Non-Adiabatic Molecular Dynamics Simulation 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 here with trajectory surface hopping the population dynamics of the molecule employing NEXMD and CP2K quantum chemistry 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.
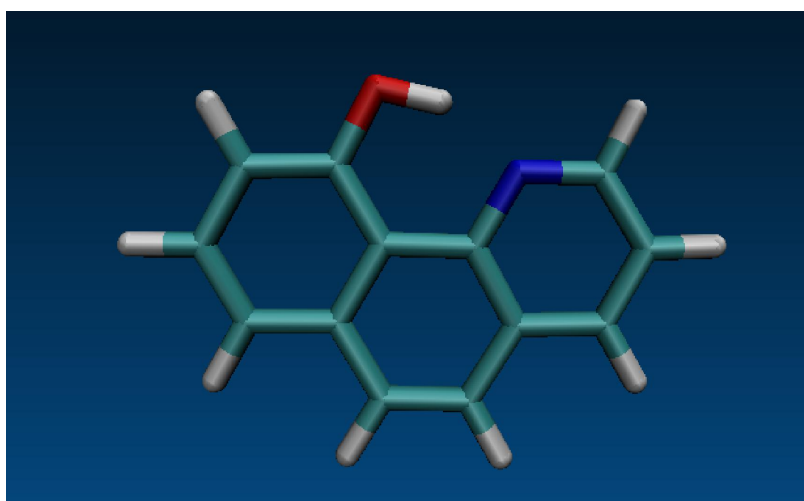

Fig. 1. Optimized geometry of HBQ

3. Absorption spectrum

To obtain the absorption spectrum of HBQ, a ground state trajectory was calculated at first during 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.
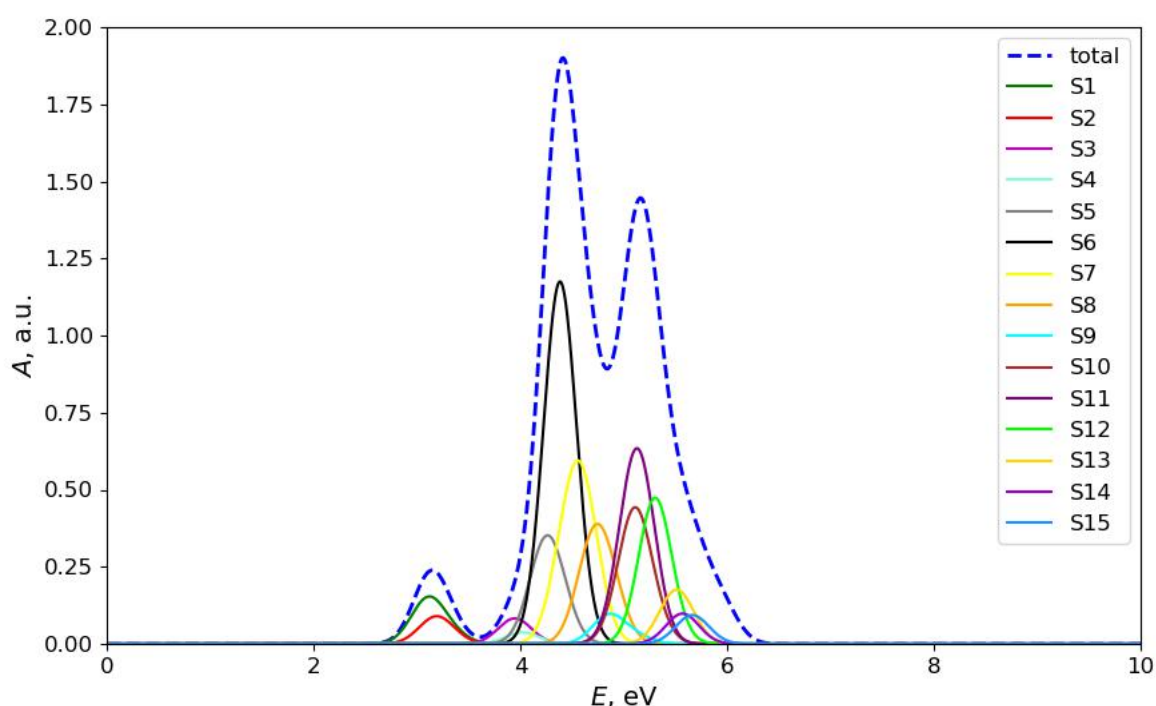

