

Non-Adiabatic Molecular Dynamics Study of HBQ Molecules

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1. Motivation

The aim of this project is to investigate the intrinsic dynamics and to calculate the ground and first excited state profiles of 10-hydroxybenzo[h]quinoline, also known as HBQ. This molecule undergoes an excited-state intra-molecular proton transfer reaction that is accompanied by a large Stokes shift which, in combination with the ultra-fast reaction dynamics, makes HBQ an ideal candidate to explore the effects of strong light-matter coupling on reactivity. As a starting point for our future research, we study the population dynamics of the molecule with trajectory surface hopping employing NEXMD and CP2K packages.

2. Geometry optimization

Geometry optimization of the initial structure was carried out with density functional theory using CP2K program. For all atoms, triple-zeta correlation-consistent basis sets and PBE functionals were used. The optimization was reached for 58 steps, the resulting structure is represented in figure 1.

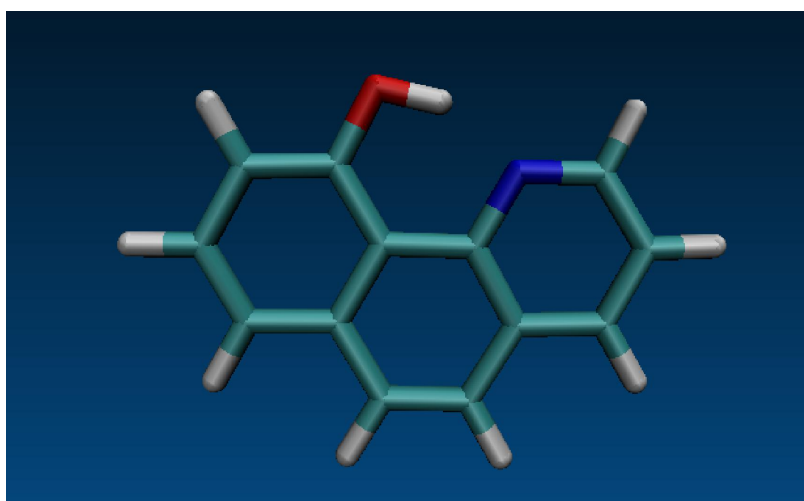


Fig. 1. Optimized geometry of HBQ

3. Absorption spectrum

To obtain the absorption spectrum of HBQ, firstly ground state dynamics were computed for 5 ps with a time step $\Delta t = 0.1$ fs. Among resulting geometries, 11 trajectories, equally distributed between 4 and 4.5 ps, were selected for single point calculations and the average absorption spectrum was generated with Gaussian lineshape chosen. As it can be seen in fig. 2, there are three absorption peaks associated with excited states S_{1-2} , S_{3-9} and S_{10-15} respectively.

