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Influence of the micro-hydration on the reactivity of carbonyls and amines: a DFT and QTAIM study

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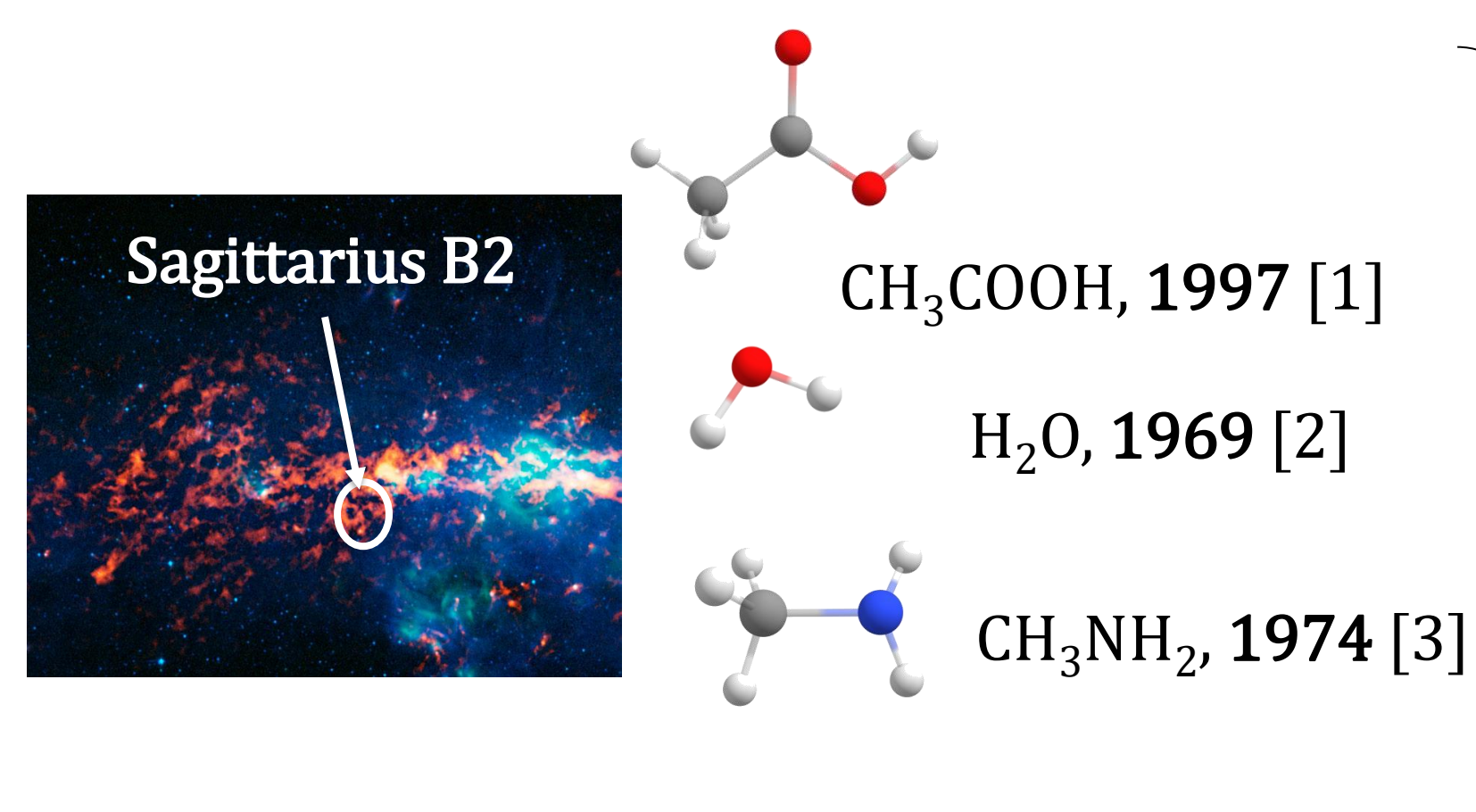
Influence of the micro-hydration on the reactivity of carbonyls and amines: A DFT and QTAIM study



