Weak intramolecular OH $\cdots \pi$ hydrogen bonding in methallyl- and allyl-carbinol

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Workshop on ”Topological approaches to intermolecular interactions”

Introduction

Hydrogen bond. The IUPAC definition[1]:

"The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation"

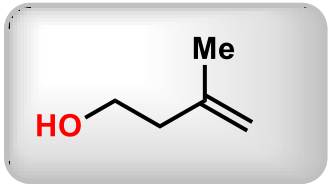
Bond critical points

[1] E. Arunan, et al., Pure Appl. Chem., 2011, 83, 1619-1636

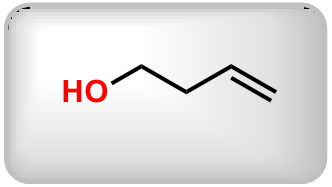
Our study

Study of intramolecular hydrogen bonding in methallyl-carbinol and allyl-carbinol

Methallyl-carbinol



Allyl-carbinol

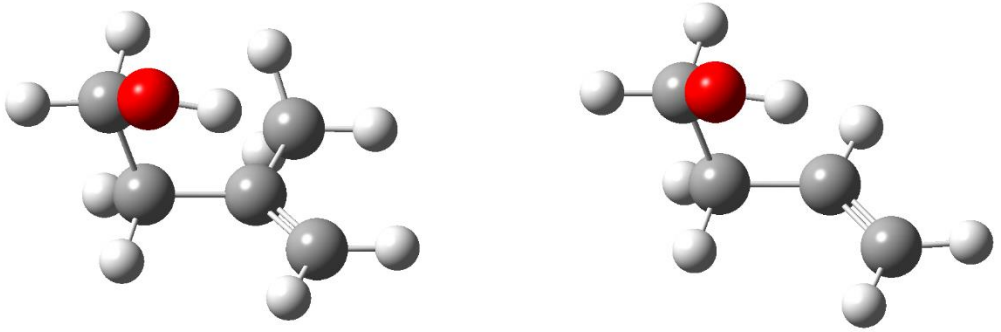


We expect an increase of the interaction due to the methyl group donating electron density into the double bond

Conformers

14 unique conformers exist for both molecules

One conformer has approximatly 30-40 % abbundance



Tools for investigating hydrogen bonding

Experimental:

- Vibrational OH-stretching overtone spectroscopy

Topological analyses:

- AIM
- NCI

Tools for investigating hydrogen bonding

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- ***Vibrational OH-stretching overtone spectroscopy***

Topological analyses:

- AIM

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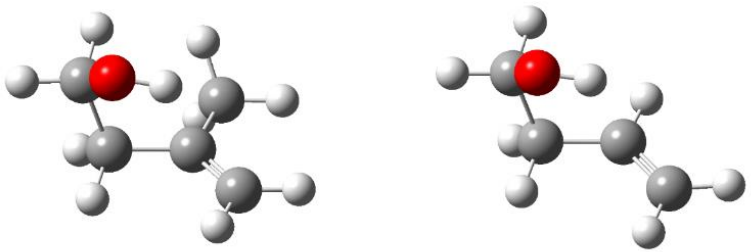
Vibrational OH-stretching overtone spectroscopy

- Anharmonicity
- Coupling

Local mode approach

$$\hat{H}_{vib} = \frac{1}{2}\sum_i G_{ii} p_i^2 \quad + \quad \sum_i V(q_i)$$



Normal mode approach

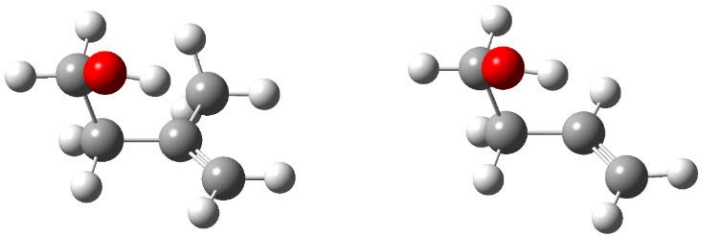
$$\hat{H}_{vib} = \frac{1}{2}\sum_i P_i^2 \quad + \quad \frac{1}{2}\sum_i F_{ii} Q_i^2$$

