Unavoidable failure of point charge descriptions of electronic density changes for out–of–plane distortions

Wagner E. Richter,[†] Leonardo J. Duarte,[‡] and Roy E. Bruns[*,‡]

† *Department of Chemical Engineering, Federal University of Technology – Paraná. Ponta Grossa–PR, Brazil.*

‡ *Institute of Chemistry, State University of Campinas. Campinas–SP, Brazil.*

E-mail: bruns@iqm.unicamp.br

Abstract

Population analyses based on point charge approximations accurately estimating the equilibrium dipole moment will systematically fail when predicting infrared intensities of out–of–plane vibrations of planar molecules, whereas models based on both charges and dipoles will always succeed. It is not a matter of how the model is devised, but on its number of degrees of freedom. Population analyses based on point charges are very limited in terms of the amount of meaningful chemical information they provide, whereas models employing both atomic charges and atomic dipoles should be preferred for molecular distortions. A good model should be able to correctly describe not only static, equilibrium structures but also distorted geometries in order to correctly assess information from vibrating molecules. The limitations of point charge models also hold for distortions much larger than those encountered vibrationally.

The relative distribution of electrons within a molecule is ubiquitous in the chemical literature. The concept of oxidation state, which is one of various ways of viewing the distribution of electrons to atoms in a molecule, is older than the actual discovery of electrons[1]. Almost 200 years later, assigning electronic populations to atoms remains a central task — actually a central challenge — for chemists.

The challenge arises from the continuum nature of the molecular electronic density: there is no unambiguous way of defining boundaries between atoms. Therefore more than twenty different models[2–19] have been proposed until now and many others may appear in the future. As far as there are new perspectives to be tested, new models will continue to be proposed.

Apart from technical features (low basis set dependence, rapid calculation, linear scaling, etc.), a good model should be able to deliver atomic charges whose interpretation follow elementary chemical concepts, such as electronegativity trends[7,18,19], as well as estimate accurate molecular properties directly related to electronic distributions, like molecular dipole moments[12,17,20], electrostatic potentials[4,5,13], core electron binding energies[21,22] and infrared intensities[23–29]. Notice that all these properties are experimentally measurable, so the failure in achieving them sounds an alert to the general and unrestricted usage of a particular charge model. Even though a charge model may be specifically designed to reproduce a given molecular property (like CM5 and ADCH charges for the dipole moment and CHELPG for the electrostatic potential), a truly good charge model should be able to perform well regardless of the property or the molecular system.

We will focus on the accurate estimation of infrared intensities as they can be measured by both FTIR and dispersive infrared spectrometers within an error of few percent[30,31]. The k^{th} IR intensity (from the k^{th} vibrational mode) depends on the square of the dipole moment derivative[32]:

$$A_k = \left(\frac{N_A \pi}{3c^2}\right)\left(\frac{\partial \vec{p}}{\partial Q_k}\right)^2 \tag{1}$$

Therefore, the ability to reproduce the molecular dipole moment is a key feature and a number of population analyses do not fulfill this initial requirement. Among those that succeed, there are two kinds of models: ones based solely on point charges (usually centered at the nuclei) and those based on both atomic charges and atomic dipoles. For an N–atom molecule:

$$\vec{p} = \sum_{i=1}^{N} \vec{p}_i \begin{cases} \vec{p} = \sum_{i=1}^{N} (q_i \cdot \vec{r}_i) & \text{(charge–only)} \\ \vec{p} = \sum_{i=1}^{N} (q_i \cdot \vec{r}_i + \vec{m}_i) & \text{(charge–and–dipole)} \end{cases} \tag{2}$$

We will demonstrate that the estimation of the correct dipole moment is a necessary but not sufficient condition for the quantitative reproduction of molecular IR intensities. These vibrational intensities depend on the dipole moment changes that is dependent on changes in the charges or both charges and dipoles. By computing these parameters for the equilibrium and several distorted geometries, one may calculate the intensities from different charge models. Since IR intensities are experimentally measurable and well–defined parameters, their accurate calculations may be used as a "standard quality test" for comparing different charge models. Here we demonstrate that reproducing the dipole moment is much easier than estimating the infrared intensity, a dynamical property.