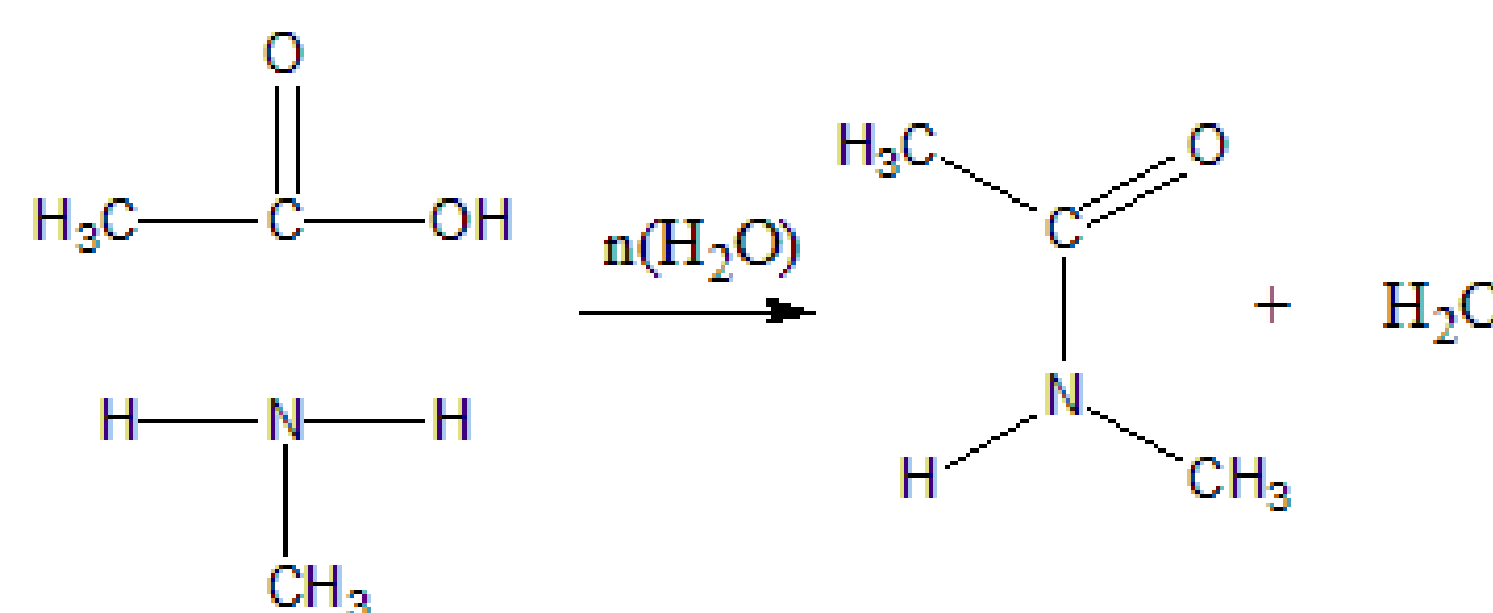
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CONTEXT AND OBJECTIVES



Could non-covalent interactions with water molecules facilitate the formation of a peptide-like C-N bond?



