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

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Supplemetary Information

Convergence of RPMD calculations

In order to determine the number of beads, N_{beads}, needed to get full convergence of the Ring Polymer Molecular Dynamics (RPMD) calculations, we have calculated the energy average using constraint Path Integral Molecular Dynamics (PIMD) calculations for a varying number of beads and different temperatures. The calculations are performed for the two reactants, with a distance between center-of-mass constraint to 120 bohr, and an Andersen thermostat,[1] as in the RPMD described in the main text. The energy is evaluated using the quantum kinetic energy estimator of Ref.[2] In each case 10^6 iterations are done, and the average energy is obtained using the energies from the step 10^4 to the final iteration considered. The results obtained for two characteristic temperatures, 100 and 300 K, are shown in Fig. 1. From this kind of analysis we determined the value of N_{beads} for each temperature and reaction. It can be observed an inverse relationship between N_{beads} and temperature as expected.

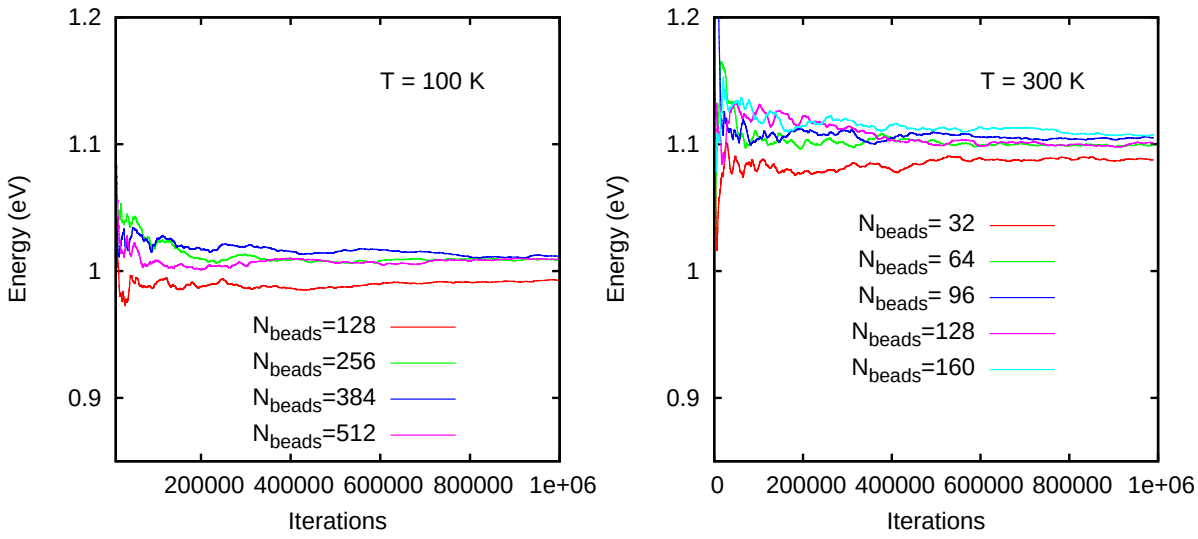

Figure 1: Average energy obtained along PIMD calculations versus iteration for a varying number of beads, N_{beads}, and for 100 K (top panel) and 300 K (bottom panel) obtained for the H_2CO + OH reaction.

To determine the time step used in the second order symplectic integration, the conservation of the total energy of the system formed by the $N_{atoms} \times N_{beads}$ is analysed. Using $\Delta t =$ 0.1 fs yields to a convergence up to the 6 or seventh significant figure of the total energy, what is considered satisfactory in this work.

Many checks have been done at 100 K for the H_2CO + OH reaction as a typical example, where the trapping mechanism starts to be important. First, about 20% of the trapped trajectories were extended up to 80 ns, with a total of 8×10^8 time steps of the propagation. Of these approximately 200 trajectories only one finished, what excludes the possibility of making converged calculations (note that more than 4 millions of CPU hours were used only for 100 K). A second check consisted in increasing the number of beads for 100 K, from 384 to 768. About 300 trajectories up to 20 ns were again propagated, and the results were the same of those listed in Table I of manuscript, whithin the statistical uncertainty. A final try to accelerate the sampling of the phase space towards reactants and products was done by switching on again the thermostat after 20 ns of real-time propagation up to 40 ns for about 100 trajectories, and again no trajectory ended. After all these checks, we conclude that for 100 K the lifetime associated to trapping must be considerable longer than 10^{-7} s since after 1 ns there is no an appreciable increase of the trapped trajectories that ended. Therefore, 10^{-7} s is considered to be hereafter a lower bound for the lifetime of the collision complexes trapped for temperatures of 100 K and below.

Finally, to check the convergence of the rate constants, the variation with the number of trajectories used in each case is represented in Fig. 2. These results give representative examples of the kind of convergence achieved in the calculations described in the manuscript.

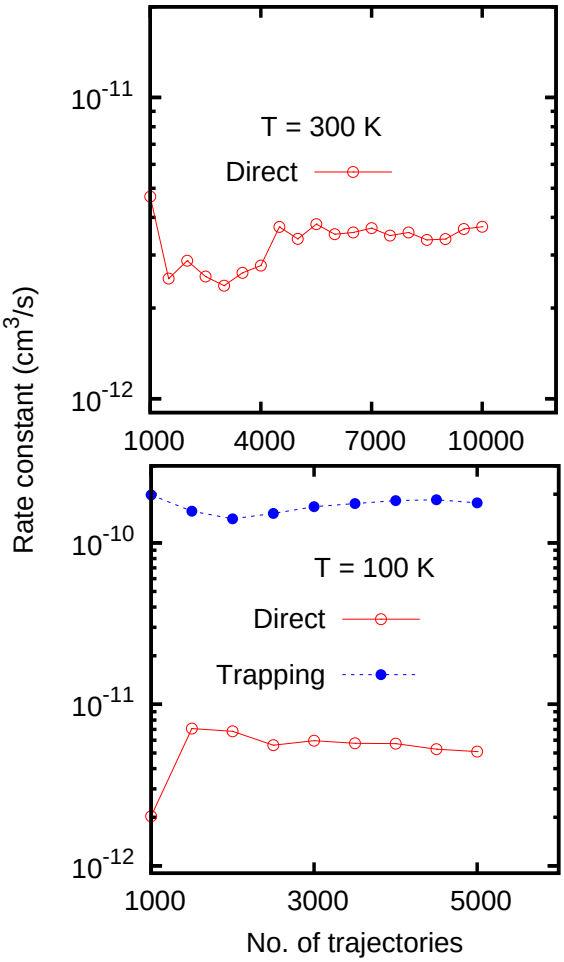

Figure 2: Direct and Trapping rates as a function of the number of trajectories obtained for the H_2CO + OH reaction at 100 and 300 K.

References

(1) Andersen, H. C. Molecular dynamics simulations at constant pressure and/or temperature. *The Journal of Chemical Physics* **1980**, *72*, 2384–2393.

(2) Ceriotti, M.; Manolopoulos, D. E. Efficient First-Principles Calculations of the Quantum Kinetic Energy and Momentum Distribution of Nuclei. *Phys. Rev. Lett.* **2012**, *109*, 100604.