

ChelpG and QTAIM atomic charge and dipole models for the infrared fundamental intensities of the fluorochloromethanes

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Abstract ChelpG atomic charges and dipoles and the charge–charge flux–dipole flux (CCFDF) model have been used to quantitatively estimate the fundamental infrared intensities of the fluorochloromethanes. Since the ChelpG calculational procedure includes the constraint that the atomic charges and dipoles reproduce the equilibrium dipole moments the model results in accurate intensity values that have a root mean square error of 0.7 km mol^{-1} compared to those determined directly from the MP2/6-311G++(3d,3p) electronic density and 23.1 km mol^{-1} relative to the experimental intensities. Although these ChelpG results for total dipole moment derivatives are almost the same as those obtained previously using QTAIM (Quantum Theory of Atoms in Molecules) atomic charges and dipoles in the CCFDF model, their charge, charge flux and dipole flux contributions are completely different. Whereas the contributions calculated using the QTAIM parameters have values following expectations based on electronegativity concepts this is not true for those obtained from the ChelpG parameters. Mean dipole moment derivatives determined from experimental fundamental infrared intensities are compared with the ChelpG and QTAIM atomic charges. Furthermore, Generalized Atomic Polar Tensor Charges (GAPT) are found to need correction for their dynamic contributions if they are to be used as static atomic charges.

Keywords Infrared intensities · Dipole moment derivatives · Atomic charges · ChelpG · QTAIM

1 Introduction

Infrared fundamental intensities provide important information on how electronic densities change as molecules vibrate. As such their interpretation can lead to the determination of atomic parameters that can simplify studies for which the knowledge of accurate electronic densities, such as those obtained from sophisticated ab initio quantum chemical models, is necessary. Accurate infrared fundamental intensities have been calculated from atomic charges and dipoles using charge–charge flux–dipole flux (CCFDF) models for a variety of small gas phase molecules [1–4]. In these investigations Bader's Quantum Theory of Atoms in Molecules [5,6] (QTAIM) has been used to determine the atomic charges and dipoles from the molecular electronic density. A fundamental question arising in many applications including those involving CCFDF models is how to calculate the atomic charges and dipoles. Alternative methods are available for doing this. Besides the QTAIM method, charges and dipoles can be obtained from the Charges from Electrostatic Potential [7,8] (Chelp and ChelpG) methods. Their charges have been widely used in molecular dynamics [9], Monte Carlo [10], molecular modeling [11] and other applications [12]. They are often preferred for applications involving large molecules owing to the modest computational effort necessary for their calculation.

Since accurate molecular dipole moments can be obtained from ChelpG atomic dipoles and charges one can also expect to calculate accurate intensity values with their application in CCFDF models. So it is tempting to substitute atomic

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dipoles and charges calculated from QTAIM by those using the ChelpG method to reduce computational requirements. However, there is no guarantee that the interpretation of the electronic changes accompanying molecular vibrations will be the same for both types of parameters. For this reason the objective of this study is to verify whether ChelpG atomic dipoles and charges are really capable of providing fundamental infrared intensities that are as accurate as those obtained using QTAIM parameters in the CCFDF model. Furthermore comparisons are made between the ChelpG and QTAIM charge, charge flux and dipole flux contributions to the electronic density changes for the vibrations of the fluorochloromethanes.

Here ChelpG atomic dipoles and charges are obtained from the MP2/6-311++G(3d,3p) level electronic densities of the fluorochloromethanes. These parameters are then used to calculate their infrared intensities. The intensity results are compared with CCFDF/QTAIM values already reported [2]. The fluorochloromethanes are an especially appropriate family of molecules for this kind of study since it contains both non-polar and very polar molecules. Specifically the existence of a strong negative correlation between charge flux and dipole flux contributions such as found for the QTAIM parameters will be investigated for the ChelpG charges and dipoles.