Objectives

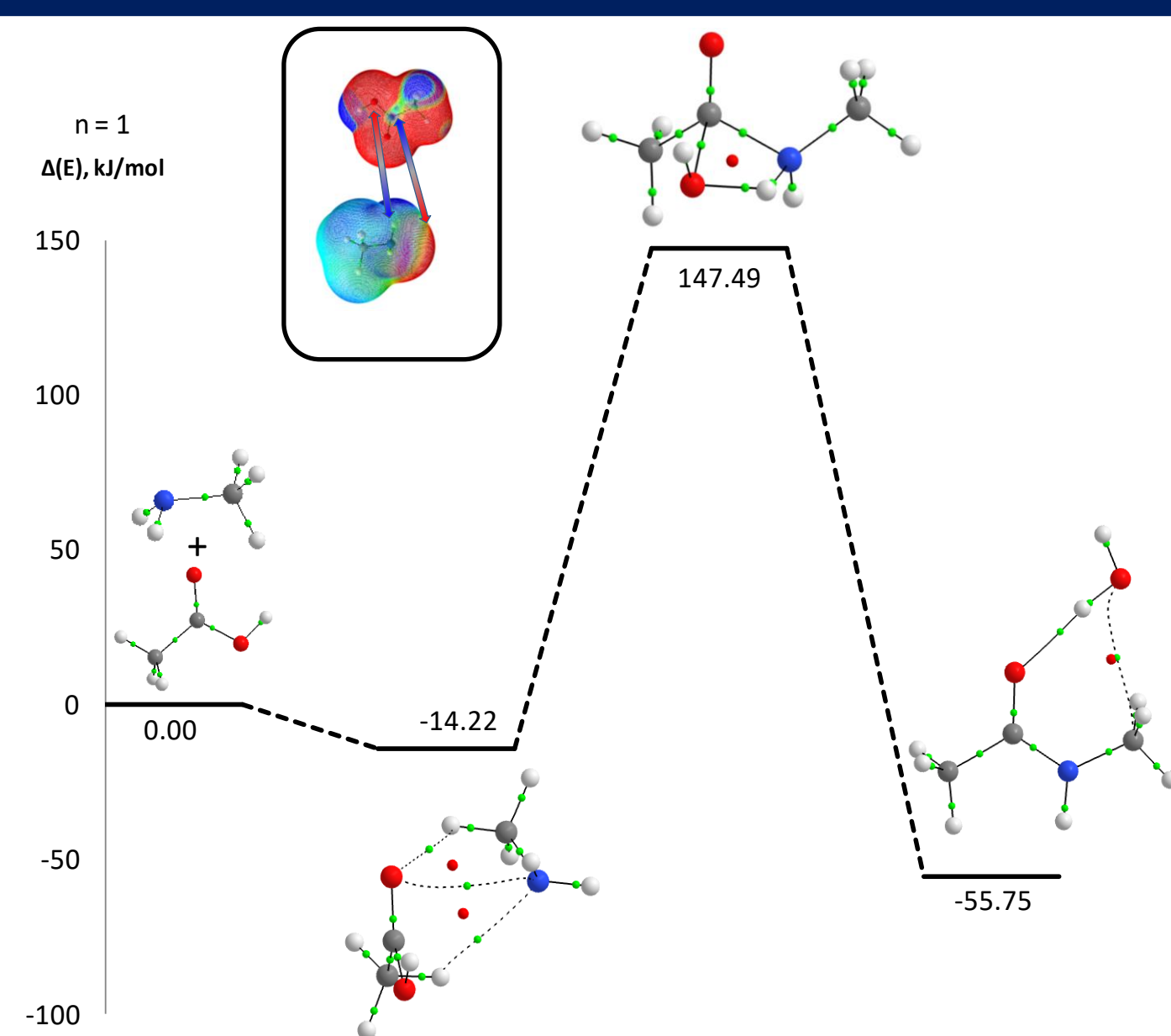
- Describing the influence of non-covalent bonds on the reactivity between a carbonyl and an amine using interpretative tools of quantum chemistry: DFT and QTAIM [4] [5]
- Understanding the role of water in lowering the energy barrier of this reaction

