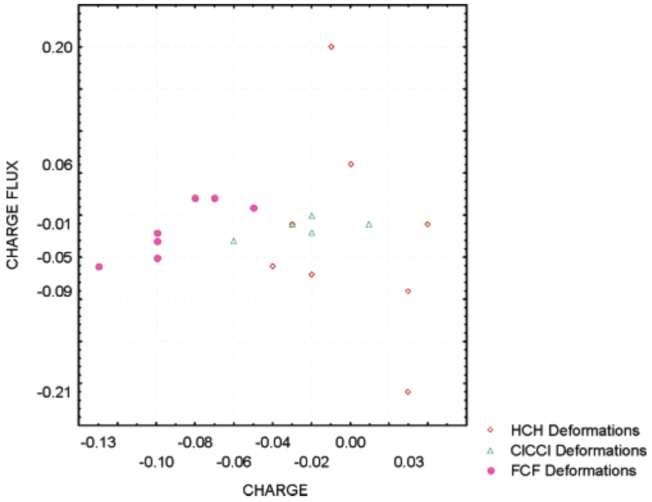

Figure 5. Charge plotted against charge flux contribution for the bending modes of the fluoro-, chloro-, and fluorochloromethanes.

The C−Cl stretching derivatives have charge, charge flux, and dipole flux contributions represented by points forming a distinct group in Figure 4. Charge contributions for this group range from −0.04 e for CH_3Cl to −0.25 e for CF_2Cl_2. The points in the right part of this group correspond to C−Cl stretches for the chloromethanes whereas the ones on the left represent C−Cl stretches for the fluorochloromethanes. The positive dipole fluxes for these stretches, +0.01 to +0.19 e, and the negative charge fluxes, −0.03 to −0.30 e, tend to cancel each other. This cancellation can be seen in Figure 3 for the C−Cl stretch of CH_3Cl.

The C−H stretching derivatives have points in the group at the bottom right of Figure 4. The charge contributions are small ranging from −0.05 to +0.04 e. On the other hand, the dipole flux contributions, ranging from −0.21 to −0.42 e, and the charge flux ones, ranging from +0.13 to +0.37 e, are much larger but cancel one another. The relative contributions of the C−H stretching derivatives of $CHCl_3$ and CHF_3 can be seen in Figure 3. The huge flux contributions cancel one another, and the direction of the dipole moment derivative vector is determined by the effectiveness of this cancellation and the direction of the charge contribution.

Figure 5 contains a graph of the charge vs charge flux contributions for those normal modes that can be securely classified as FCF, ClCCl, and HCH bending vibrations. The FCF and ClCCl deformations have points falling in distinct groups whereas the HCH deformation points form a diffuse group. The charge contributions normally have larger magnitudes for FCF deformations relative to the ClCCl ones, which are, in turn, usually larger than the HCH ones. Whereas the FCF and ClCCl deformations have moderate ranges for their charge and dipole fluxes, these contributions are more variable for the HCH deformations. The largest magnitudes of the charge fluxes in Figure 5 correspond to HCH deformations of the chloromethanes with the fluoromethane points being positioned closer to the zero charge flux line.

Finally, the charge flux−dipole flux cancellations are helpful in understanding why the carbon mean dipole moment derivatives of the fluorochloromethanes are so well correlated with the electrostatic potentials near the carbon nuclei of these molecules.[30] Graphs of the experimental carbon 1s electron ionization energies corrected for their neighboring atom electrostatic potentials against the corresponding carbon mean dipole moment derivatives determined from IR intensities are surprisingly very linear. Siegbahn's simple potential model[37] predicts this linear relationship to be expected if the carbon atomic charge is used instead of its mean dipole moment derivative. Of the 66 derivatives in Table 4, charge flux and dipole flux cancellations occur for 52 or almost 80% of the derivatives. It is not surprising then that the mean dipole moment derivatives are expected to be correlated with carbon atomic charges and would provide good fits to Siegbahn's simple potential model for carbon 1s electron ionization energies. A graph of the charge flux contributions against the dipole flux ones for the carbon mean dipole moment derivatives (not shown here) shows an even more negative correlation than the one illustrated in Figure 2.

Conclusions

The charge−charge flux−dipole flux (CCFDF) model quantified with QTAIM parameters at the MP2/6-311++G(3d,3p) level provides accurate estimates of the IR fundamental intensities of the fluorochloromethane molecules. This accuracy can be expected to improve upon using higher level quantum methods. Atomic dipoles and dipole fluxes are shown to be very important in modeling the molecular dipole moment and its derivatives. Charge flux−dipole flux cancellations are shown to be important in describing electronic density changes during molecular vibrations and seem to be important for explaining why mean dipole moment derivatives work so well in Siegbahn's simple potential model for calculating the 1s carbon electron ionization energies for the fluorochloromethanes. Atomic dipoles and their fluxes as well as atomic charges and charge fluxes are seen to be important in describing the electronic densities of the fluorochloromethane vibrational distortions. As such, one should consider their use in models of electronic structures for even larger molecular distortions that are important for describing complex chemical phenomena.