If the chosen charge model employs both atomic charges and atomic dipoles, then inserting this expression in Eq. (1) will lead to three sets of derivatives: the first is associated with the movements of static equilibrium charges along the normal coordinate (C), the second with the changes in these charges, called charge transfers (CT) and the third with the changes in the atomic dipoles (called dipolar polarization, DP)[26,33,34]:

$$\left(\frac{\partial \vec{p}}{\partial Q_k}\right) = \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{C} + \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{CT} + \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{DP} \tag{3}$$

A detailed, step–by–step derivation on this subject may be found in a recent report[34]. On the other hand, if a model describes the molecular dipole moment from a distribution of net point charges centered at the nuclei, then the total derivative will be described solely by the first two derivatives. There are several papers in the literature dealing with this approach, often known as *Equilibrium Charge, Charge Flux*[23,24,27–29] models. Regardless of the name, the equations and interpretations are equivalent.

If the molecule is planar, a well established result from Dinur and Hagler[35] ensures that the charge transfer term must vanish for out–of–plane vibrations due to symmetry constraints. For charge–only models, this means that the IR intensity for the out–of–plane mode will be described solely by equilibrium atomic charges, whereas the models based on charges–and–dipoles will describe this intensity by a combination of equilibrium charges and changes in the atomic polarizations.

In order to compare these two types of models, we performed complete IR intensity analyses for three planar systems, ethene, *cis*–difluoroethene and benzene. These molecules had their geometries optimized and standard vibrational analysis carried out at the m06–2X/aug–cc–pVTZ level by Gaussian09[36]. From the equilibrium (optimized) geometry, the Placzek[37,38] program generated additional 6N (N being the number of atoms) distorted geometries regarding positive and negative displacements of each atom along the Cartesian axes. All these 6N+1 geometries had their atomic charges and dipoles computed from different models and, along with the Hessian matrix, Placzek numerically calculated the intensities from each charge model. QTAIM[8], Hirshfeld[9], DDEC6[15], CM5[12], ADCH[17], VDD[11] and CHELPG[5] models were investigated. QTAIM, Hirshfeld and DDEC6 will automatically reproduce the dipole moment if both charges and dipoles are employed. ADCH also satisfies the static dipole, but employing only atomic charges, whereas CM5 aims to reproduce the experimental molecular dipole moment, which may not have the same value determined from the wavefunction. CHELPG parameters, on the other hand, were computed under three different situations: point charges, without constraint to reproduce the dipole moment from the wavefunction (labeled CHELPG–q); point charges, but constrained to reproduce the dipole moment (CHELPG–qcd); and atomic charges and atomic dipoles, again constraining the entire set to reproduce the dipole moment (CHELPG–qmcd). Gaussian09, AIMAll[39], Chargemol[15] and Multiwfn[40] were used to compute all charges and atomic dipoles. Table S1 (Supp. Info.) shows the software used to compute each set of atomic charges and atomic dipoles. In order to avoid favour for any of the charge models all of them were evaluated using default approaches (*i.e.* default grids, meshs, initial densities, etc.). Slightly different numerical results could be achieved by modifying some (or various) of these parameters, but the overall conclusions described in the following should hold.

It is important to stress that the inclusion of atomic polarizations does not make the atomic charges and dipoles from QTAIM, Hirshfeld, DDEC6 and CHELPG–qmcd conceptually equivalent. They belong to a common group but their electronic density changes can be completely different and even incompatible with one another, depending on the relative magnitudes of their charges and dipoles. The same can be said about the different models with only point charges. Table 1 shows the amount of the total dipole moment attributed to charges and atomic dipoles for *cis*–difluoroethene.

Table 1: Total dipole moment contributions of atomic charges ($\vec{p}_q$) and atomic dipoles ($\vec{p}_{\vec{m}}$) for *cis*–difluoroethene, in units of Debye (D), from m06–2X/aug–cc–pVTZ calculations.