IDENTIFYING A REACTION PATH

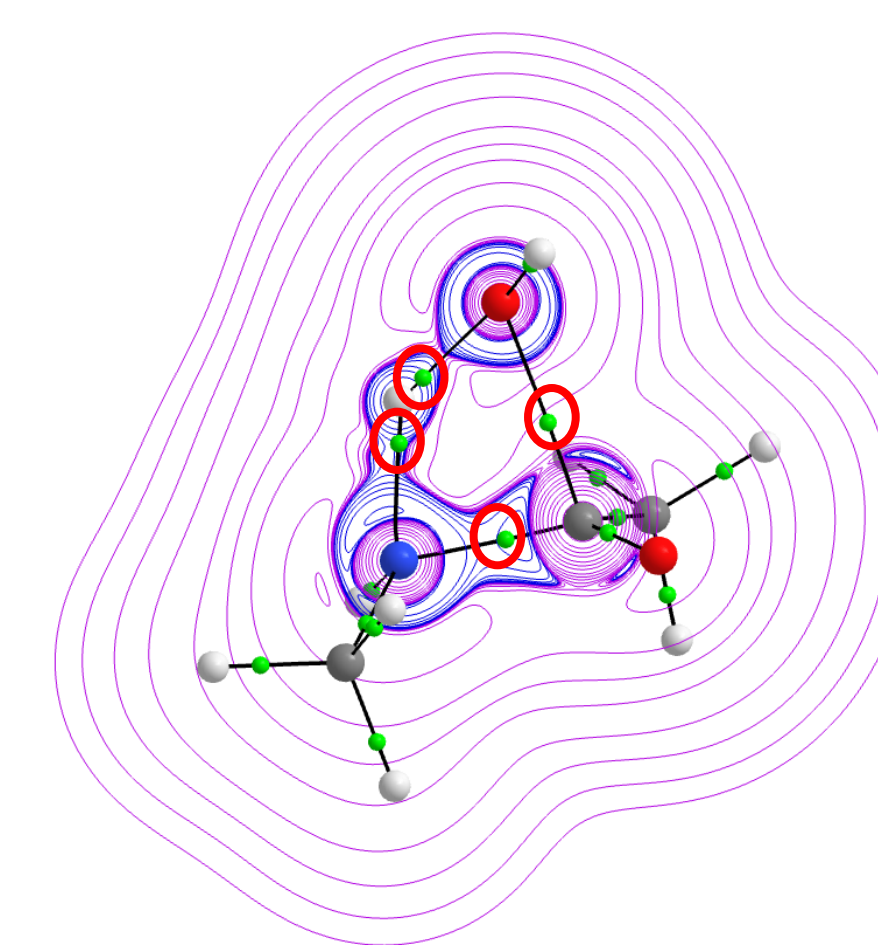
- Experimental demonstration of the formation of a peptide-type bond from acetic acid and methylamine by mass spectrometry, and identification of a possible reaction path. [6]

Computing level: LC- ω PBE/6-311++G(d,p) GD3BJ

- For the uncharged system: Identification of preferred directions of approach from the molecular electrostatic potential. [7]



