IL 6

Quantum Roaming in the complex forming mechanism of the reactions of OH with Formaldehyde and Methanol at low temperature and Zero Pressure: a ring polymer molecular dynamics approach

Octavio Roncero

Instituto de Física Fundamental, CSIC
Serrano 123, 28006 Madrid (Spain)

The quantum dynamics of the title reactions are studied[1]using the ring polymer molecular dynamics (RPMD) method from 20 to 1200 K using recently proposed full dimensional potential energy surfaces[2,3] which include longrange 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. The long lifetimes of these complexes are comparable to the time scale of the tunnelling to form reaction products. These complexes are formed at zero pressure because of quantum effects and not only at high pressure as suggested by transition state theory (TST) calculations for OH + methanol and other OH
reactions. The zero-pressure rate constants reproduce quite well measured ones below 200 K, and this agreement opens the question of how important the pressure eff ects on the reaction rate constants are, as implied in TST-like formalisms. The zeropressure mechanism is applicable only to very low gas density environments, such as the interstellar medium, which are not repeatable by experiments.

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)