2 Calculations

The basic equations relating charge, charge flux and dipole flux contributions to the molecular dipole moment derivatives [13] and atomic polar tensors [14, 15] have been published previously [1, 2]. Within the harmonic oscillator-linear dipole moment approximation, fundamental infrared intensities, A_j , are directly related to the squares of the molecular dipole moment derivatives with respect to the normal coordinates, $\partial \vec{p} / \partial Q_j$,

$$A_j = \frac{N_A \pi}{3c^2} \left(\frac{\partial \vec{p}}{\partial Q_j} \right)^2 \quad j = 1, 2, \dots, 3N - 6 \quad (1)$$

where N_A and c are Avogadro's number and the velocity of light, respectively [2]. These derivatives can be transformed to atomic Cartesian coordinates. These derivatives make up the polar tensor [14, 15] and can be decomposed into contributions from the movement of equilibrium charge (charge contribution), intramolecular charge transfer occurring during the vibration (charge flux contribution) and changes in polarizations of the electron clouds during the vibrations (dipole flux contribution) [1]. For diagonal polar tensor elements

$$\frac{\partial p_r}{\partial r_a} = q_a + \sum_i r_i \left(\frac{\partial q_i}{\partial r_a} \right) + \sum_i \frac{\partial m_{i,r}}{\partial r_a} \quad (2)$$

and for the off-diagonal ones

$$\frac{\partial p_s}{\partial r_a} = \sum_i s_i \left(\frac{\partial q_i}{\partial r_a} \right) + \sum_i \frac{\partial m_{i,s}}{\partial r_a} \quad (3)$$

where $r, s = x, y, z$, a refers to the displaced atom, q_a and q_i are atomic charges and $m_{i,r}$ and $m_{i,s}$ are Cartesian components of the atomic dipole moments.

Since polar tensor element values depend on the orientation of the molecule in the Cartesian coordinate system it is convenient to use the rotationally invariant atomic mean dipole moment derivative, \bar{p}_a , in comparing polar tensors results where

$$\bar{p}_a = 1/3 \left[\left(\frac{\partial p_x}{\partial x_a} \right) + \left(\frac{\partial p_y}{\partial y_a} \right) + \left(\frac{\partial p_z}{\partial z_a} \right) \right] \quad (4)$$

The atomic mean dipole moment derivative has also been interpreted as an atomic charge, the so-called generalized atomic polar tensor (GAPT) charge [16]. This quantity also has additive charge, charge flux and dipole flux contributions [17].

Geometry optimizations were carried out at the MP2/6-311++G(3d,3p) level using the Gaussian 03 electronic structure program [18]. The ChelpG atomic charges and dipoles were calculated from the electronic density implementing the ChelpG routine of the Gaussian package imposing the restriction that the ChelpG molecular dipole moment reproduce the MP2/6-311++G(3d,3p) molecular dipole moment calculated directly from the electronic density. The numerical derivatives of the molecular dipole moment with respect to atomic Cartesian coordinates (polar tensor elements) were calculated using the Placzek [19, 20] program from atomic charges and dipoles obtained from the molecular equilibrium geometry and geometries with atomic Cartesian coordinates displaced by ± 0.01 Å for all molecules except for the CF₄ molecule. The CCFDF/ChelpG calculated intensities for CF₄ using the ± 0.01 displacements were much different than those obtained directly from the MP2 electronic density. Displacements of ± 0.005 Å for CF₄ yielded CCFDF/ChelpG results in almost exact agreement with the MP2 values and these are reported here. Averages of numerical derivatives calculated from the positive and negative displacements of each atomic Cartesian coordinate were used to estimate the polar tensor elements. For a molecule with N atoms molecular electronic calculations for $6N$ geometries slightly distorted from equilibrium would be necessary. However, the Placzek program is capable of exploiting molecular symmetry eliminating redundant calculations. As such only 12 non-equilibrium calculations were performed for the T_d molecules and 18 for the C_{2v} and C_{3v} symmetry molecules, rather than 30 calculations for each molecule. This reduced the computational effort by about half.

Table 1 ChelpG and QTAIM charge and dipole contributions calculated at the MP2/6-311++G(3d,3p) level and their sums along with total molecular dipole moments calculated directly from the MP2/6-