TOPOLOGICAL ANALYSIS

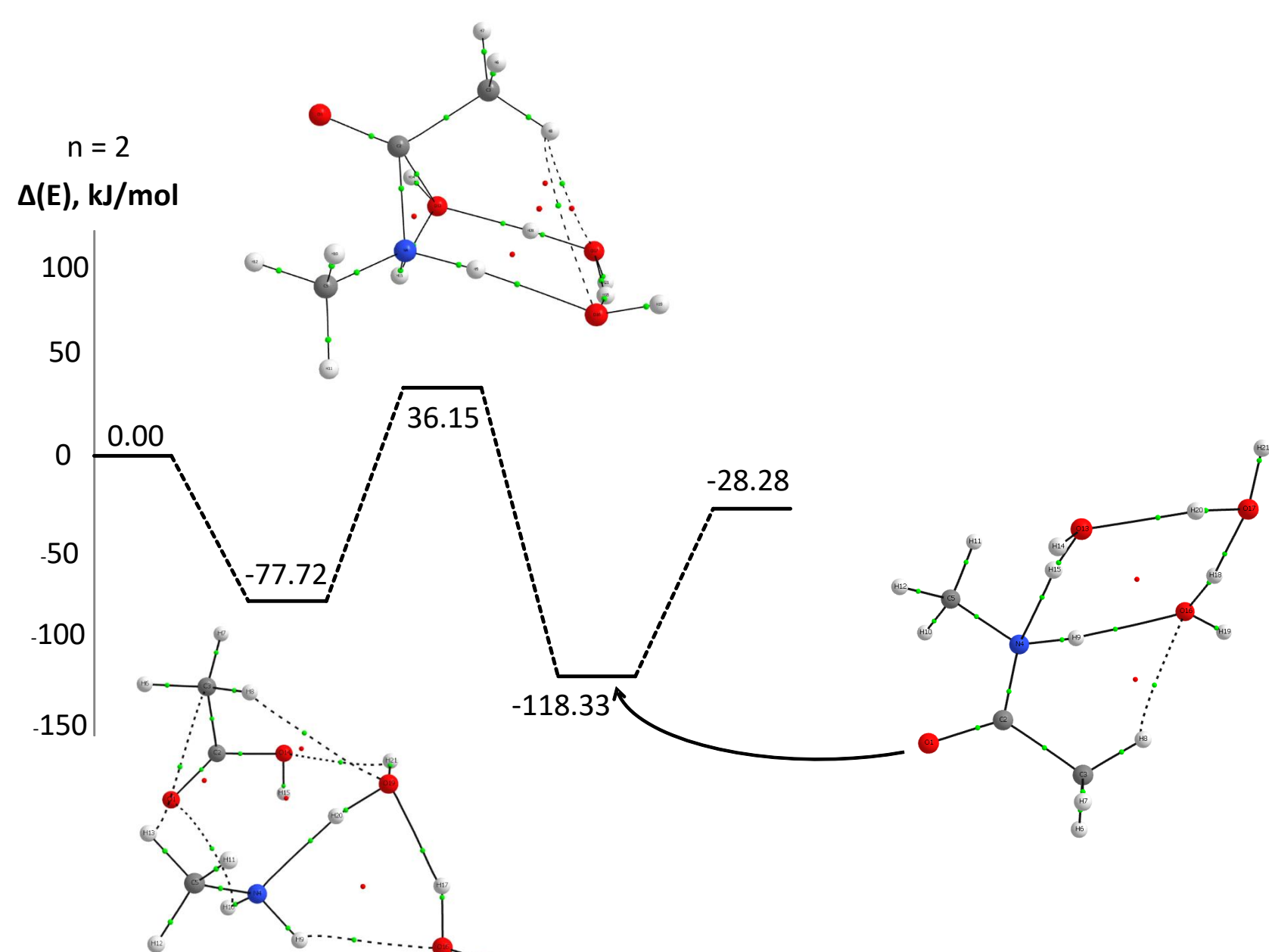


- QTAIM study. Electronic density and its Laplacian

$$2G(\mathbf{r}) + V(\mathbf{r}) = \frac{1}{4}\nabla^2\rho(\mathbf{r})$$

- Analysis at bond critical points: C-N, C-O, N-H, O-H

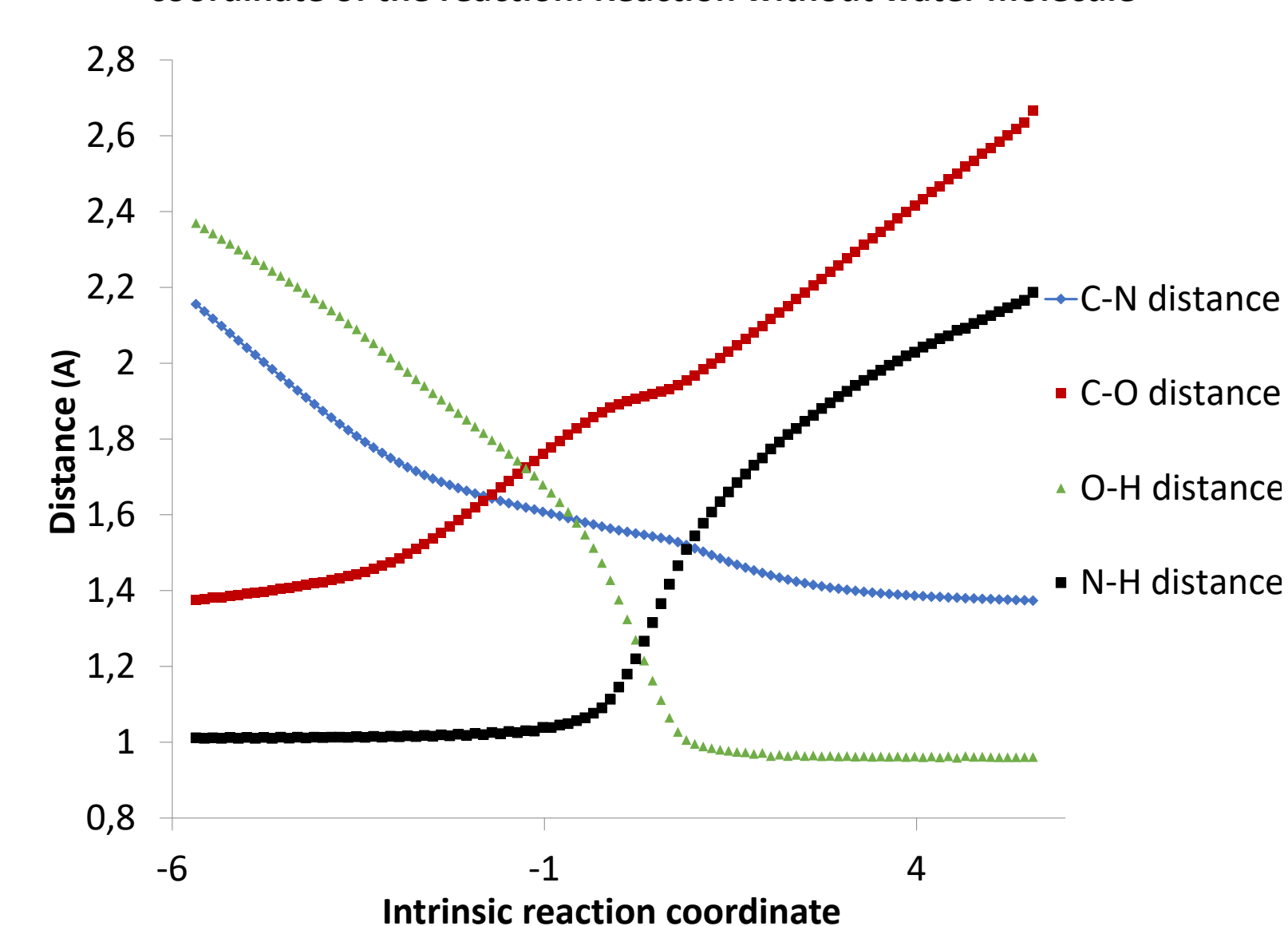