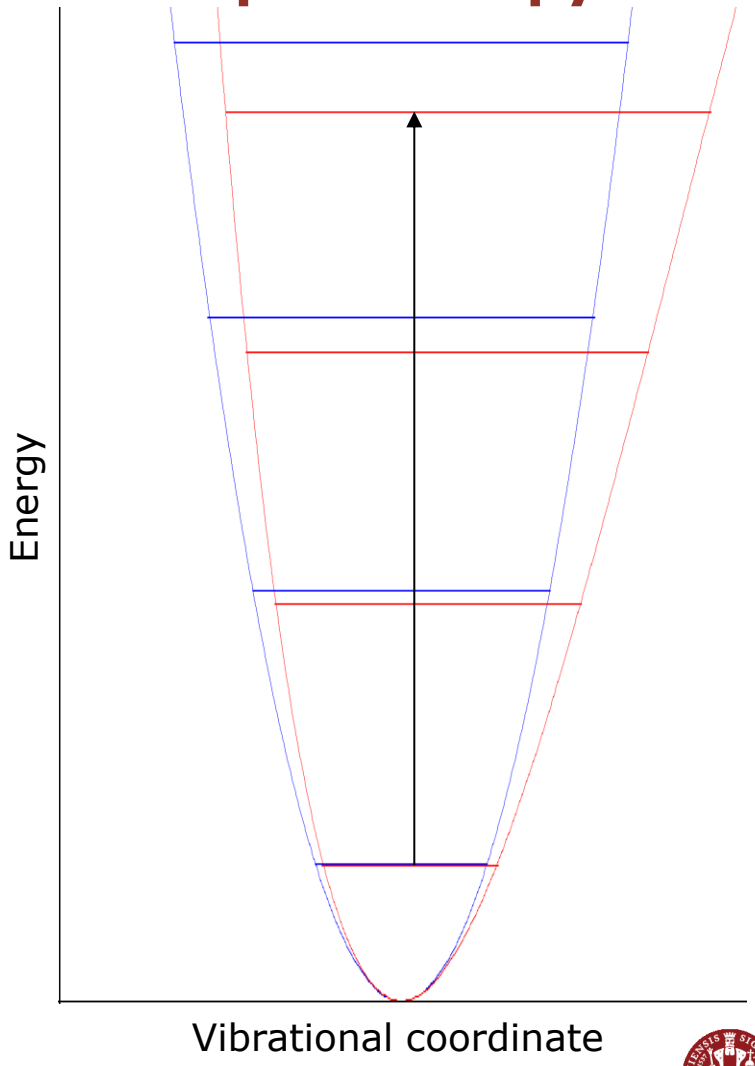
Vibrational OH-stretching overtone spectroscopy