Model	$\vec{p}_q$	$\vec{p}_{\vec{m}}$	$\vec{p}_{total}$
Wavefunction	—	—	2.4068
QTAIM	8.1878	–5.7825	2.4053
Hirshfeld	1.6854	0.7205	2.4059
DDEC6	2.1509	0.2551	2.4060
CHELPG–qmcd	5.9131	–3.5072	2.4059
CHELPG–qcd	2.4059	0.0000	2.4059
CHELPG–q	2.3032	0.0000	2.3032
ADCH	2.4040	0.0000	2.4040
VDD	1.6526	0.0000	1.6526
CM5	2.4366	0.0000	2.4366
Experimental	—	—	2.42[41]

The magnitudes of the charge and dipole contributions are very different for these models. More interestingly, their relative orientations are not always the same. Consider, for example, QTAIM and Hirshfeld models, whose charges are quite often claimed to be too high and too low, respectively. The large QTAIM charge contribution is partially cancelled by the atomic dipoles, whose net polarization is in the opposite direction. In contrast, these Hirshfeld contributions are alligned, reinforcing each other to yield the correct dipole moment value. DDEC6 has slightly higher charges than Hirshfeld, but also a slightly lower net polarization, resulting in the same total dipole moment as well. It is important to understand that stating QTAIM charges are too high or Hirshfeld charges are too low is pointless if their associated atomic dipoles are not considered as well.

For the charge–only models, one can see the CHELPG–qcd and ADCH results agree with the equilibrium dipole moment from the wavefunction, whereas the remaining ones do not. CHELPG–q and CM5 yield values close to the target value, but these differences are large enough to compromise the accuracy of the infrared intensity analysis, as seen in Table 2. We stress that the CM5 model does not aim to reproduce the dipole from the wavefunction, but actually the experimental dipole. Its results are indeed closer to the experimental value than the wavefunction's value, as expected from its parametrization. The molecular dipoles from VDD charges are far from the target value, but it is worth mentioning that the Voronoi cells used to calculate VDD charges are not necessarily symmetric and thus could admit internal atomic dipoles to be therein defined[11]. Unfortunately, to the best of our knowledge this feature has not been computationally implemented yet.

The charges and dipoles from these models were used to calculate the electronic density changes accompanying vibrations, in order to determine their infrared intensities. Table 2 shows the wavenumbers and intensities for some of the IR active vibrations of ethene, *cis*–difluoroethene and benzene. Only vibrations with intensities are larger than 10.00 $km.mol^{-1}$ were considered so inherent numerical errors will be small compared to the total intensities.

The table was divided and colored in a way to ease the interpretation of the results. The second and third columns show the raw data from Gaussian09, obtained from the standard vibrational analysis delivered by this code. Columns 4–7 show the results for the four models which employ both atomic charges and atomic dipoles, whereas columns 8–12 show the results from the models employing only atomic charges. The intensities from Gaussian are colored blue, meaning they are the "target" values from the wavefunction. The intensities from the models are colored according to their agreement to the target data: green (0 to 4 $km.mol^{-1}$), orange (4 to 8 $km.mol^{-1}$) and red (8+ $km.mol^{-1}$).

It is evident that models including atomic dipoles perform much better. Except for a few results from CHELPG–qmcd, all results approach the target values within numerical accuracy. Notice that the ways in which these models are defined may be completely different (starting from reference atomic densities for DDEC6 and Hirshfeld, from ESP fit for CHELPG–qmcd and from the topology of the molecular density for QTAIM), but nearly all of them are equally capable of accurately reproducing all these intensities.

A totally different situation is found for the results from the point charge models. Both CHELPG–q and VDD charges disagree with the target intensities for almost all vibrations. Only two intensities from CHELPG–q agree with the wavefunction, but this seems to be more a coincidence than reliable agreement. One might expect CM5 charges to perform better than CHELPG–q and VDD, since CM5 charges were developed to reproduce the experimental dipole moment, but this is not the case. Probably the parametrization for the experimental dipole moment prevents these charges from capturing the real modifications in the wavefunctions of the distorted geometries.

Finally, we compare the point charge models that *do* reproduce the dipole moment of the wavefunction, CHELPG–qcd and ADCH. One can see that both are capable of accurately calculating the intensities of all vibrations for each molecule but one, specifically the out–of–plane mode (which is italic). This may seem surprising at first, but we are able to rationalize why this happens.

The static charges from the equilibrium geometry completely determine the first terms in RHS of Eq. (3). Since the distortions lead to rearrangements in the electronic density, the charges must vary, and the new charges calculated for the distorted geometries are also constrained to agree with the non–equilibrium dipole moments; the difference be-

Table 2: IR wavenumbers (in cm^{-1}) and intensities (in $km.mol^{-1}$) from Gaussian (the target data) and from various charge models as calculated by Placzek[a], for ethene, *cis*–difluoroethene and benzene.