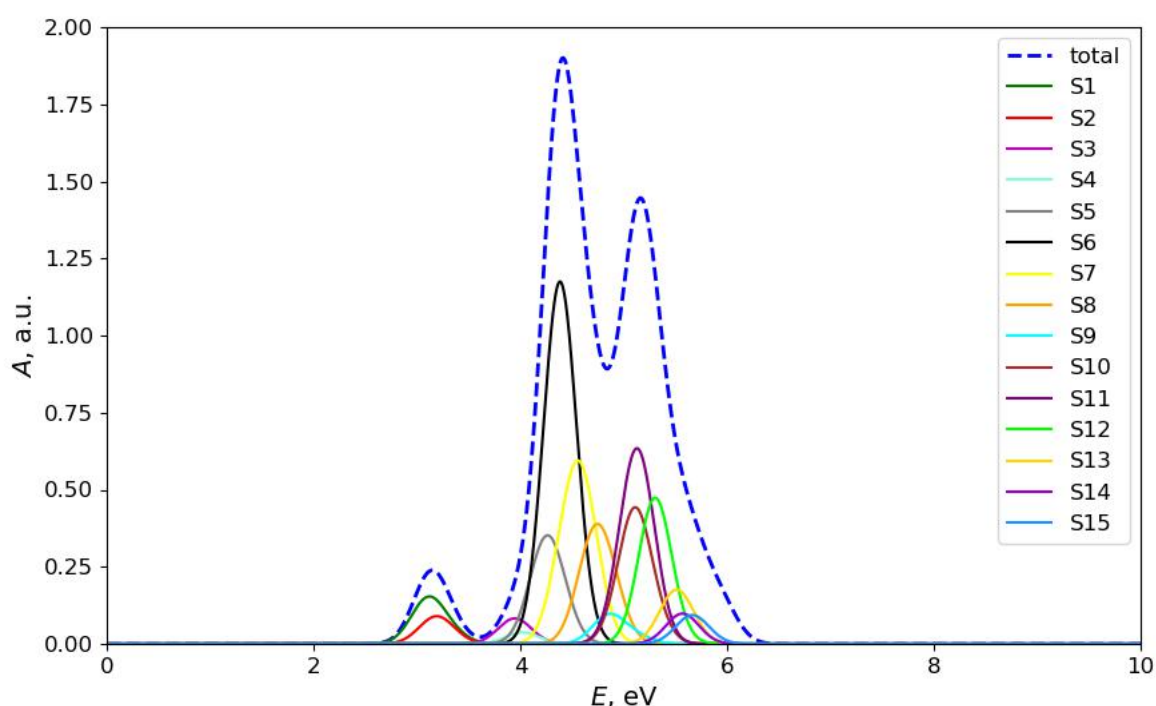


Fig. 2. Absorption spectrum of HBQ

4. Non-adiabatic molecular dynamics simulations

Non-adiabatic MD simulations were performed for the same geometries as in the previous step. The system was evolved during 100 fs after an initial excitation at $E = 5.16$ eV, that corresponds to the third peak of the absorption spectrum. This peak is predominantly associated with the excited states S_{10} , S_{11} and S_{12} , as seen in fig. 3. In less than 40 fs, population moves to lower excited states and, after 100 fs, more than 60 % of the initial excitation is concentrated on the first excited state.