311++G(3d,3p) level electron density and experimental dipole moments (units of Debye, D)

| Molecule | $P_{\text{ChelpG}}^{\text{charge}}$ | $P_{\text{ChelpG}}^{\text{dipole}}$ | $P_{\text{QTAIM}}^{\text{charge}}$ | $P_{\text{QTAIM}}^{\text{dipole}}$ | $P_{\text{ChelpG}}, P_{\text{MP2}}$ and P_{QTAIM} | $P_{\text{exp}}^{\text{a}}$ |
|---------------------------------|-------------------------------------|-------------------------------------|------------------------------------|------------------------------------|--|-----------------------------|
| CH ₃ F | -1.42 | -0.52 | -4.31 | 2.38 | -1.93 | 1.86 |
| CH ₂ F ₂ | -2.78 | 0.74 | -5.11 | 3.07 | -2.04 | 1.98 |
| CHF ₃ | 2.53 | -0.85 | 4.72 | -3.04 | 1.68 | 1.65 |
| CH ₃ Cl | -3.09 | 1.16 | -2.27 | 0.34 | -1.93 | 1.89 |
| CH ₂ Cl ₂ | -3.15 | 1.52 | -2.20 | 0.57 | -1.63 | 1.60 |
| CHCl ₃ | 1.94 | -0.90 | 1.62 | -0.57 | 1.05 | 1.04 |
| CFCl ₃ | 0.49 | -0.99 | -3.15 | 2.65 | -0.50 | 0.46 |
| CF ₂ Cl ₂ | 0.52 | -1.12 | -3.80 | 3.20 | -0.60 | 0.51 |
| CF ₃ Cl | -0.51 | 1.06 | 3.43 | -2.87 | 0.56 | 0.50 |

^a Estimated experimental errors for these molecules range from ± 0.01 to ± 0.03 D [21]

3 Results

Table 1 contains the ChelpG and QTAIM charge and dipole contributions to the molecular dipole moment, their sum and the dipole moments of the fluorochloromethanes calculated directly from the MP2/6-311++G(3d,3p) electron density as well as the experimental values [21]. The ChelpG values in this table were obtained using the constraint that the calculated moment be the same as the one calculated from the electron density. As such the ChelpG atomic charges and dipoles result in molecular dipole moment values in exact agreement with the values calculated directly from the electron density. They are also in exact agreement with those calculated [2] using the QTAIM method for which no such constraint is imposed. Similar to the results obtained from QTAIM, both charge and dipole contributions are significant in determining the total ChelpG molecular moment. Except for methyl fluoride, the charge and dipole contributions have opposite signs as do the QTAIM parameters. The dipole directions owing to charge separation are opposite the resultants of the atomic dipoles. However, individual contributions have quite different values depending on which method is used in their calculation. Even the relative signs of the contributions are not always the same. ChelpG charge and dipole contributions have smaller magnitudes for the fluoromethanes and fluorochloromethanes but larger ones for the chloromethanes. There is no evidence of significant correlation ($r = 0.43$) between the ChelpG and QTAIM atomic parameters.

The fluorochloromethane fundamental infrared intensities calculated using the ChelpG atomic charges and dipoles are presented in Supplementary Table A1 of the supporting information along with the experimental values, those obtained using the CCFDF/QTAIM model and those calculated directly from the molecular wavefunction.

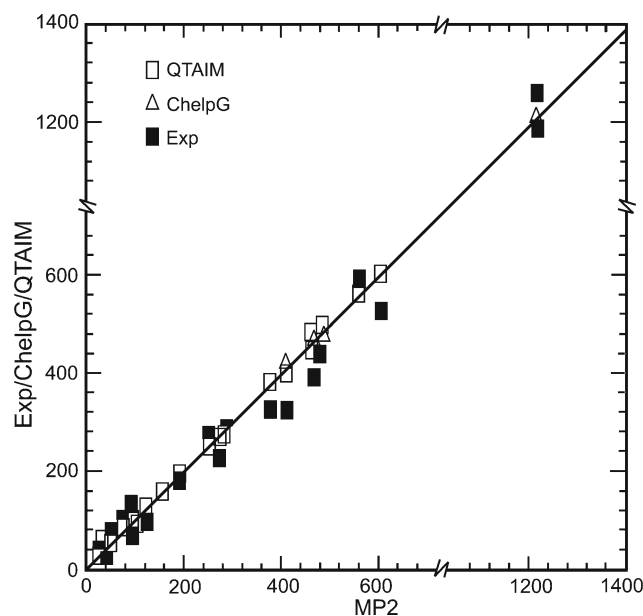


Fig. 1 Infrared intensities calculated from ChelpG and QTAIM atomic charges and dipoles using the CCFDF model along with experimental values plotted against those obtained directly from the MP2/6-311++G(3d,3p) electron density

Figure 1 summarizes these results with a graph of the MP2 analytical intensities plotted against the CCFDF/ChelpG, CCFDF/QTAIM and the experimental intensities. The agreement of the CCFDF/ChelpG and CCFDF/QTAIM values with the MP2 intensities is excellent with root mean square errors (rms) of 0.7 and 5.6 km mol^{-1} , respectively. The rms error of the CCFDF/ChelpG values relative to the experimental values, 23.1 km mol^{-1} , is almost exactly the same as the error for the QTAIM values, 23.0 km mol^{-1} .

