
Automatic computation of global intermolecular potential energy surfaces for non-covalently bound systems

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Résumé

We aim at simulating full quantum mechanically (nuclei and electrons) the processes of adsorption and photoreactivity of NO₂ adsorbed on soot (modeled as large Polycyclic Aromatic Hydrocarbons, PAHs) in atmospheric conditions. A detailed description of these processes is necessary to understand the differential day-nighttime behavior of the production of HONO [1, 2], which is a precursor of the hydroxyl radical (OH) [3]. In particular, the specific mechanism of the soot-mediated interconversion between NO₂ and HONO is to date not fully understood. Due to its relevance, we have chosen the NO₂-Pyrene system [1]. The first stage in this study has consisted in the determination of the stable configurations (transition states and minima) of the NO₂-Pyrene system. To this end, we have used the van der Waals Transition State Search Using Chemical Dynamics (vdW-TSSCDS) method [4], the non-covalent version of the TSSCDS algorithm [5]. Starting from a single input geometry, vdW-TSSCDS permits the characterization of the topography of a intermolecular Potential Energy Surface (PES) in a fully automated fashion. This topographical information will be used to obtain a global description (fit) of the interaction potential, necessary for the dynamical elucidation of spectroscopic properties and reactivity of the adsorbed species. For this, we have developed the Specific Reaction Parameter Multigrid POTFIT (SRP-MGPF) algorithm and software (SRPTucker) [6]. This method computes chemically accurate (intermolecular) PESs through reparametrization of semiempirical methods which are subsequently tensor decomposed using MGPF [7]. This software has been interfaced with the Heidelberg version of the Multiconfiguration Time-Dependent Hartree (MCTDH) software [8].

References

C. Guan, X. Li, W. Zhang and Z. Huang, *J. Phys. Chem. A*, 121, 482-492 (2017).

M. E. Monge et al , *PNAS*, 107, 6605 (2010)

*Intervenant

A. M. Holloway and R. P. Wayne, *Atmos. Chem.* (2010)

S. Kopec, E. Martínez-Núñez, J. Soto, D. Peláez, *Int. J. Quant. Chem.*, e26008 doi:10.1002/qua.26008

E. Martínez-Núñez, *Phys. Chem. Chem. Phys.* ,17.22 (2015)

R.L.Panadés-Barrueta, E. Martínez-Núñez, D. Peláez, *Front. Chem.*, (Minor corrections)

D. Peláez, H.-D. Meyer, *J. Chem. Phys.* 138, 014108 (2013)

M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, *Phys. Rep.*, 324 (2000)

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