	G09 Freq	G09 Inten	QTAIM	Hirshfeld	DDEC6	CHELPG–qmcd[b]	CHELPG–qcd[c]	CHELPG–q[d]	ADCH	VDD	CM5
Ethene	3251.4	12.64	13.89	13.79	13.79	14.82	13.79	21.34	13.79	14.70	0.13
	3148.4	8.53	9.99	10.00	10.03	10.59	10.01	12.39	9.99	24.77	2.08
	1476.3	10.76	10.25	10.26	10.25	9.33	10.26	4.84	10.48	0.48	0.20
	1002.1	*98.12*	*99.16*	*98.03*	*97.63*	*98.12*	*74.30*	*73.92*	*70.37*	*4.34*	*38.05*
cis–$C_2H_2F_2$	1802.6	66.25	66.06	65.61	65.65	67.90	65.56	70.47	65.72	140.96	26.98
	1413.7	35.57	36.04	37.16	37.23	41.80	37.04	28.17	36.72	37.50	28.48
	1297.1	42.36	43.37	42.67	42.67	38.56	42.78	34.59	42.15	0.99	25.17
	1170.3	121.17	119.36	119.89	119.88	115.56	120.00	121.63	119.94	68.57	95.88
	1054.9	65.04	64.11	64.59	64.69	64.97	64.57	75.20	64.78	148.15	30.68
	817.9	*47.17*	*47.01*	*47.52*	*47.54*	*45.85*	*21.85*	*21.21*	*32.13*	*4.54*	*19.14*
	785.2	31.74	32.13	31.91	31.96	30.81	31.93	37.46	31.85	15.93	18.10
Benzene	3199.9	20.10	22.32	22.31	22.20	25.22	22.23	29.01	22.64	24.58	0.15
	3198.4	19.07	21.08	22.23	22.24	18.29	22.55	27.21	22.35	901.09	0.14
	699.0	*112.70*	*114.95*	*112.19*	*112.17*	*107.42*	*40.81*	*45.97*	*101.67*	*11.06*	*59.69*

[a] Green cells show agreement within 4 $km.mol^{-1}$; orange cells between 4 and 8 $km.mol^{-1}$, and red cells 8+ $km.mol^{-1}$.
[b] CHELPG with atomic charges (q) and atomic dipoles (m), constrained (c) to reproduce the correct dipole (d) moment, calculated by Gaussian09.
[c] CHELPG with only atomic charges (q), constrained (c) to reproduce the correct dipole (d) moment, calculated by Gaussian09.
[d] CHELPG with only atomic charges (q), without constraining to reproduce the correct dipole moment, calculated by Multiwfn.

tween these charges and equilibrium ones determines the charge transfer term. Therefore, for in–plane vibrations, C+CT (or C+CT+DP) satisfactorily reproduce the correct dipole moment derivative and thus the correct IR intensity. Out–of–plane vibrations also display rearrangements in the electronic density, but CT term vanishes, and equilibrium charges cannot describe these changes resulting in errouneous intensity values.

The reason why all charge–dipole models accomplish this task is now evident. Even though the CT term must vanish (see Eq. (3)), there is still a single degree of freedom available in the form of the DP term, which ensures the correct calculation of the dipole moments of distorted geometries and hence the intensities. In other words, explicit consideration of atomic polarizations is necessary for quantitative assessment of IR intensities of out–of–plane vibrations. The popular claim that *some models can only reproduce the dipole moment if atomic dipoles are included*, usually presented as a disadvantage, is rather the sole reason of the superiority of all these models compared to those based solely on point charges. Therefore, a general conclusion is that reproducing the dipole moment is a necessary, but not sufficient condition for accurate and meaningful prediction of infrared intensities. The inclusion of atomic dipoles is mandatory for accurate intensity estimates as well as for any study focused on the electronic density changes accompanying molecular distortions, including (but not restricted to) vibrations. These findings may be summarized as:

$$\left(\frac{\partial \vec{p}}{\partial Q_k}\right)_{\text{wavef}} \neq \left(\frac{\partial \vec{p}}{\partial Q_k}\right)_{\text{charge–only}} = \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{C} \tag{4}$$

$$\left(\frac{\partial \vec{p}}{\partial Q_k}\right)_{\text{wavef}} = \left(\frac{\partial \vec{p}}{\partial Q_k}\right)_{\text{charge–dipole}} = \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{C} + \left(\frac{\partial \vec{p}}{\partial Q_k}\right)^{DP} \tag{5}$$