Fig. 2. Absorption spectrum of HBQ

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 the initial excitation at $E = 5.16$ eV, that corresponds to the thirs peak of the absorption spectrum predominantly associated with the excited states S_{10}, S_{11} and S_{12}, that is why it is they that are populated initially, as seen in fig. 3. However, in less than 40 fs the population moves to lower excited states and after 100 fs more than 60 % of the population is concentrated on the first excited state.
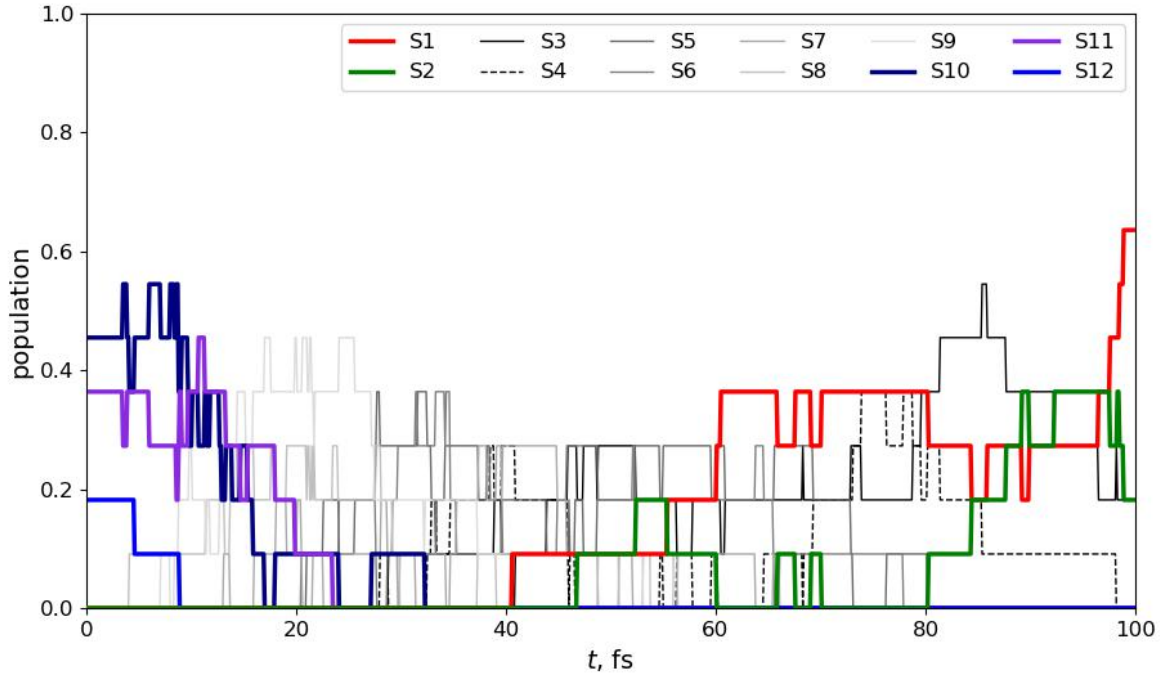
Fig. 3. Population dynamics of HBQ

Fig. 4 depicts excited state energies as funtions of time for one certain geometry. The vertical lines correspond to the moments when hops between states occur (table 1). Despite the energy difference between states S_3 and S_2 rather large, during the time interval between 38 and 52 fs corresponding potential curves approach each other that facilitates the population transition and its further movement towards the first excited state.