Vibrational transitions between the ground state and an excited state

We are looking at the OH-stretch: Anharmonic

Local mode description

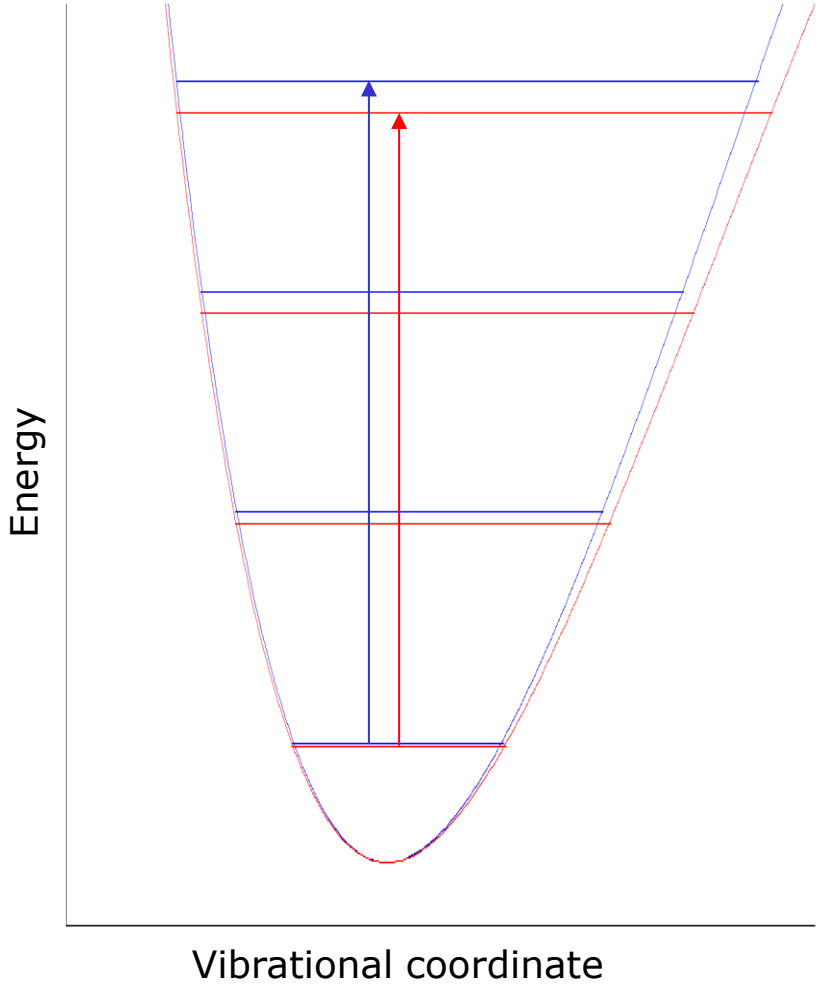




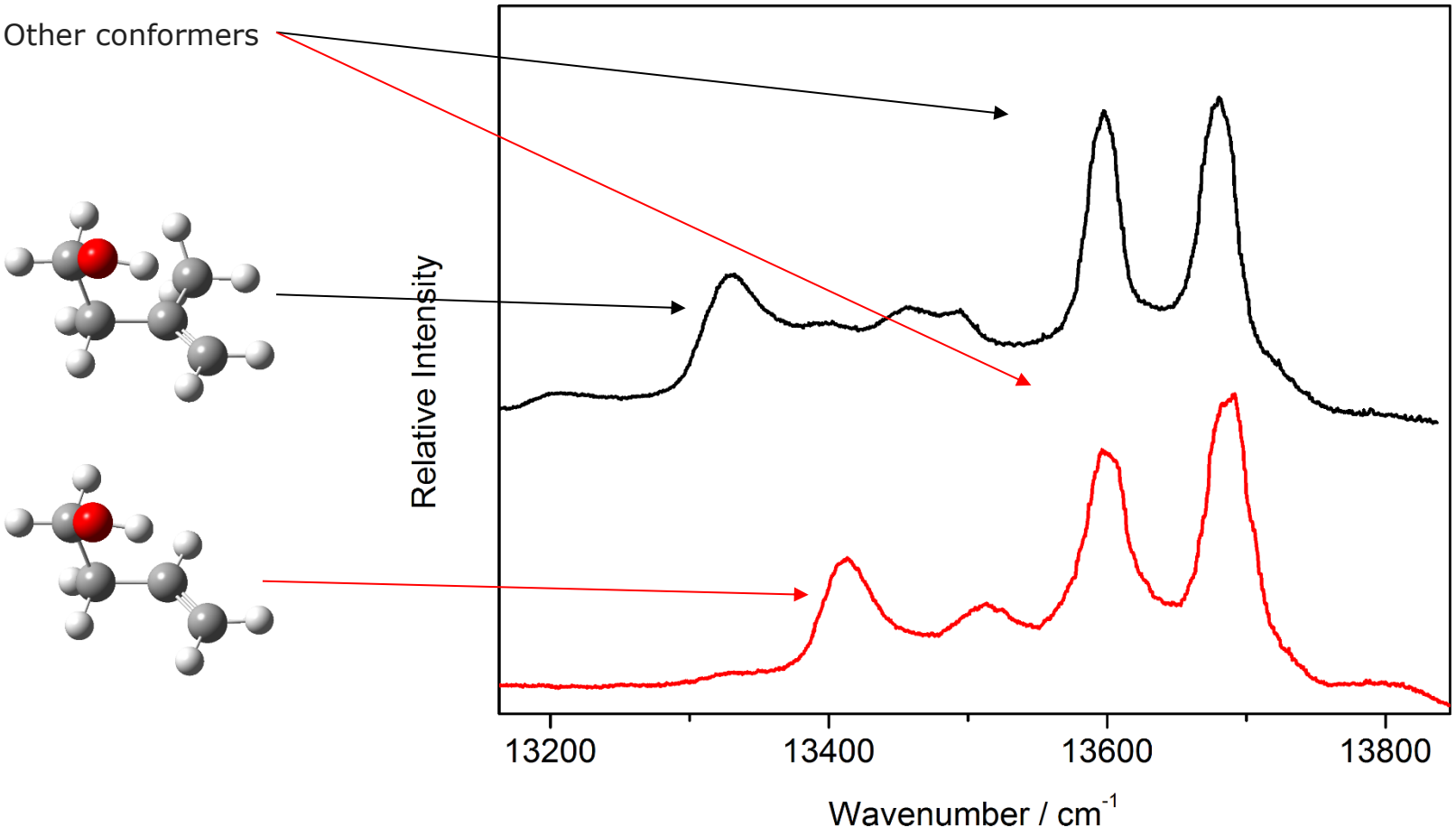
Vibrational OH-stretching overtone spectroscopy