The dispute for the “better” charge model seems endless. Most of the defenders of a particular charge model stress only its advantages, which quite often summarizes to calculational convenience, basis set independence or transferability among different atoms. These are of course desirable features, but the ability of reproducing experimentally verifiable properties should be a most important feature in this pursuit, because if the charges themselves cannot be observed experimentally, at least some properties dependent on the charges can be measured with high precision. Dipole moments, infrared intensities and core–electron binding energies, which are experimentally measurable and unambiguosly defined, depend on the distribution of the electronic density which is not static in nature, as molecules are vibrating. All these properties are better rationalized if atomic dipoles are considered[42]. Therefore, much effort should be directed at how to describe the charge distributions of distorted geometries. Unfortunately, most of the times the importance of this feature is largely underestimated by researchers when presenting new charge models.

By demonstrating that models based on a point charge approach will systematically fail for out–of–plane intensities shows that the point charge approximation is in general very limited and efforts towards a deeper understanding of the role of atomic polarizations in chemistry is needed. Furthermore one cannot expect charge–only models to accurately describe electronic density changes for large out–of–plane distortions if they fail for small vibrational displacements. Force field development, which is historically associated with charge modelling, has experienced growing interest in charge fluxes in recent years[43–48]. We also advocate in favour of atomic polarizations as a rich source of information not only about static electronic density but also its dynamics. Infrared intensity analyses show that atomic polarizations are as important as charge fluxes in describing the dynamics of the electronic density.

Acknowledgements

WER thanks *Fundação Araucária de Apoio ao Desenvolvimento Científico e Tecnológico* (FAADCT/PR) for a research fellowship (89–2019/FA) and finantial support to computational facilities. LJD thanks *Fundação de Amparo à Pesquisa do Estado de São Paulo* (FAPESP) for a BEPE doctoral fellowship (2018/24844–7). REB acknowledges FAPESP for funding research grant (2018/08861–9) and *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq) for a research fellowship (302574/2019–0).

References

(1) Karen, P. Oxidation State, A Long-Standing Issue! Angewandte Chemie International Edition **2015**, 54, 4716–4726.

(2) Mulliken, R. Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. The Journal of Chemical Physics **1955**, 23, 1833.

(3) Montgomery, J.; Frisch, M.; Ochterski, J.; Petersson, G. A complete basis set model chemistry. VII. Use of the minimum population localization method. The Journal of Chemical Physics **2000**, 112, 6532.

(4) Chirlian, L.; Francl, M. Atomic charges derived from electrostatic potentials: A detailed study. Journal of Computational Chemistry **1987**, 8, 894.

(5) Breneman, C.; Wiberg, K. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. Journal of Computational Chemistry **1990**, 11, 361.

(6) Stone, A.; Alderton, M. Distributed multipole analysis: Methods and applications. Molecular Physics **1985**, 56, 1047.

(7) Cioslowski, J. A new population analysis based on atomic polar tensors. Journal of the American Chemical Society **1989**, 111, 8333.

(8) Bader, R. Atoms in Molecules: a quantum theory.; Clarendon Press, Oxford, 1994; p 292.

(9) Hirshfeld, F. Bonded-atom fragments for describing molecular charge densities. Theoretica Chimica Acta **1977**, 44, 129.

(10) Bultinck, P.; Alsenoy, C.; Ayers, P.; Carbo-Dorca, R. Critical analysis and extension of the Hirshfeld atoms in molecules. The Journal of Chemical Physics **2007**, 126, 144111.

(11) Guerra, C.; Handgraaf, J.-W.; Baerends, E.; Bickelhaupt, F. Voronoi deformation density (VDD) charges: Assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD methods for charge analysis. Journal of Computational Chemistry **2004**, 25, 189.

(12) Marenich, A.; Jerome, S.; Cramer, C.; Trhular, D. Charge Model 5: An Extension of Hirshfeld Population Analysis for the Accurate Description of Molecular Interactions in Gaseous and Condensed Phases. Journal of Chemical Theory and Computation **2012**, 8, 527.

(13) Singh, U.; Kollman, P. An approach to computing electrostatic charges for molecules. Journal of Computational Chemistry **1984**, 5, 129.

