Characteristic behavior of carbonyl stretching IR absorption intensities

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INTRODUCTION

Vibrational frequencies are readily related to chemical groups and therefore called spectros–copic fingerprints. Infrared intensities, on the other hand, do not show such a characteristic pattern for their numerical values. In this work, the IR intensities of the carbonyl stretches in mono and dicarbonyl molecules are studied using the QTAIM/CCFDF and QTAIM/CCTCP models. Our efforts were directed to understand why this fingerprint feature does not hold for the absorption intensities as for the frequencies.

METHODOLOGY

The theoretical methodology is described in more detail in recent reports by our group[1,2]. Shortly, one can split the infrared intensity of any vibrational mode in terms of CCFDF contributions as presented in Eq. (1):

$$A_j = A_j^{(C^2)} + A_j^{(CF^2)} + A_j^{(DF^2)} \\ + A_j^{(C \times CF)} + A_j^{(C \times DF)} + A_j^{(CF \times DF)} \quad (1)$$

Due to their high correlation, one can sum the CF², DF² and CFxDF terms in a unique portion called *Charge Transfer–Counterpolarization*, and the CxCF and CxDF terms can be summed to form an interaction term:

$$A_j = A_j^{(C)} + A_j^{(CTCP)} + A_j^{(C \times CTCP)} \quad (2)$$

The results show how these two models can reproduce the infrared intensities of several carbonyl stretches with the advantage of a reliable physical interpretation for them.

RESULTS

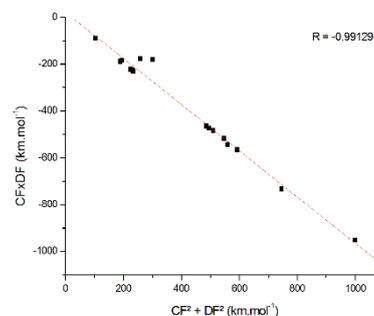Figure 1 and 2 summarizes the results obtained in this work for the CCFDF and CCTCP models.

Figure 1. Correlation between the CF² + DF² and CFxDF yielding an almost perfect cancellation. The term CTCP (of the CCTCP model) is therefore almost null.

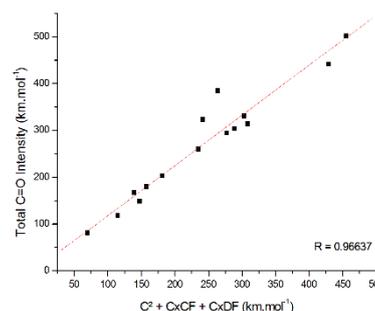**Figure 2.** Correlation between the C + CxCF + CxDF (on the CCTCP model: C + CxCTCP) and the total intensity of the vibrational modes. The overall agreement is very good.

CONCLUSIONS

The results show that the intensity is widely dominated by the charge term, followed by the CxCP interaction, while the polarization itself is negligible in almost all cases. Even though the values of the intensities are not characteristic, their contributions behave in a characteristic way among the different molecules. Therefore, the contribution patterns can be visualized as charac–teristic for this kind of stretch, an unpublished result in the IR research field.

ACKNOWLEDGEMENTS

[1] AF Silva, WE Richter, RE Bruns. *PCCP*, 16, 23224, 2014.

[2] AF Silva, WE Richter, RE Bruns. *PCCP*, submitted.