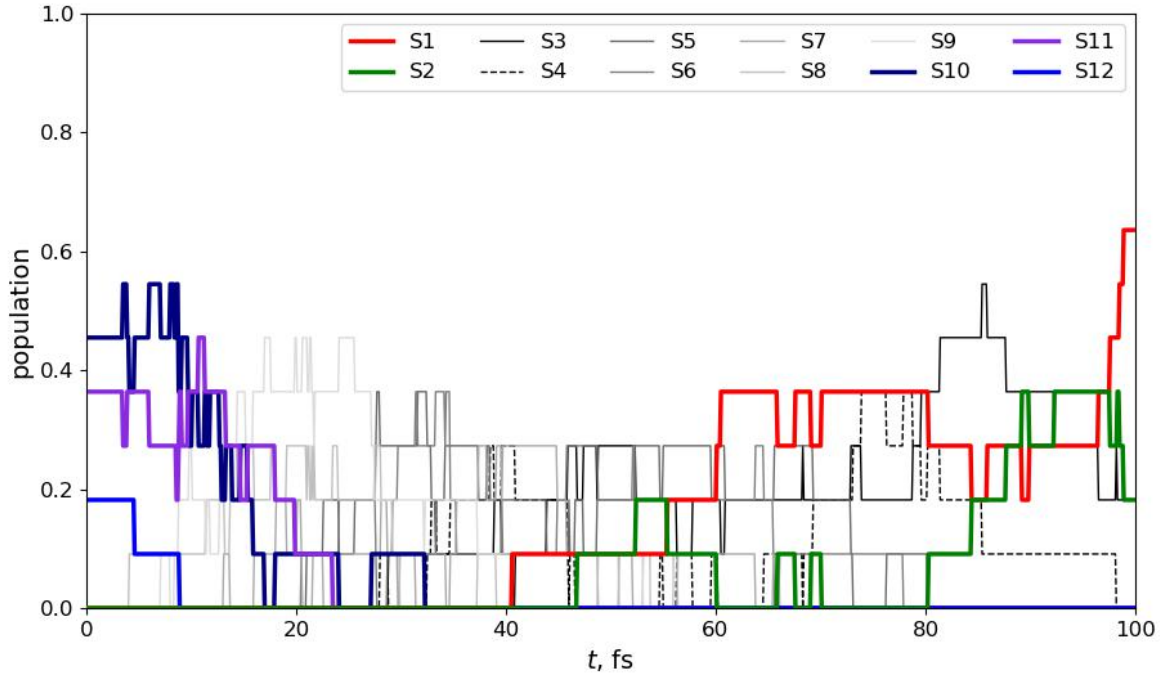


Fig. 3. Population dynamics of HBQ

Fig. 4 depicts excited state energies as functions of time for a given geometry. Vertical lines correspond to hops between states (table 1). Despite the energy difference between states S_3 and S_2 that is rather large, during the time interval 38 to 52 fs, potential energy curves approach each other thereby facilitating population transfers ultimately reaching the first excited state.

table 1

t, fs	state from	state to	t, fs	state from	state to
8.8	10	9	46.8	3	2
13.8	9	8	55.4	2	1
14.4	8	9	65.9	1	2
15.2	9	8	67.6	2	1
21.0	8	5	69.1	1	2
34.7	5	4	70.1	2	1
45.9	4	3	84.4	1	2

