

SUPPLEMENTARY MATERIAL

A non-adiabatic quantum-classical dynamics study of the intramolecular excited state hydrogen transfer in *ortho*- Nitrobenzaldehyde

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Trajectories launched from the FC equilibrium structure.

Here, we describe the results from the trajectories started from the FC structure. The electronic deactivation of *o*-NBA was also studied assuming an instantaneous excitation (δ -pulse) from the equilibrium minimum in the S_0 to the S_1 state, i.e. the trajectories generated at the ground state minima are integrated starting in the S_1 potential. Figure S1 shows the O_9-H_8 and C_6-H_8 distances involved in the ESIHT of *o*-NBA at the final time of the simulation, crosses and circles symbolize trajectories ending up in the S_1 and S_0 electronic states, respectively. From the 179 initial conditions of the Wigner distribution centered at the ground state geometry, only two trajectories are able to overcome the barrier, go through the CI, and end in the electronic ground state; these trajectories show a long C_6-H_8 distance and a short O_9-H_8 one at the end of the propagation, indicating that the HT is complete. This shows that the HT takes place together with the decay to the ground state, in agreement with the mechanism of Figure 1. The rest of the trajectories clearly remain localized in the S_1 state with a C_6-H_8 bond of ca. 1.1 Å, as in the equilibrium geometry in the S_0 . In this set of localized trajectories, the O_9-H_8 distances range from 2 to 3 Å, as a consequence of a strong vibration in the excited state around the equilibrium distance of ca. 2.3 Å. Clearly, the maximum C_6-H_8 distance obtained in most of the cases (ca. 1.3 Å) is not enough to reach the TS, and therefore the system is trapped in the $(n\pi^*)_{Min}$.

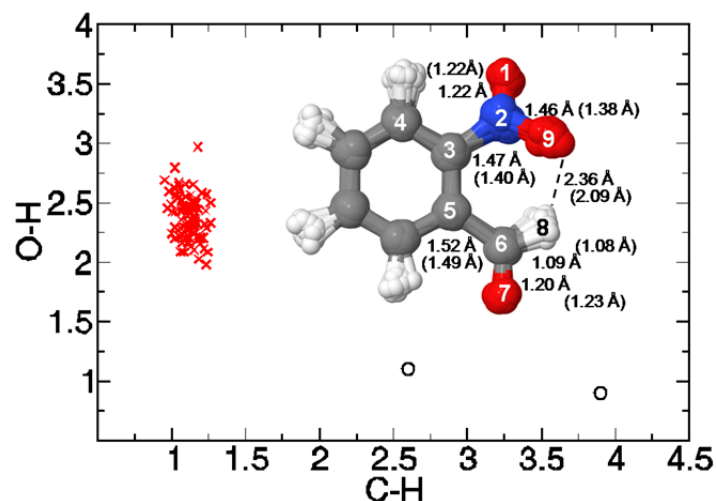


Figure S1. O_9-H_8 and C_6-H_8 bond distances at the final time of the simulation for the set of trajectories propagated from the *o*-NBA equilibrium geometry (FC). The crosses and circles indicate trajectories ending in the S_1 and S_0 , respectively. The inset shows a superposition of the corresponding geometries at the end of the propagation, indicating the average bond distances (values in parenthesis correspond to the structure optimized at CASSCF(14,12) level of theory).

The inset of Fig. S1 displays a superposition of all geometries corresponding to each of the trajectories in the S_1 state at the end of the propagation. In parenthesis, we report the values of the structure optimized at CASSCF(14,12) level of theory. The averaged geometry corresponds to the system confined in $(n\pi^*)_{\text{Min}}$, with approximately 0.2 Å elongated N_2-O_9 distances as a consequence of populating the antibonding $\pi_{\text{NO}_2^*}$ orbital. Moreover, the nitro and aldehyde groups, which lie in planes forming 30° dihedral angles with respect to benzene in the ground state, planarize by approximately 10 and 20° in the $(n\pi^*)_{\text{Min}}$, respectively.