X-H

X-H ··· Y

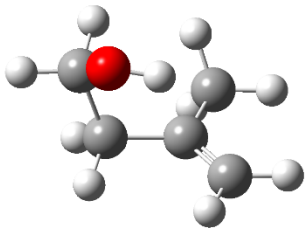


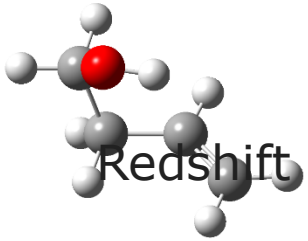
Vibrational overtone spectrum of methallyl-carbinol and allyl-carbinol

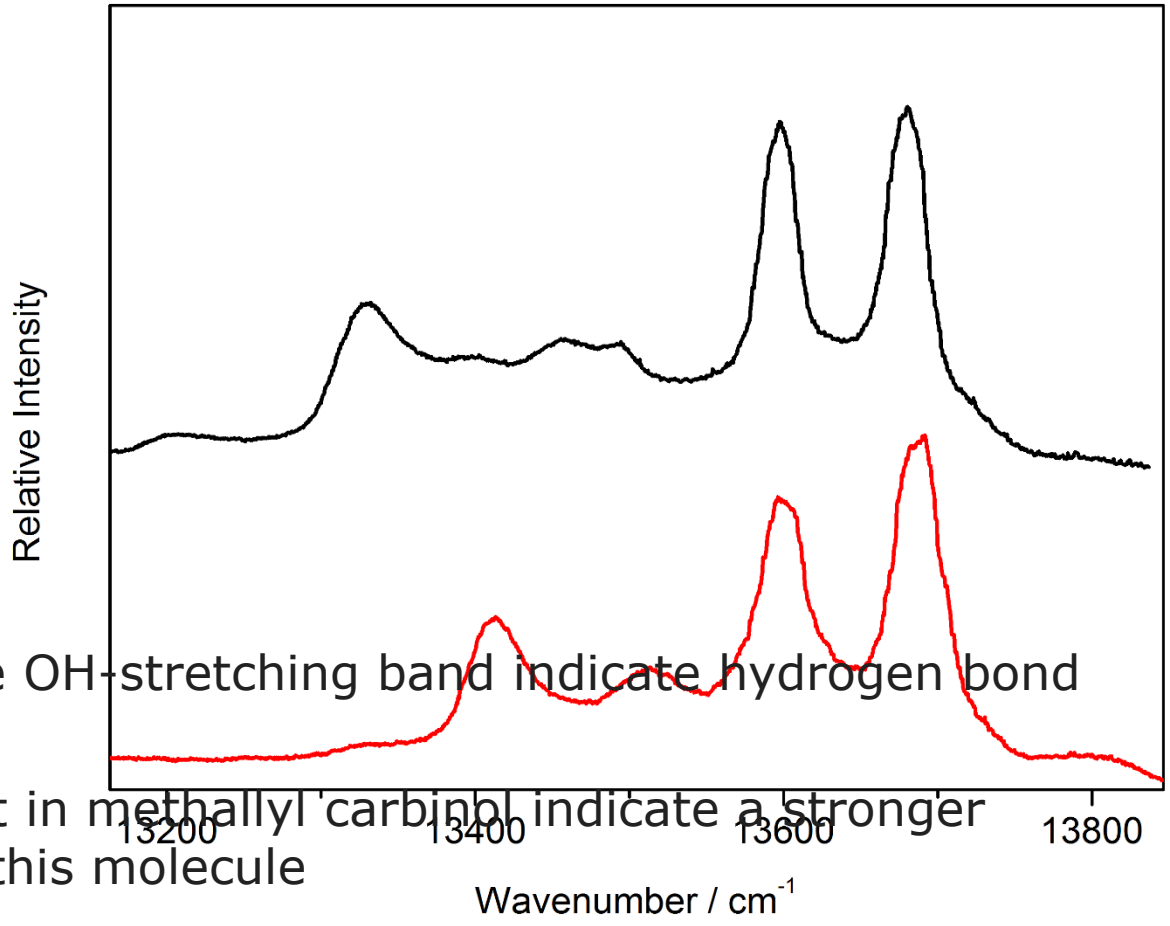


Band assignment is based on local mode calculation at the CCSD(T)-F12a/VDZ-F12 level.

Vibrational overtone spectrum of methallyl-carbinol and allyl-carbinol







Redshift of the OH-stretching band indicate hydrogen bond

Larger redshift in methallyl carbinol indicate a stronger interaction in this molecule

Tools for investigating hydrogen bonding

Experimental:

- Vibrational OH-stretching overtone spectroscopy

Topological analyses*:*

- ***AIM***

- ***NCI***

AIM

Very popular tool for investigating hydrogen bonding

In 2011 an account and revised definition of the hydrogen bond is made by IUPAC[1]

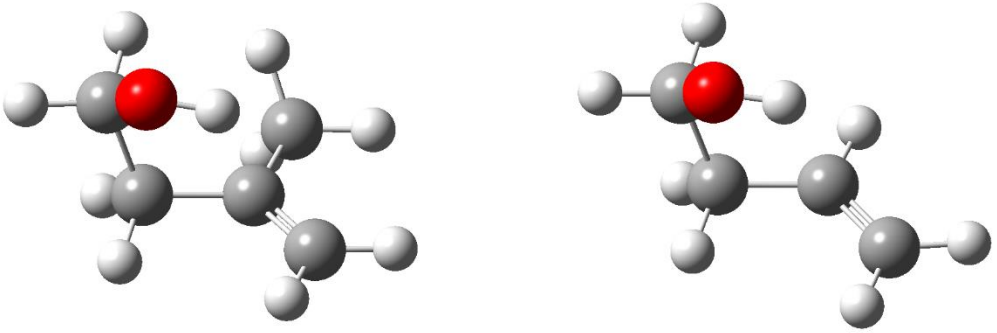
- Bond critical points are discussed. It is stated that they are usually found in hydrogen-bonded systems

Debated in the litterature whether they are nessecary or not [2,3]

