

## Quantum Theory of Atoms in Molecules charge-charge transfer-dipolar polarization classification of infrared intensities

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Abstract: Fundamental infrared intensities of gas-phase molecules are sensitive probes of changes in electronic structure accompanying small molecular distortions. Models containing charge, charge transfer and dipolar polarization effects are necessary for a successful classification of the C-H, C-F and C-Cl stretching and bending intensities. C-H stretching and in-plane bending vibrations involving  $sp^3$  carbon atoms have small equilibrium charge contributions and are accurately modeled by the charge transfercounterpolarization contribution and its interaction with equilibrium charge movement. Large C-F and C=O stretching intensities have dominant equilibrium charge movement contributions compared to their charge transfer-dipolar polarization ones and are accurately estimated by equilibrium charge and the interaction contribution. The C-F and C-Cl bending modes have charge and charge transfer-dipolar polarization contribution sums that are of similar size but opposite sign to their interaction values resulting in small intensities. Experimental in-plane C-H bends have small average intensities of 12.6±10.4 km mol<sup>-1</sup> owing to negligible charge contribuions and charge whereas transfer-counterpolarization cancellations, their average out-of-plane experimental intensities are much larger,  $65.7\pm20.0$  km mol<sup>-1</sup>, as charge transfer is zero and only dipolar polarization takes place. The C-F bending intensities have large charge contributions but very small intensities. Their average experimental out-of-plane intensity of 9.9±12.6 km mol<sup>-1</sup> arises from the cancellation of large charge contributions by dipolar polarization contributions. The experimental average in-plane C-F bending intensities,  $5.8\pm7.3$  km mol<sup>-1</sup> is also small owing to charge and charge transfercounterpolarization sums being cancelled by their interaction contributions. Models containing only atomic charges and their fluxes are incapable of describing electronic structure changes for simple molecular distortions that are of interest in classifying infrared intensities. One can expect dipolar polarization effects to also be important for larger distortions of chemical interest.



Key-words: Charge transfer, polarization, infrared intensities, QTAIM..

**Support:** A. F. S. and L. J. D. thank São Paulo's FAPESP for the award of postdoctoral grant number 2014/21241-9 and undergrad fellowship 2016/07411-4, and R. E. B. acknowledges FAPESP for funding through the award 2009/09678 and Brazil's CNPq for research fellowship, 304518/2014-0. **References:** 

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