

Analysis of charge, charge flux and dipole flux contributions for infrared intensities of the OH stretching mode in carboxylic acid dimers

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The relevance of hydrogen bonds for chemical and biological systems motivates several experimental or theoretical studies on the nature of this type of interaction which governs not only the integrity of the genetic code of living beings, but also allows a variety of flat polycyclic aromatic molecules to intersect between the nitrogen bases of deoxyribonucleic acid (DNA) [1]. IUPAC defines hydrogen bonding as an "*attractive interaction between a hydrogen atom of a molecule or a molecular fragment XH, where X is more electronegative than H, and an atom or group of atoms of the same or different molecules*" [2]. This type of interaction can be represented simply by X-H ... Y, where X-H refers to the proton donor monomer and Y is the end of the acceptor unit where the interaction occurs.

The stretching of the X-H bond is usually the mode that shows larger intensity increments in the infrared spectra during the formation of hydrogen bonds when compared to the data of the respective isolated donor monomer. Thus, the partitioning of dipole moment derivatives in contributions of charge, charge flux and dipole flux (CCFDF), [3] from multipoles of the Quantum Theory of Atoms in Molecules (QTAIM), allows a deeper understanding of the reasons for the increase in infrared intensities of certain vibrational bands during the dimerization process of carboxylic acids.

All electronic structure calculations were performed in the *Gaussian 09* program [4] using the B2PLYP hybrid functional with the aug-cc-pVTZ base set. The QTAIM parameters of charge and atomic dipole were obtained with the AIMAll program [5] at the equilibrium positions of the atoms and in structures distorted by individual displacements of ± 0.01 Å along the three Cartesian axes. Finally, the infrared intensities were estimated by the CCFDF/QTAIM model using dipole moment derivatives in relation to the normal vibration coordinate.

The variations of infrared intensities for the analyzed vibrational modes can be understood in terms of dipole moment derivatives in relation to the normal mode of vibration (Equation 1) [6]. The contributions of charge, charge flux, dipole flux and the cross terms between these quantities can be visualized in Table 1.

$$A = \frac{N\pi}{3c^{2}} \left[\left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{C}^{2} + \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{CF}^{2} + \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{DF}^{2} + 2 \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{C} \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{CF} + 2 \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{DF} + 2 \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{CF} \left(\frac{\partial \vec{\mu}}{\partial Q_{i}} \right)_{DF} \right]$$
(1)



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Table 1: Variations of charge (C), charge flux (CF), dipole flux (DF) contributions and cross terms for the intensity, A, (km mol⁻¹) of O-H stretching mode during dimerization according to the CCFDF/QTAIM model

System	$\Delta A^{\rm C}$	ΔA^{CF}	ΔA^{DF}	$\Delta A^{C \times CF}$	$\Delta A^{C \times DF}$	$\Delta A^{CF \times DF}$	ΔA^{a}
BrCOOHBrCOOH	126.1	-159.0	59.3	2672.1	249.3	727.9	3675.9
CICOOHCICOOH	127.2	-239.9	65.1	2450.9	276.9	632.6	3312.8
FCOOHFCOOH	123.8	-405.1	80.3	1834.3	350.5	392.7	2376.6
HCOOHHCOOH	90.0	-469.1	-32.9	2222.1	-191.3	399.1	2017.8
ClCOOHBrCOOH	126.7	-207.4	61.9	2551.7	262.1	676.5	3471.4
CICOOHFCOOH	125.2	-337.5	74.1	2152.4	315.5	516.8	2846.6
CICOOHHCOOH	150.3	-382.1	48.7	2288.8	196.9	565.0	2867.6
BrCOOHHCOOH	150.2	-344.6	48.5	2416.8	193.3	621.3	3085.4
FCOOHBrCOOH	124.9	-299.2	69.1	2293.2	294.8	571.3	3054.1
FCOOHHCOOH	144.8	-458.3	50.6	1972.6	216.7	445.3	2371.8
CH ₃ COOHBrCOOH	145.0	-117.4	37.8	2744.4	171.6	722.8	3704.2
CH ₃ COOHClCOOH	132.6	-178.1	29.2	2630.3	146.1	646.0	3406.1
CH ₃ COOHFCOOH	144.2	-322.7	44.6	2265.9	212.8	541.5	2886.3
CH ₃ COOHHCOOH	177.6	-417.9	37.2	2361.3	48.7	487.5	2694.5
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^a $\Delta A = \left[\left(A_{O-H}(s) + A_{O-H}(as) \right)_{Dimer} - \left(A_{O-H}(a) + A_{O-H}(b) \right)_{Monomer} \right].$

The dimerization process results in an expressive increment in infrared intensities of the O-H stretching. The main factor responsible for these changes in intensities after the formation of the two hydrogen bonds is the charge variation of each atom during dimerization along with changes in the cross term between charge and fluxes of charge and atomic dipole (Figure 1).

Figure 1: Variations of the infrared intensity of the O-H stretching modes during dimerization as a function of the sum of changes in the charge contribution and its cross terms with charge and dipole fluxes



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