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References and Notes

(1) Haiduke, R. L. A.; de Oliveira, A. E.; Bruns, R. E. *J. Phys. Chem. A* **2004**, *108*, 6788.
(2) Haiduke, R. L. A.; Bruns, R. E. *J. Phys. Chem. A* **2005**, *109*, 2680.
(3) César, P. H.; Faria, S. H. D. M.; da Silva, J. V., Jr.; Haiduke, R. L. A.; Bruns, R. E. *Chem. Phys.* **2005**, *317*, 35.
(4) King, W. T.; Mast, G. B. *J. Phys. Chem.* **1976**, *80*, 2521.
(5) Bode, J. H. G.; Smit, W. M. A. *J. Phys. Chem.* **1980,** *84*, 198.
(6) Saëki, S.; Mizuno, S.; Kondo, S. *Spectrochim. Acta, Part A* **1976,** *32*, 403.
(7) Heicklen, J. *Spectrochim. Acta, Part A* **1961**, *17*, 201.
(8) Russell, J. W.; Needham, C. D.; Overend, J. *J. Chem. Phys.* **1966**, *45*, 3383.
(9) Barrow, G. M.; McKean, D. C. *Proc. R. Soc. London, Ser. A* **1952**, *213*, 27.
(10) Mizuno, M.; Saëki, S. *Spectrochim. Acta, Part A* **1976**, *32*, 1077.
(11) Morcillo, J.; Zamarano, L. R.; Heredia, J. M. V. *Spectrochim. Acta, Part A* **1966**, *22*, 1969.
(12) Kondo, S.; Saëki, S. *J. Chem. Phys.,* **1981** *74*, 6603.
(13) Levine, R. W.; Person, W. B. *J. Phys. Chem.* **1977**, *81*, 1118.
(14) Morcillo, J.; Herranz, J.; Biarge, F. *Spectrochim. Acta* **1959**, *15*, 110.
(15) Schurin, B. *J. Chem. Phys.* **1959**, *30*, 1.
(16) Dickson, A. D.; Mills, I. M.; Crawford, B. L., Jr. *J. Chem. Phys.* **1957**, *27*, 445.
(17) Saëki, S.; Tanabe, K. *Spectrochim. Acta, Part A* **1969**, *25*, 1325.
(18) Tanabe, K.; Saëki, S. *Spectrochim. Acta, Part A* **1970**, *26*, 1469.
(19) Kim, K.; King, W. T *J. Chem. Phys.*, **1984** *80*, 978.
(20) Person, W. B.; Rudys, S. K.; Newton, J. H. *J. Phys. Chem.* **1975**, *79*, 2525.
(21) Golden, W. G.; Horner, D.; Overend, J. *J. Chem. Phys.* **1978**, *68*, 964.
(22) Varanasi, P.; Ko, F. K. *J. Quant. Spectrosc. Radiat. Transfer* **1977**, *17*, 385.
(23) Varanasi, P.; Chudamani, K. *J. Quant. Spectrosc. Radiat. Transfer* **1988**, *39*, 193.
(24) Person, W. B.; Rudys, S. K.; Newton, J. H. *J. Phys. Chem.*, **1975**, *79*, 2525.
(25) Li, Z.; Varanasi, P. *J. Quant. Spectrosc. Radiat. Transfer* **1994**, *52*, 137.
(26) Names, R.; Silvaggio, P. M.; Boese, R. W. *J. Quant. Spectrosc. Radiat. Transfer* **1980**, *23*, 211.
(27) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory;* Clarendon Press: Oxford, U.K., 1990.
(28) Bader, R. F. W.; Matta, C. F. *J. Phys Chem. A* **2004**, *108*, 8385.
(29) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; Macdougall, P. J.; Wiberg, K. B. *J. Chem. Phys***.**, **1987**, *87*, 1142.
(30) Guadagnini, P. H.; de Oliveira, A. E.; Bruns, R. E.; Neto, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 4224.
(31) Person, W. B.; Newton, J. H. *J. Chem. Phys.* **1974**, *61*, 1040.
(32) Biarge, J. F.; Herranz, J.; Morcillo, J. *An. R. Soc. Esp. Fis. Quim., Ser. A* **1961**, 57, 81.
(33) Wilson, E. B.; Decius J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955.
(34) Overend, J. In *Infrared Spectroscopy and Molecular Structure*; Davis, M., Ed.; Elsevier: New York, 1963; Chapter 10, p 354.
(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, 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.; Liashenko, A.; Piskorz, P.; Komaromi, 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.; Chen, 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.
(36) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Hauper Collins College Publishers: New York, 1993; p 393−394, 425.
(37) Siegbahn, K.; Nordling, C.; Johanson, G.; Hedmar, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werne, L. O.; Mann, R.; Baer, Y. *ESCA Applied to Free Molecules*; North-Holland: Amsterdam, The Netherlands, 1969.