(14) Reed, A.; Weinstock, R.; Weinhold, F. Natural population analysis. The Journal of Chemical Physics **1985**, 83, 735.

(15) Limas, N.; Manz, T. Introducing DDEC6 atomic population analysis: part 1. Charge partitioning theory and methodology. RSC Advances **2016**, 6, 47771–47801.

(16) Vyboishchikov, S.; Voityuk, A. Iterative Atomic Charge Partitioning of Valence Electron Density. Journal of Computational Chemistry **2019**, 40, 875–884.

(17) Lu, T.; Chen, F. Atomic dipole moment corrected Hirshfeld population method. Journal of Theoretical and Computational Chemistry **2012**, 11, 163–183.

(18) Cho, M.; Sylvetsky, N.; Eshafi, S.; Santra, G.; Efremenko, I.; Martin, J. The Atomic Partial Charges Arboretum: Trying to See the Forest for the Trees. ChemPhysChem **2020**, 21, 688–696.

(19) Manz, T. Seven confluence principles: a case study of standardized statistical analysis for 26 methods that assign net atomic charges in molecules. RSC Advances **2020**, 10, 44121–44148.

(20) Bader, R.; Larouche, A.; Gatti, C.; Carroll, M.; MacDougall, P.; Wiberg, K. Properties of atoms in molecules: Dipole moments and transferability of properties. The Journal of Chemical Physics **1987**, 87, 1142.

(21) Saethre, L.; Siggel, M.; Thomas, T. Molecular charge distribution, core-ionization energies, and the point-charge approximation. Journal of the American Chemical Society **1991**, 113, 5224–5230.

(22) Guadagnini, P.; Oliveira, A.; Bruns, R.; Barros Neto, B. Core electron energies, infrared intensities and atomic charges. Journal of the American Chemical Society **1997**, 119, 4224–4231.

(23) Decius, J. An effective atomic charge model for infrared intensities. Journal of Molecular Spectroscopy **1975**, 57, 348.

(24) Milani, A.; Castiglioni, C. Atomic charges from atomic polar tensors: A comparison of methods. Journal of Molecular Structure:THEOCHEM **2010**, 955, 158.

(25) King, W.; Mast, G. Infrared intensities, polar tensors, and atomic population densities in molecules. Journal Physical Chemistry **1976**, 88, 2521.

(26) Haiduke, R.; Bruns, R. An atomic charge-charge flux-dipole flux atom-in-molecule decomposition for molecular dipole moment derivatives and infrared fundamental intensities. The Journal of Physical Chemistry A **2005**, 109, 2680.

(27) Milani, A.; Galimberti, D.; Castiglioni, C.; Zerbi, G. Molecular charge distribution and charge fluxes from Atomic Polar Tensors: The case of OH bonds. Journal of Molecular Structure **2010**, 976, 342–349.

(28) Milani, A.; Castiglioni, C. Modeling of Molecular Charge Distribution on the Basis of Experimental Infrared Intensities and First-Principles Calculations: The Case of CH Bonds. The Journal of Physical Chemistry A **2010**, 114, 624–632.

(29) Milani, A.; Tommasini, M.; Castiglioni, C. Atomic charges from IR intensity parameters: theory, implementation and application. Theoretical Chemistry Accounts **2012**, 131, 1139.

(30) Duarte, L.; Silva, A.; Richter, W.; Bruns, R. FTIR and dispersive gas phase fundamental infrared intensities of the fluorochloromethanes: Comparison with QCISD/cc-pVTZ results. Spectrochimica Acta Part A **2018**, 205, 269–275.

(31) Duarte, L.; Bruns, R. FTIR and dispersive gas phase absolute infrared intensities of hydrocarbon fundamental bands. Spectrochimica Acta Part A **2019**, 214, 1–6.

(32) Overend, J. In Infrared Spectroscopy and Molecular Structure; Davies, M., Ed.; Elsevier, 1963.

(33) Silva, A.; Richter, W.; Meneses, H.; Faria, S.; Bruns, R. How Accessible Is Atomic Charge Information from Infrared Intensities? A QTAIM/CCFDF Interpretation. The Journal of Physical Chemistry A **2012**, 116, 8238.