Table 2 ChelpG and QTAIM charge, charge and dipole flux contributions, total mean dipole moment derivatives and mean derivatives determined from experimental infrared intensities for the fluorochloromethanes (units of electrons, e)

| Molecule | ChelpG | | | | QTAIM | | | | Exp. |
|---------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | C | CF | DF | Total | C | CF | DF | Total | |
| Carbon | | | | | | | | | |
| CH ₄ | 1.243 | 0.685 | -1.926 | 0.002 | 0.086 | -0.484 | 0.393 | -0.005 | 0.016 |
| CH ₃ F | 1.839 | 0.537 | -1.826 | 0.550 | 0.641 | -0.515 | 0.374 | 0.500 | 0.541 |
| CH ₂ F ₂ | 1.919 | 0.684 | -1.514 | 1.089 | 1.222 | -0.545 | 0.409 | 1.086 | 1.014 |
| CHF ₃ | 2.249 | 0.919 | -1.584 | 1.584 | 1.846 | -0.692 | 0.428 | 1.582 | 1.523 |
| CF ₄ | 2.570 | 1.213 | -1.743 | 2.040 | 2.512 | -0.981 | 0.495 | 2.026 | 2.049 |
| CH ₃ Cl | 2.230 | 0.453 | -2.405 | 0.278 | 0.190 | -0.186 | 0.267 | 0.271 | 0.277 |
| CH ₂ Cl ₂ | 2.620 | 0.351 | -2.385 | 0.586 | 0.271 | 0.233 | 0.075 | 0.579 | 0.527 |
| CHCl ₃ | 2.853 | 0.428 | -2.383 | 0.898 | 0.338 | 0.728 | -0.175 | 0.891 | 0.827 |
| CCl ₄ | 3.005 | 0.718 | -2.524 | 1.119 | 0.397 | 1.251 | -0.458 | 1.190 | 1.043 |
| CFCl ₃ | 2.897 | 1.012 | -2.463 | 1.446 | 0.900 | 0.821 | -0.296 | 1.425 | 1.367 |
| CF ₂ Cl ₂ | 2.821 | 1.134 | -2.287 | 1.668 | 1.420 | 0.304 | -0.052 | 1.672 | 1.636 |
| CF ₃ Cl | 2.668 | 1.218 | -2.023 | 1.863 | 1.958 | -0.299 | 0.203 | 1.862 | 1.863 |
| Hydrogen | | | | | | | | | |
| CH ₄ | -0.311 | -0.131 | 0.441 | -0.001 | -0.021 | 0.121 | -0.099 | 0.001 | -0.004 |
| CH ₃ F | -0.431 | -0.046 | 0.461 | -0.016 | 0.000 | 0.114 | -0.126 | -0.012 | -0.017 |
| CH ₂ F ₂ | -0.342 | -0.053 | 0.369 | -0.026 | 0.032 | 0.115 | -0.167 | -0.020 | -0.018 |
| CHF ₃ | -0.339 | -0.078 | 0.406 | -0.011 | 0.077 | 0.141 | -0.229 | -0.011 | 0.004 |
| CH ₃ Cl | -0.533 | -0.253 | 0.784 | -0.002 | 0.021 | 0.089 | -0.110 | 0.000 | -0.002 |
| CH ₂ Cl ₂ | -0.604 | 0.423 | 0.171 | -0.010 | 0.061 | 0.052 | -0.119 | -0.006 | -0.015 |
| CHCl ₃ | -0.704 | 0.178 | 0.493 | -0.033 | 0.097 | 0.008 | -0.128 | -0.023 | -0.022 |
| Fluorine | | | | | | | | | |
| CH ₃ F | -0.536 | -0.566 | 0.600 | -0.502 | -0.645 | 0.159 | -0.016 | -0.502 | -0.49 |
| CH ₂ F ₂ | -0.617 | -0.506 | 0.600 | -0.523 | -0.644 | 0.157 | -0.038 | -0.525 | -0.488 |
| CHF ₃ | -0.636 | -0.174 | 0.288 | -0.522 | -0.641 | 0.183 | -0.066 | -0.524 | -0.506 |
| CF ₄ | -0.642 | -0.263 | 0.396 | -0.510 | -0.628 | 0.245 | -0.118 | -0.501 | -0.512 |
| CFCl ₃ | -0.790 | -0.943 | 1.165 | -0.568 | -0.607 | 0.107 | -0.059 | -0.559 | -0.486 |
| CF ₂ Cl ₂ | -0.750 | -0.503 | 0.697 | -0.556 | -0.617 | 0.133 | -0.067 | -0.551 | -0.585 |
| CF ₃ Cl | -0.682 | -0.269 | 0.412 | -0.539 | -0.624 | 0.177 | -0.083 | -0.530 | -0.59 |
| Chlorine | | | | | | | | | |
| CH ₃ Cl | -0.662 | 0.002 | 0.386 | -0.274 | -0.253 | -0.080 | 0.055 | -0.278 | -0.271 |
| CH ₂ Cl ₂ | -0.706 | -0.046 | 0.468 | -0.284 | -0.197 | -0.168 | 0.080 | -0.285 | -0.248 |
| CHCl ₃ | -0.705 | -0.420 | 0.836 | -0.289 | -0.145 | -0.245 | 0.107 | -0.283 | -0.267 |
| CCl ₄ | -0.751 | -0.039 | 0.492 | -0.298 | -0.099 | -0.313 | 0.130 | -0.282 | -0.261 |
| CFCl ₃ | -0.700 | -0.209 | 0.604 | -0.305 | -0.098 | -0.309 | 0.148 | -0.259 | -0.294 |
| CF ₂ Cl ₂ | -0.660 | -0.227 | 0.604 | -0.283 | -0.096 | -0.286 | 0.095 | -0.287 | -0.233 |
| CF ₃ Cl | -0.609 | -0.095 | 0.456 | -0.248 | -0.091 | -0.235 | 0.069 | -0.257 | -0.139 |