table 1

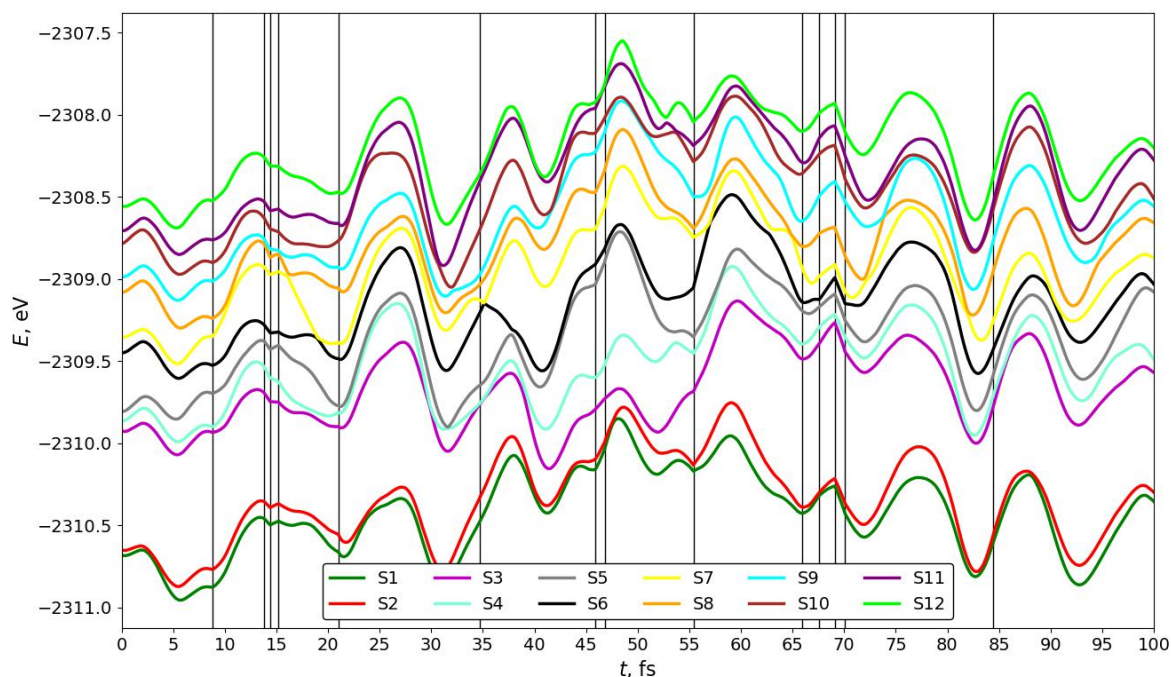| t, fs	state *from*	state *to*	t, fs	state *from*	state *to*
8.8	10	9	46.8	3	2
13.8	9	8	55.4	2	1
14.4	8	9	65.9	1	2
15.2	9	8	67.6	2	1
21.0	8	5	69.1	1	2
34.7	5	4	70.1	2	1
45.9	4	3	84.4	1	2

Fig. 4. Potential energy surfaces

5. Strong coupling between S_1 excited state and external light

As was mentioned above, HBQs undergoe an excited-state intra-molecular proton transfer reaction. To study investigate the possibility of strong coupling to affect this process, we built potential energy plots for both a neutral HBQ molecule and a negative ion (HBQ⁻) along the reaction coordinate which is the O-H bond length over the interval 0.95—1.70 Å with a step 0.5 Å. Calculations were carried out in CP2K with TDDFPT 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 situations when 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, further we consider only HBQ⁻ ion.
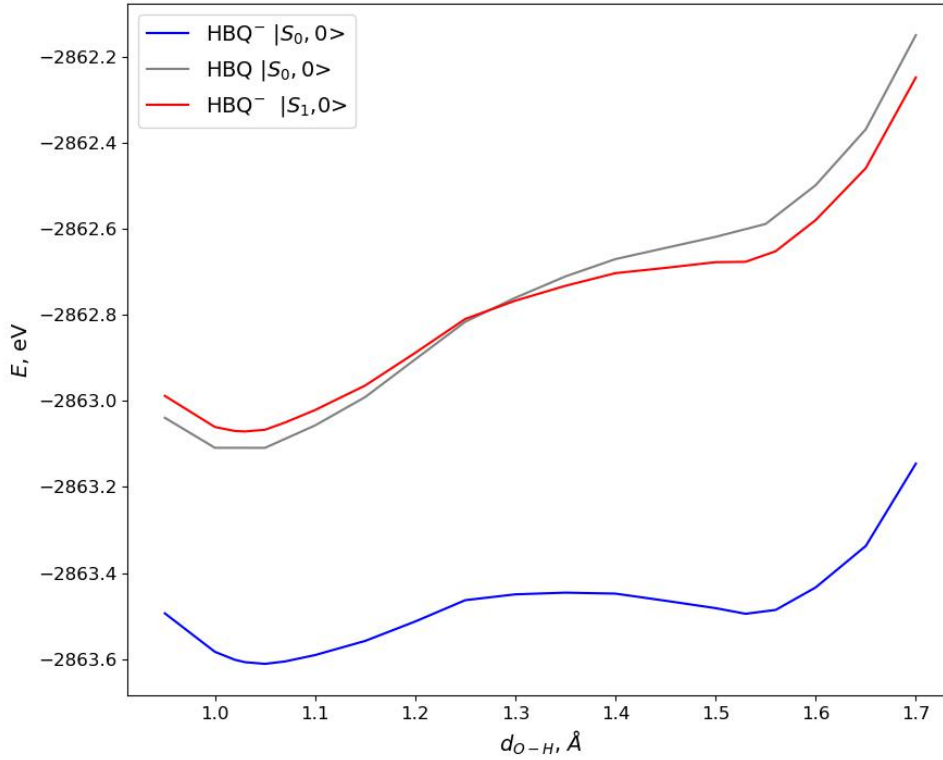
Fig. 5. Energies along the reaction coordinate