RESULTS AND ANALYSIS



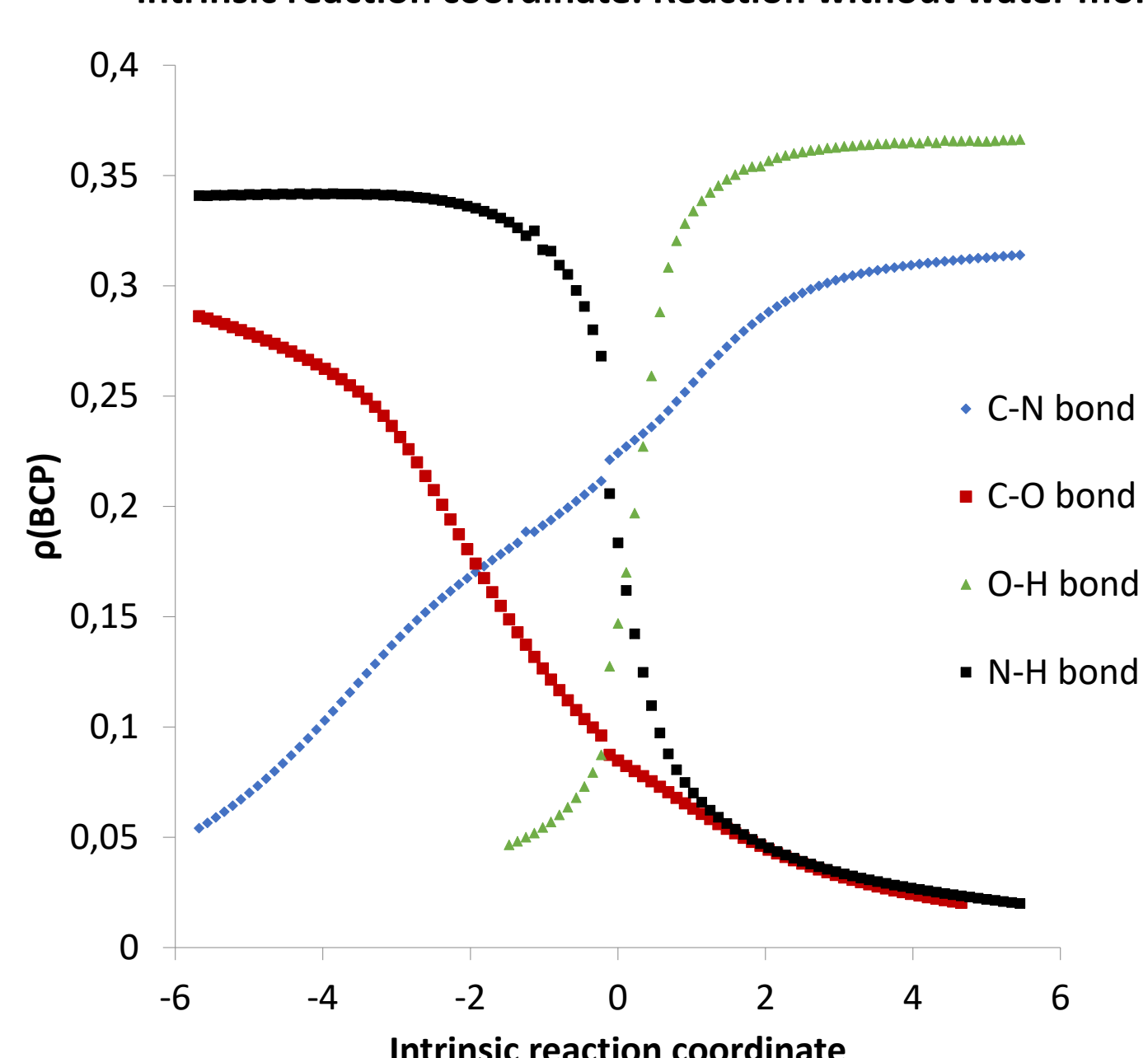
- Close monitoring of bonds during the reaction
- A concerted evolution of the 4 bonds, regardless of the number of water molecules
- A similar evolution regardless of the number of water molecules

Properties n(H ₂ O)	Energetic	Geometric	Topological	
	E	d	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$
n = 0 to 4	A single transition state	A concerted evolution of the 4 bonds	2 covalent bonds and 2 non-covalent interactions	
n(H ₂ O) ↑	Lowering of the energy barrier	Evolution becomes "synchronous" with the addition of n(H ₂ O)		