Estimated experimental errors given in Ref. [24] for the fluorochloromethanes range between ± 0.01 and $\pm 0.04e$ [22–24]

The atomic mean dipole moment derivatives and their charge, charge flux and dipole flux contributions calculated from the CCFDF/ChelpG and CCFDF/QTAIM models are given in Table 2 along with the mean derivatives determined from the experimental infrared fundamental intensities

of the gas-phase fluorochloromethane molecules [2]. The ChelpG and QTAIM total mean dipole moment derivatives are in excellent agreement. Furthermore both sets of calculated values agree very well with the experimentally derived values with rms errors of 0.050 and 0.048e for the ChelpG

and QTAIM values, respectively. The agreement between the theoretical values can be seen in Fig. 2 where the QTAIM and ChelpG values are plotted against one another. All the solid squared points representing total mean derivatives fall close to the diagonal line representing exact agreement. However, this is not true for the charge, charge flux and dipole flux contributions to the mean dipole moment derivatives that have points falling far from this line. The carbon charge contributions are represented by the solid triangles in the upper right corner of the graph. In all cases except for the carbon mean dipole moment derivatives for CF_4 , the ChelpG charge contributions are much larger than the QTAIM ones. The ChelpG fluorine and chlorine charge contributions to the mean dipole moment derivatives have very similar values ranging between -0.54 to $-0.79e$ whereas the QTAIM method predicts very different values for the fluorine, between -0.61 and $-0.65e$, and chlorine, -0.09 and -0.25 . It should be emphasized that these charge contributions are equivalent to the ChelpG and QTAIM atomic charges.

The ChelpG charge flux contributions to the mean dipole moment derivative are always positive for the carbon atom whereas the corresponding QTAIM contributions have both positive and negative values. In most cases, the dipole flux contributions for the ChelpG mean derivatives have a much larger absolute magnitude than the QTAIM values and for the carbon and fluorine atoms often have opposite signs.

