Quantum Roaming in the complex forming mechanism of the reactions of OH with Formaldehyde and Methanol at low temperature and the effect of pressure

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The quantum dynamics of the title reactions is studied[1]using the ring polymer molecular dynamics (RPMD) method from 20 to 1200 K using full dimensional potential energy surfaces[2,3] which include long-range dipole− dipole interactions. A V-shaped dependence of the reaction rate constants is found with a minimum at 200−300 K, in rather good agreement with the current experimental data[4,5,6,7]. For temperatures above 300 K the reaction proceeds following a direct H-abstraction mechanism. However, below 100 K the reaction proceeds via organic-molecule··· OH collision complexes, with very long lifetimes, longer than 10−7 s, associated with quantum roaming arising from the inclusion of quantum effects by the use of RPMD. New results are obtained in a new Neural-Network PES recently proposed, increasing the accuracy of the fit and including the long-range interactions[8]. The same trapping mechanism is found [8], and it is associated to spurious RPMD resonances[9]. Thermostated RPMD method[9] has been applied and compared to previous RPMD results. Also, preliminary results on the reaction of OH with the $(H_2CO)_2$ dimer will be presented.

References

[1] P. del Mazo-Sevillano, A. Aguado, E. Jiménez, Y. V. Suleimanov, O. Roncero, J. Phys. Chem. Lett. **10**,1900 (2019)
[2] A. Zanchet, et al. PCCP **20**, 5415 (2018)
[3] O. Roncero, A. Zanchet and A. Aguado, PCCP 20, 25951 (2018)
[4] A. J. Ocaña, et al. AstroPhys. J. **850,** 28 (2017)
[5] R.J. Shannon, M. A. Blitz, A Goddard, D. E. Heard, Nat. Chem. **5**, 750 (2013)
[6] M. Antiñolo et al., AstroPhys. J. **823**, 25 (2016)
[7] A. J. Ocaña et al. PCCP **21**, 6942 (2019)
[8] P. del Mazo-Sevillano, A. Aguado, O. Roncero, J. Chem. Phys, **154**, 094305 (2021)
[9] M. Rossi, M. Ceriotti, D. E. Manolopoulos, J. Chem. Phys., **140**, 234116 (2014).