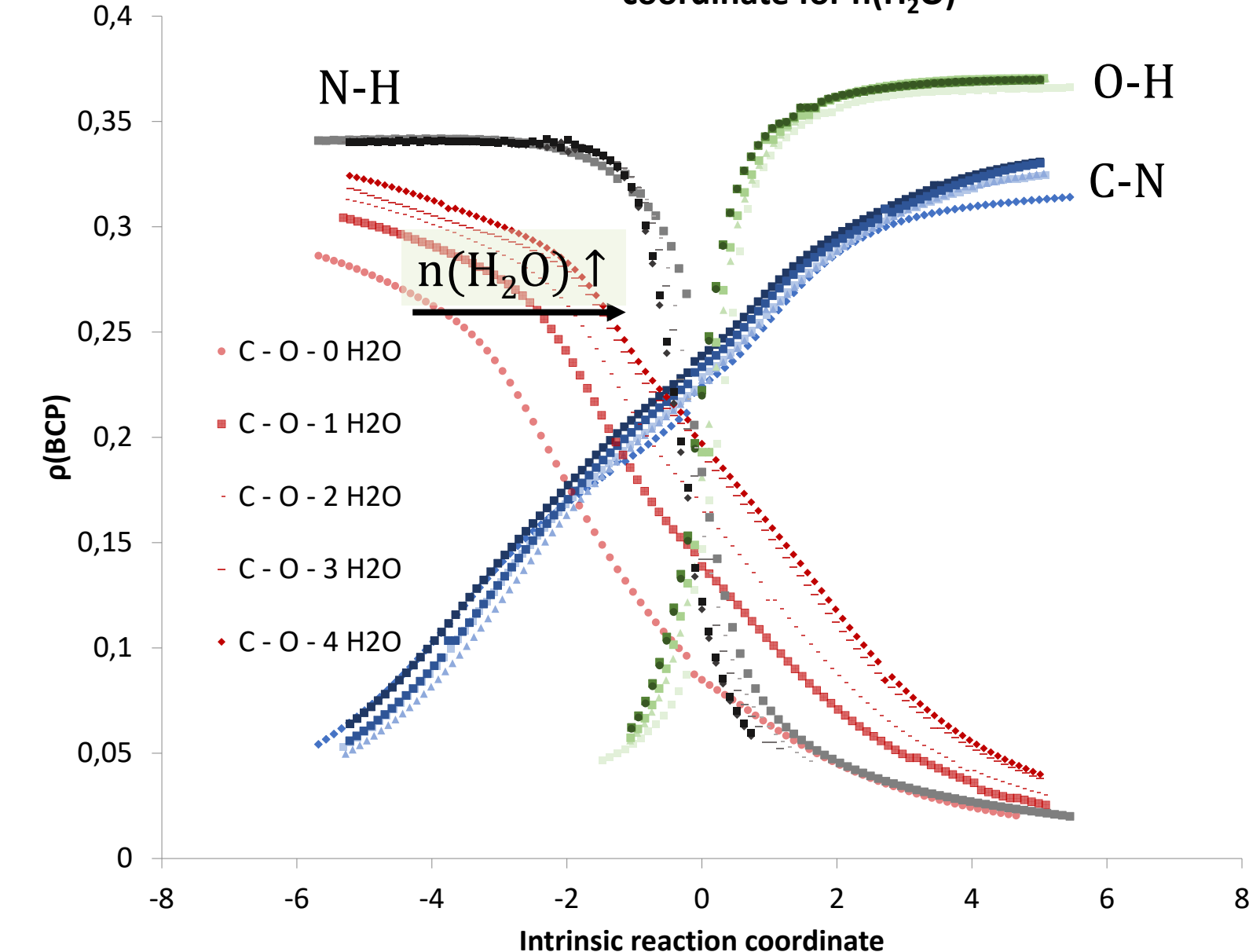
Evolution of the distance of 4 bonds along the intrinsic coordinate of the reaction. Reaction without water molecule



Evolution of the electron density at the 4 BCPs along the intrinsic reaction coordinate. Reaction without water molecule



Evolution of the electron density at the 4 BCPs along the intrinsic reaction coordinate for n(H₂O)



CONCLUSIONS AND PERSPECTIVES

- Adding an increasing number of water molecules particularly affects the breaking of the C-O(H) bond: with 3 or 4 water molecules, the breaking of this bond and the loss of a water molecule occur almost synchronously.
- Coupling theory and experimentation by studying the reactivity of micro-hydrated complexes, mass-selected using a mass spectrometer along with synchrotron radiation.

References:

- [1] D. M. Mehringer, L. E. Snyder, Y. Miao, and F. Lovas, *ApJ*, 480, 1997
[2] A. C. Cheung, D. M. Rank, C. H. Townes, D. D. Thornton, and W. J. Welch, *Nature*, 221, 1969
[3] N. Kaifu, M. Morimoto, K. Nagane, K. Akabane, T. Iguchi, and K. Takagi, *ApJ*, 191, 1974
[4] P. Hohenberg, *Physical Review*, 136, 1964, B864-B871 ; W. Kohn, *Physical Review*, 140, 1965

[5] R. Bader, *Oxford University Press*, 1994

[6] I. Derbali, R. Thissen, C. Alcaraz, C. Romanzin, E-L. Zins, *The Journal of Physical Chemistry A*, 125, 2021

[7] I. Derbali, O. Aroule, G. Hoffmann, R. Thissen, C. Alcaraz, C. Romanzin, E-L. Zins, *Theor Chem Acc*, 141, 2022 (Accepted)