The strong negative correlations observed previously [1–4] between the charge flux and dipole flux contributions to the QTAIM dipole moment derivatives of the fluorochloro-

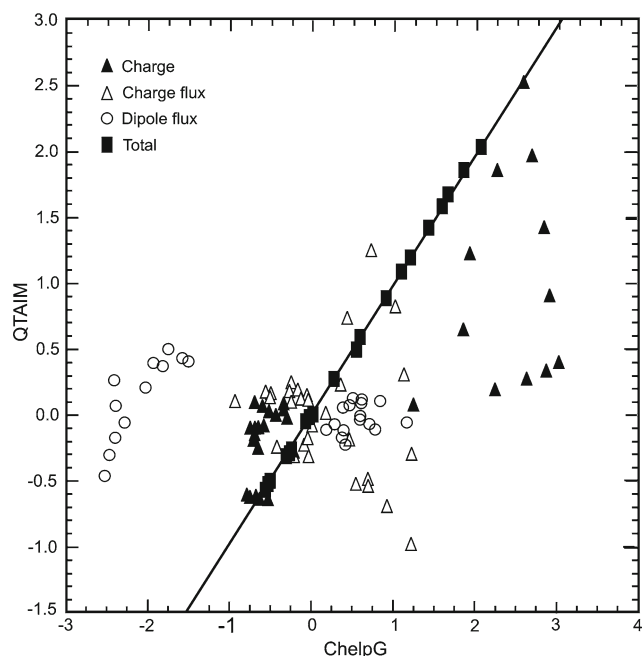


Fig. 2 ChelpG versus QTAIM charge, charge flux and dipole flux contributions for the polar tensor elements of the fluorochloromethanes

romethanes, difluoro- and dichloroethylenes and the X_2CY ($\text{X}=\text{H}, \text{F}$ and Cl ; $\text{Y}=\text{O}$ and S) molecules are also found for the ChelpG mean derivatives. For the values in Table 2 a $r = -0.87$ correlation coefficient is calculated for the ChelpG values compared with $r = -0.90$ for the corresponding QTAIM values.

4 Discussion

Infrared fundamental intensities of gas phase molecules provide quantitative information that is related to the atomic charges in molecules. The CCFDF model suggests that the atomic mean dipole moment derivative is a sum of contributions from its static atomic charge and the dynamic charge and dipole fluxes. As stated earlier the dynamic contributions have been calculated to be negatively correlated and have opposite signs for the fluorochloromethanes as well as for other molecules. Intramolecular electron transfers in a certain direction during the molecular vibrations is interpreted as being accompanied by changes in electron density polarizations, which occur in the opposite direction. If this cancellation of dynamic effects would be perfectly efficient the atomic mean dipole moment derivatives determined from experimental intensities are expected to be the same as the static atomic charges. This would allow an experimental, although indirect, determination of atomic charge values. Indeed the GAPT charges, often used in theoretical treatments, would be identical to these static charges.

In Fig. 3, a graph of the QTAIM and ChelpG calculated atomic charges plotted against the experimentally derived mean dipole moment derivatives for the carbon, hydrogen, fluorine and chlorine atoms is presented. The fluorine, chlorine and hydrogen QTAIM charges are very close to the line representing exact agreement with the atomic mean dipole moment derivatives. The QTAIM flux terms for the fluorine atoms have flux sums that vary from 0.05 to $+0.14e$. For this reason all of the QTAIM fluorine static charges are somewhat more negative than their corresponding mean dipole moment derivatives calculated at the MP2/6-311++G(3d,3p) level or these derivatives determined from the infrared intensities. The ChelpG dynamic contributions vary from $+0.03$ to $+0.22e$ and are positioned close to or a bit lower than the fluorine charges in Fig. 3. The QTAIM dynamic contributions for the chlorine atoms cancel each other more efficiently than do the ChelpG ones. The QTAIM dynamic sums vary from -0.03 to $-0.19e$ whereas the ChelpG ones vary from 0.36 to $0.45e$. For this reason the QTAIM chlorine charges are a bit above or close to the diagonal line whereas the ChelpG charges are well below it. A similar situation occurs for the hydrogen atomic charges. QTAIM dynamic contribution sums range from $+0.02$ to $-0.12e$ for hydrogen whereas the ChelpG ones range from 0.31 to $0.67e$.