Useful insight can be extracted from the simple Jaynes-Cummings model, in which a molecule considering as a two level system interacts with a single light mode. As a result of such synergy, two polaritonic states appear, 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 coupling strength.

We fitted the energy profiles and made diagonalization along the reaction coordinate with a step 0.01 Å, light mode energy 0.7 eV and coupling strength 0.01 eV. With this parameters Rabi splitting reaches 0.02 eV. The potential barrier for the lower polariton of the same order as for the ground state is clearly seen in fig. 6. Thus, stroung coupling impedes the photoinduced proton transfer unlike its absense. However, to approve or refute this conclusion as well as to research the system in realistic conditions (the presence of solvent, thermal motion accounting,

influence of the dark states) molecular dynamic calculation is requirer that is our purpose for the future.
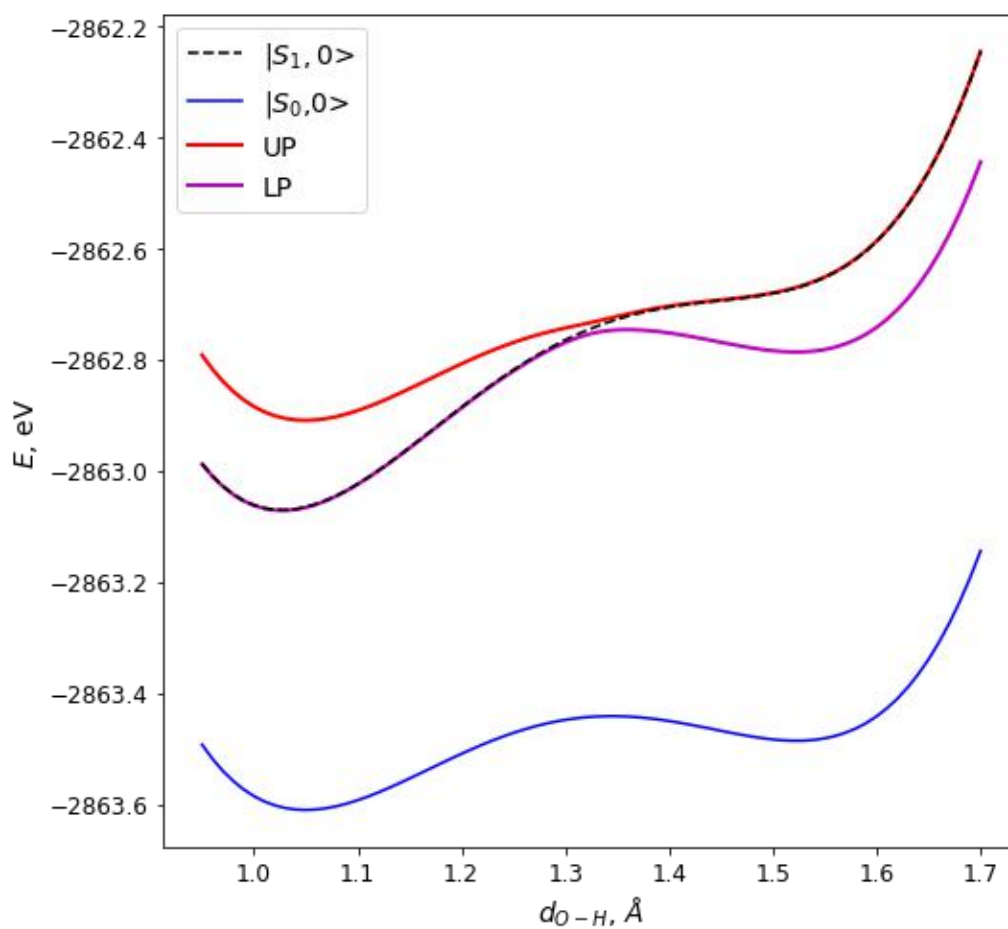

Fig. 6. Energy splitting and the change of the energy profile due to strong coupling