

Understanding the Hydrogen-Bond by means of Infrared intensities: A Quantum Theory CCTDP approach.

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Abstract

The linear correlation between the energy and the absorption of the hydrogen symmetric stretching vibrational mode was studied by means of the CCTDP model. The model indicates that the hydrogen atom contribution to this normal mode is the only one necessary to describe this a correlation and also predicts that for shorter bond lengths the charge transfer contribution becomes more relevant, indicating certain degree of covalency.

Key words:

Dynamic atomic contribution; Hydrogen bonding energy; Quantum Theory

Introduction

In the past decades, many studies were dedicated to the study of the hydrogen-bond^[1]. A.V logansen reported a linear correlation between the H-bond formation enthalpy and the increase of the donor symmetric stretch intensity^[2].

This correlation seems to be logical, since the intensities are correlated to the molecular electronic structure, which is also fundamental to the reactivity of chemical systems.

The Charge - Charge Transfer - Dipolar Polarization (CCTDP) model allows us to analyze the intensity of a vibrational mode in terms of these components, which has already proved to be adequate to provide fundamental information on similar systems^[3].

$$\frac{\partial p}{\partial Q} = \sum_i^N q_i + \sum_i^N \sigma \frac{\partial q_i}{\partial Q} + \sum_i^N \frac{\partial m_{i,\sigma}}{\partial Q} \quad (1)$$

The first term in equation (1) is the Charge, the second is the Charge-Transfer and the third one is the Dipolar Polarization Contribution.

Results and Discussion

In this work, two molecular groups were analyzed. The first are compounds with HF adducts and the others are compounds with HCl adducts.

Solving equation (1) for only the hydrogen atom of the donor molecule, we find that the linear correlation reported by logansen can be expressed only in terms of the Hydrogen atom contributions, as shown in Figure 1.

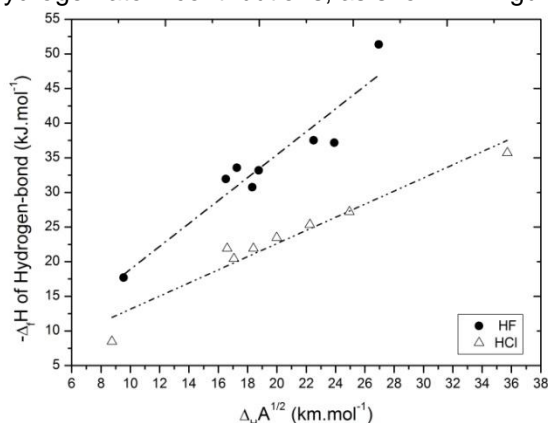


Figure 1: Plot of $-\Delta H$ (kJ.mol⁻¹) versus variation of square root of hydrogen contribution to the total intensity $\Delta H A^{1/2}$ (kJ.mol⁻¹).

For shorter adduct bond lengths we notice that the charge transfer contributions to the total intensity of the hydrogen symmetric stretching modes become more important while the charge term becomes less relevant, suggesting a predominant covalent character.

Chart 1: Calculated bond lengths for adducts in Angstroms

Acceptor	HCl	HF
HCl	2.53	N.A
HF	N.A	1.85
NH ₃	1.77	1.69
H ₂ O	1.91	1.73
HCN	2.04	1.85
Acetonitrile	1.98	1.81
Acetaldehyde	1.80	1.70
Formaldehyde	1.86	1.73
Formic acid	1.95	1.77

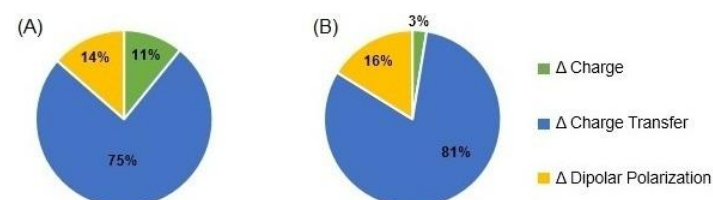


Image 2: Dynamic Atomic Contributions variation for HCl (A) and HF (B) (e.amu^{-1/2}).

Conclusions

For both groups the intensity increase is proportional to the H-bond energy, but there are physical differences between the two systems. The CCTDP model appears to be a good tool for understanding these interactions and perhaps different kinds of chemical bonds.

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