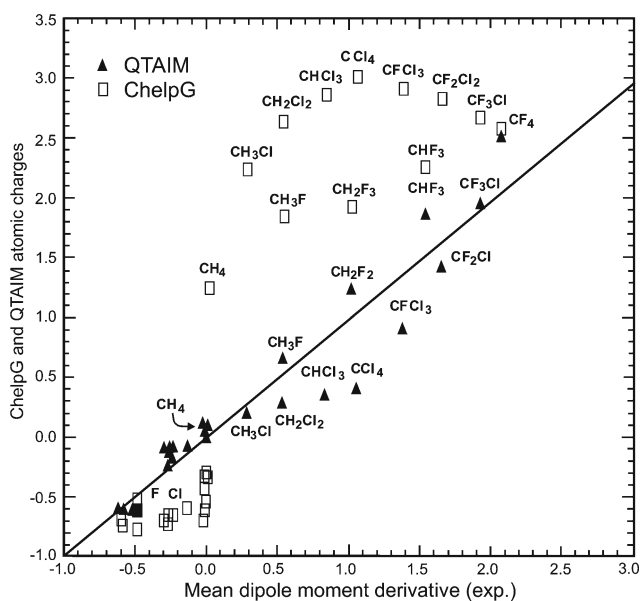


Fig. 3 Graph of the ChelpG and QAIM atomic charges against the mean dipole moment derivatives calculated from experimentally measured infrared intensities

The QAIM static charge values seem reasonable in the light of electronegativity arguments for these terminal atoms, between -0.02 to $+0.10e$ for hydrogen, -0.61 to $-0.65e$ for fluorine and -0.09 to $-0.25e$ for chlorine. This is not the case for the ChelpG static charges where the fluorine range of values, -0.54 to $-0.79e$, is about the same as the chlorine range, -0.61 to $-0.75e$, and just a bit more negative than the hydrogen ones, -0.31 to $-0.71e$.

The QAIM static carbon charges are also much closer to the diagonal line than the ChelpG ones. They are a bit larger than the fluoromethane carbon mean derivatives obtained from the experimental intensities. The dynamic contributions becomes less effective with increasing fluorine substitution with the methane and methyl fluoride points falling close to the diagonal line while the ones for CHF_3 and CF_4 are positioned farthest from it. The chloromethanes have positive sums for their QAIM flux contributions. As such their QAIM charges are less than their mean derivatives and their points fall below the diagonal. CFCl_3 and CF_2Cl_2 have positive total dynamic contributions whereas CF_3Cl , that is close to the diagonal, has a small negative one. On the other hand all the sums of the ChelpG dynamic contributions are large and negative. For this reason the ChelpG points for the static carbon charges fall well above the diagonal line.

Two articles have been published some time ago showing linear relationships between both theoretically and experimentally determined carbon mean dipole moment derivatives and the average electronegativities of the terminal atoms of the fluorochloromethanes [21,22]. The QAIM carbon static charges in Fig. 3 show behaviors one would expect

based on simple electronegativity arguments. As chlorines are substituted for hydrogens in the chloromethanes, fluorine substituted for hydrogen in the fluoromethanes and fluorine substituted for chlorine in the fluorochloromethanes the carbon charge increases in a linear manner, at a much lower rate for the chloromethanes than for the fluoromethanes and fluorochloromethanes. The ChelpG carbon static charges present a much different behavior for these substitutions. The carbon charge increases as the average electronegativity of the terminal atoms increases but more rapidly for chlorine substitution in the chloromethanes than fluorine substitution in the fluoromethanes. As a consequence the carbon charge calculated for CCl_4 is larger than the one for CF_4 with the carbon charge decreasing as fluorine is substituted for chlorine in the fluorochloromethanes contrary to expectations based on electronegativity arguments. It seems clear that even though both the ChelpG and QAIM atomic charges and dipoles are capable of providing accurate estimates of the dipole moments and infrared intensities of the fluorochloromethanes, only the QAIM description of the electronic densities of molecules near the molecular equilibrium configurations is consistent with our classical understanding of chemical bonding.

5 Conclusions

Even though both the ChelpG and QAIM methods are capable of providing atomic charges and dipoles that can be used to calculate accurate equilibrium dipole moments and infrared intensities of the fluorochloromethanes they predict very different electronic structures and changes in these structures on molecular vibrations. Only the QAIM parameters are consistent with classical chemical experience based on the electronegativity concept. As such one must be cautious in using ChelpG atomic charges and dipoles in chemical applications for which chemical interactions take place at distances shorter than the van der Waal radii of these molecules. One might expect this caution to be advisable for similar molecules. Furthermore GAPT charges should be corrected for their dynamic contributions if they are to be used to represent static charges.

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