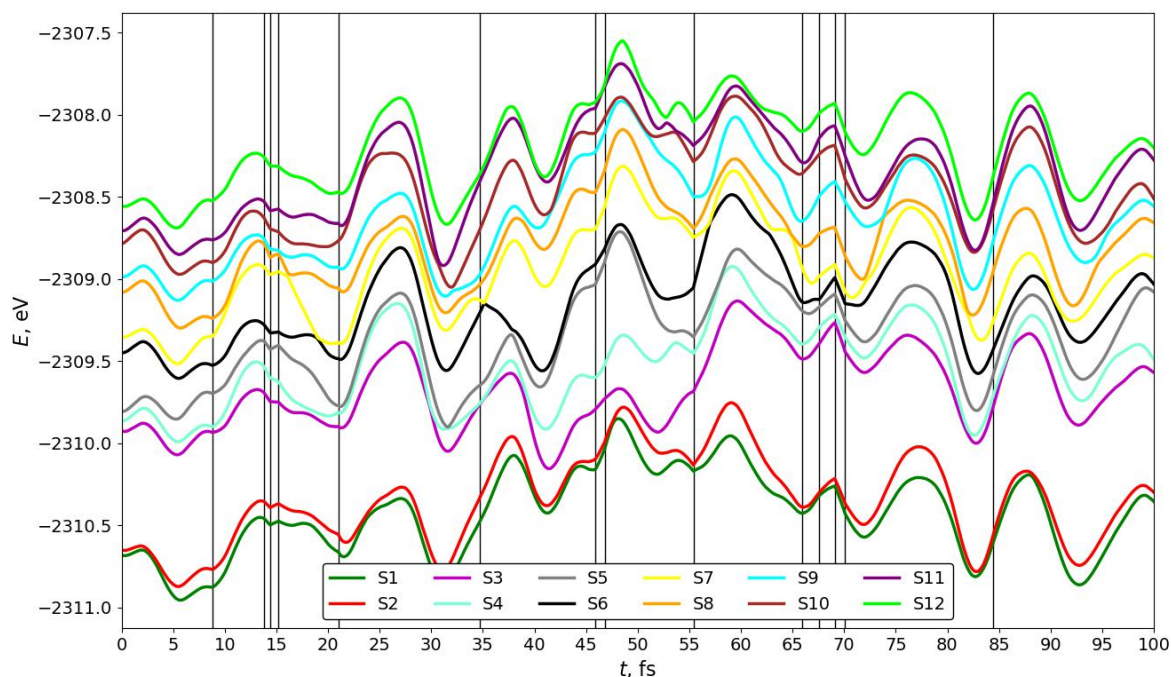


Fig. 4. Potential energy surfaces

5. Strong coupling between S_1 excited state and external light

As mentioned above, HBQ molecules undergo an excited-state intra-molecular proton transfer reaction. To investigate how strong coupling to potentially affects this process, we built potential energy plots for both neutral HBQ and a negative ion (HBQ^-) along the reaction coordinate defined to be the O-H bond length over the interval 0.95–1.70 Å with a step of 0.5 Å. Calculations were carried out employing CP2K with a TDDFT approach. As we can see in fig. 5, the neutral HBQ has only one energy minimum, while for HBQ^- there are 2 minima corresponding to conformations where the hydrogen atom is bound to either oxygen (total minimum at 1.05 Å) or nitrogen (local minimum at 1.55 Å). For this reason, in what follows we consider HBQ^- ion only.

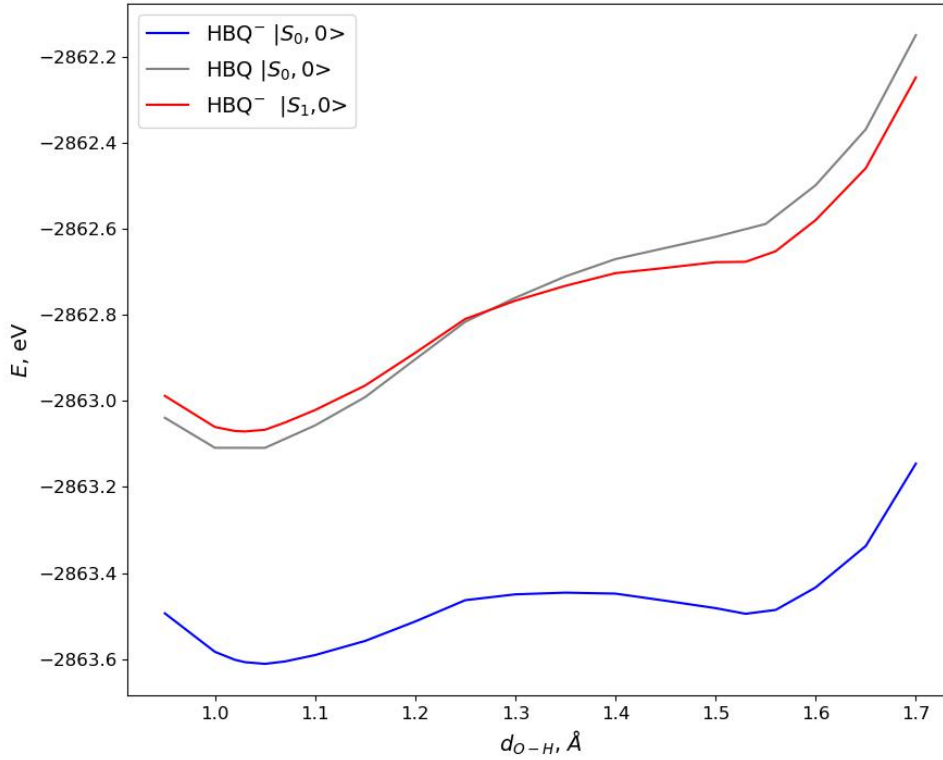


Fig. 5. Energies along the reaction coordinate

In the Jaynes-Cummings model, in which a molecule is considered as a two level system interacting with a single light mode. Fast energy exchanges result in two polaritonic states, which energies can be obtained by diagonalization of the system Hamiltonian

$$\widehat{H} = \begin{pmatrix} E_{mol} & g \\ g & E_{ph} \end{pmatrix},$$

where g is the coupling strength.

