Quantum Roaming in the Complex Forming Mechanism of Reactions of OH with H_2CO and CH_3OH at Low Temperature in the Low Pressure Limit: A Ring Polymer Molecular Dynamics Approach

Pablo del Mazo-Sevillano[1] , A. Aguado[1] and Octavio Roncero[2*]

[1]*Departament of Applied Physical Chemistry, Universidad Autónoma de Madrid, Facultad de Ciencias M-14, 28049 Madrid, Spain.*
[2]*Instituto de Física Fundamental, CSIC, Serrano 123, 28006 Madrid, Spain.*
[*]*octavio.roncero@csic.es*

The quantum dynamics of the title reactions are studied using the Ring Polymer Molecular Dynamics method from 20 to 1200 K using a recently proposed full dimensional potential energy surfaces which includes long range dipole-dipole interactions[1,2]. For H_2CO a V-shaped dependence of the the reaction rate constant is found with a minimum at 200-300 K, in rather good agreement with the experimental data available[3]. For temperatures above 300 K the reaction proceeds following a direct mechanism. However, below 100 K the reaction proceed via collision complexes, with very long lifetimes, longer than 10^{-7} s for 100 K, and even more for lower temperatures. These long lifetimes are considered to be of the order of tunneling rates at energies above the re-dissociation limit, and open the possibility of a low pressure mechanism which compete withs the high pressure mechanism already used within transition state theory to reproduce the experimental rate constants. Such low pressure mechanism is the only valid in the dilute astrophysical objects, and it is crucial to unravel this question, theoretically as well as experimentally.

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