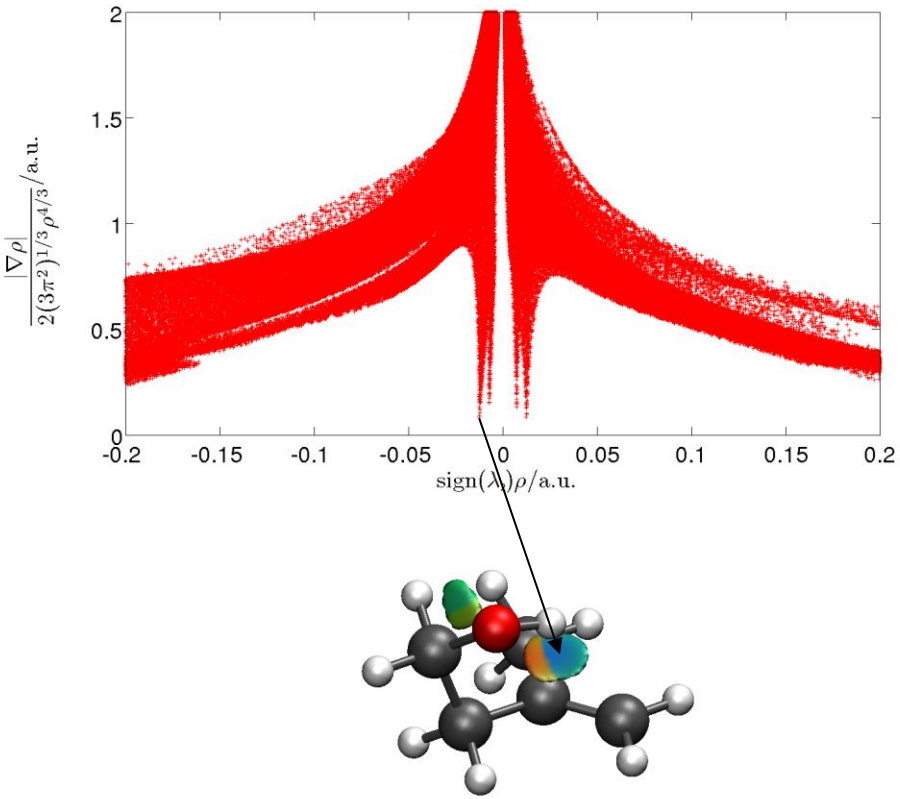
[1] E. Arunan, et al., Pure Appl. Chem., 2011, 83, 1619-1636
[2] R. A. Klein, J. Comput. Chem. 2002, 23, 585–599
[3] D. L. Howard, et.al., J. Am. Chem. Soc. 2005, 127, 17096–17103

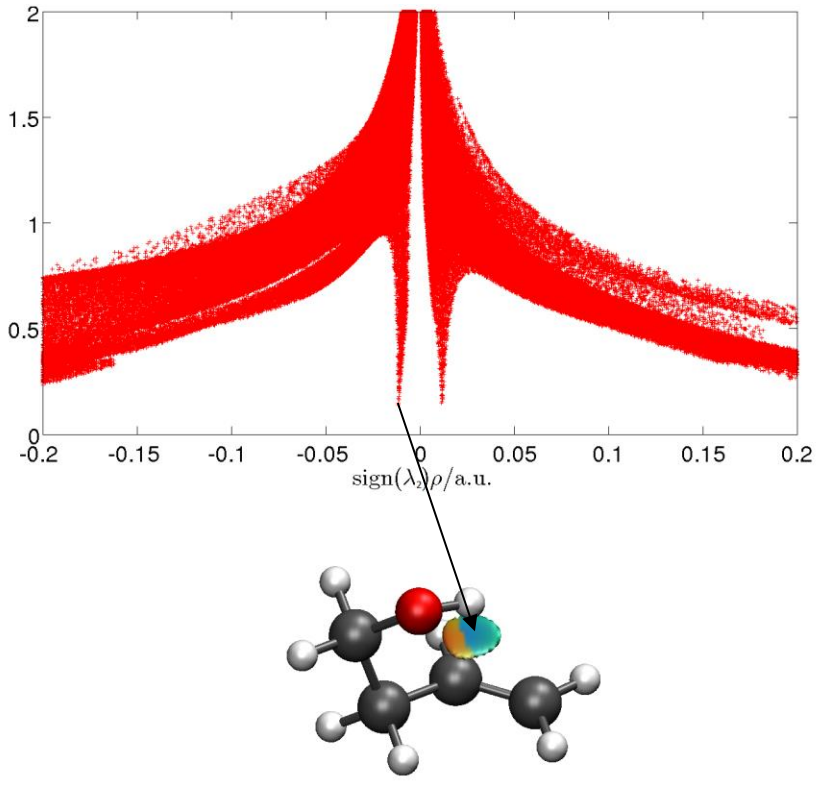
AIM

No bond critical point is found between the O-H group and the π-electrons in either of the two molecules



NCI





10 % increase in electron density

Summary

Experimental observations indicates hydrogen bond formation between the alchol group and the π-electrons in methallyl-carbinol and allyl-carbinol

The experiments predicts that the interaction is increased in methallyl-carbinol relative to that in allyl-carbinol

These observations are supported by theoretical NCI analysis, which as well predict increased intramolecular interaction in methallyl carbinol

Acknowledgement

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