(34) Richter, W.; Duarte, L. J.; Vidal, L. N.; Bruns, R. AC/DC analysis: broad and comprehensive approach to analyze infrared intensities at atomic level. The Journal of Physical Chemistry A **2021**, 125, 3219.

(35) Dinur, U.; Hagler, A. Determination of atomic point charges and point dipoles from the Cartesian derivatives of the molecular dipole moment and second moments, and from energy second derivatives of planar dimers. I. Theory. The Journal of Chemical Physics **1989**, 91, 2949–2958.

(36) Frisch, M. et al. Gaussian09, Revision B.01. Gaussian, Inc., Wallingford CT, 2009.

(37) Gomes, T.; Silva, J.; Vidal, L.; Vazquez, P.; Bruns, R. ChelpG and QTAIM atomic charge and dipole models for the infrared fundamental intensities of the fluorochloromethanes. Theoretical Chemistry Accounts **2008**, 121, 173.

(38) Gomes, T.; Silva, J.; Vidal, L.; Vazquez, P.; Bruns, R. Implementação computacional do modelo carga-fluxo de carga-fluxo de dipolo para cálculo e interpretação das intensidades do espectro infravermelho. Química Nova **2008**, 31, 1750.

(39) Keith, T. AIMAll (Version 14.11.23), TK Gristmill Software, Overland Park KS, USA, 2014 (aim.tkgristmill.com).

(40) Lu, T.; Chen, F. Multiwfn, a multifunctional wavefunction analyzer. Journal of Computational Chemistry **2012**, 33, 580–592.

(41) Laurie, V. Microwave Spectrum of cis-Difluoroethylene. Structures and Dipole Moments of Fluoroethylenes. The Journal of Chemical Physics **1961**, 34, 291.

(42) Richter, W.; Duarte, L.; Bruns, R. Are GAPT charges really just charges? Submitted for publication **2021**,

(43) Kim, S.; Rhee, Y. Modeling Charge Flux by Interpolating Atomic Partial Charges. Journal of Chemical Information and Modeling **2019**, 59, 2837–2849.

(44) Sedghamiz, E.; Ghalami, F. Evaluating the Effects of Geometry and Charge Flux in Force Field Modeling. The Journal of Physical Chemistry A **2018**, 122, 4647–4653.

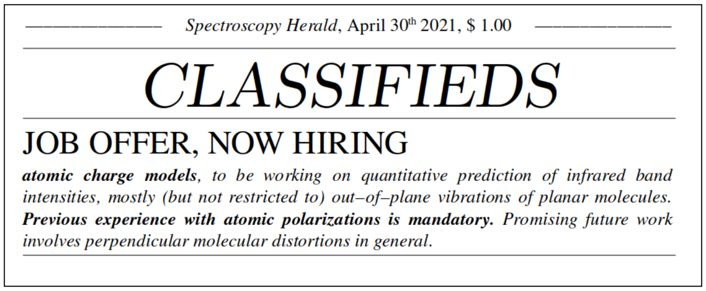
(45) Sedghamiz, E.; Nagy, B.; Jensen, F. Probing the Importance of Charge Flux in Force Field Modeling. Journal of Chemical Theory and Computation **2017**, 13, 3715–3721.

(46) Palmo, K.; Mannfors, B.; Mirkin, N.; Krimm, S. Inclusion of charge and polarizability fluxes provides needed physical accuracy in molecular mechanics force fields. Chemical Physics Letters **2006**, 429, 628–635.

(47) Hagler, A. Quantum Derivative Fitting and Biomolecular Force Fields: Functional Form, Coupling Terms, Charge Flux, Nonbond Anharmonicity, and Individual Dihedral Potentials. Journal of Chemical Theory and Computation **2015**, 11, 5555–5572.

(48) Hagler, A. Force field development phase II: Relaxation of physics-based criteria... or inclusion of more rigorous physics into the representation of molecular energetics. Journal of Computer-Aided Molecular Design **2019**, 33, 205–264.

Graphical TOC Entry



Spectroscopy Herald, April 30th 2021, $ 1.00

CLASSIFIEDS

JOB OFFER, NOW HIRING

atomic charge models, *to be working on quantitative prediction of infrared band intensities, mostly (but not restricted to) out–of–plane vibrations of planar molecules.* ***Previous experience with atomic polarizations is mandatory.*** *Promising future work involves perpendicular molecular distortions in general.*