We fitted the energy profiles and diagonalized along the reaction coordinate with a step 0.01 Å (light mode energy 0.7 eV and coupling strength 0.01 eV). With these parameters a Rabi splitting of 0.02 eV is obtained. The energy barrier for the lower polariton is of the same order as the barrier for the ground state, see fig. 6. Thus, strong coupling should prevent photoinduced proton transfer. However, to validate this conclusion further simulations need to be carried out improving the level of theory and accounting for more realistic conditions (presence of solvent, thermal motions, role of dark states).

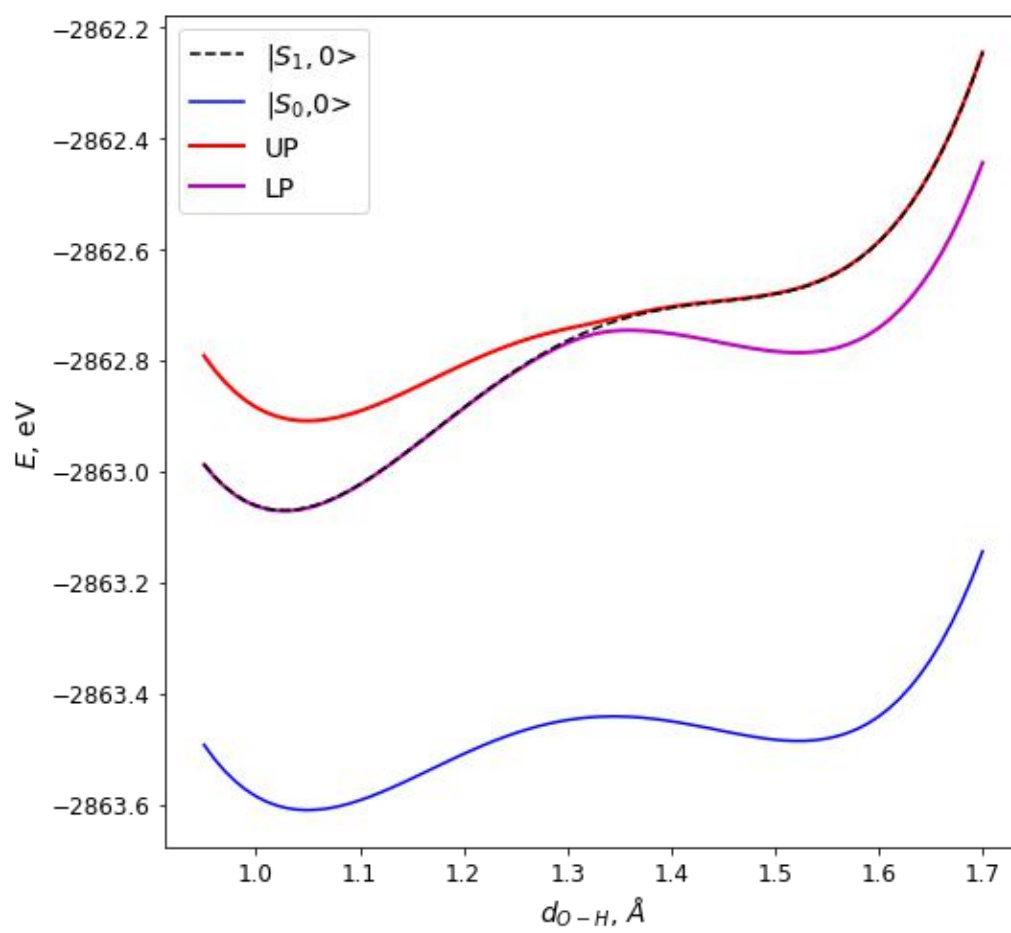


Fig. 6. Change of the energy profile due to strong coupling