Vibrational structure of absorption spectrum of 2,5-bis(2-benzoxazolyl)hydroquinone

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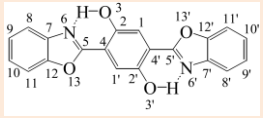
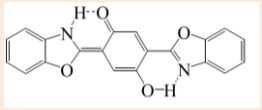
Introduction

Photoinduced excited state intramolecular proton transfer (ESIPT) has attracted attention of researchers for several decades as an ultrafast photochemical reaction and a process that could be utilized for a number of applications. 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) has been extensively studied for several decades by theoretical calculations and experiments in various environments as a substance that exhibits the ESIPT. The preferable structure of the BBHQ molecule in the ground state is an enol form, whereas the enol and keto forms are in dynamical equilibrium in the first excited state, the equilibrium is shifted towards to the keto form. In this study we consider application of TDDFT approach and harmonic approximation for vibronic states of the enol form of the molecule of BBHQ.



enol form



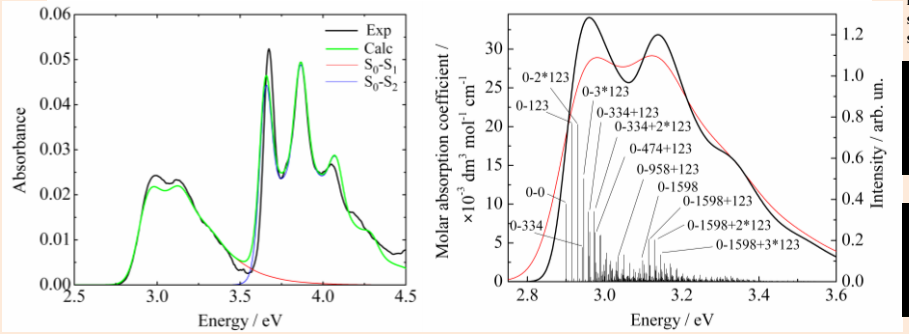
keto form

Computational methods

The calculations were performed for an isolated molecule using the ORCA software package [1,2], the def2-SVP basis set and ωB97X-D3 functional. The vibrations were calculated in harmonic approximation using analytical second energy derivatives for the ground state and numerical ones with default parameters for the excited states. Frequencies of the vibrations are unscaled. Vibronic structure of the absorption spectra was calculated with the harmonic model and the Franck-Condon approximation. The vibronic structure calculations were performed with the FCclasses3 code [3,4] using the time-independent and time-dependent methods. The spectrum was modeled assuming inhomogeneous broadening by Gaussian function with the half width at half maximum of 0.035 eV.

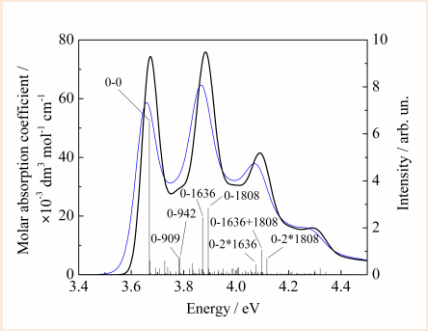
Calculated geometrical parameters (bond length, Å; angle, degree) of the enol structure of the molecule of BBHQ in the ground S_0, first S_1 and second S_2 excited states

Parameter	S_0	S_1	S_2	Parameter	S_0	S_1	S_2	Parameter	S_0	S_1	S_2
C_1-C_2	1.393	1.403	1.386	C_{12}-C_7	1.398	1.404	1.412	O_{13}-C_5-N_6	114.6	114.0	113.7
C_2-C_4	**1.418**	**1.457**	1.425	C_{12}-O_{13}	1.363	1.365	1.357	C_7-C_8-C_9	117.1	117.3	117.3
C_4-$C_{1'}$	**1.399**	1.401	**1.443**	O_{13}-C_5	1.352	1.358	1.367	C_8-C_9-C_{10}	121.7	121.8	121.9
C_4-C_5	**1.457**	**1.422**	**1.409**	**C_2-O_3**	**1.336**	**1.310**	1.335	C_9-C_{10}-C_{11}	121.7	121.5	121.6
C_5-N_6	**1.300**	**1.321**	**1.329**	**C_1-C_2-C_4**	**117.9**	**120.5**	118.4	C_{10}-C_{11}-C_{12}	115.6	115.9	115.8
N_6-C_7	**1.389**	1.377	**1.365**	**C_2-C_4-C_5**	**118.7**	118.2	**119.8**	C_{11}-C_{12}-C_7	123.8	123.7	123.8
C_7-C_8	1.397	1.398	1.405	C_4-C_5-N_6	126.0	125.3	126.1	C_{12}-C_7-C_8	120.1	119.8	119.6
C_8-C_9	1.391	1.393	1.389	C_5-N_6-C_7	105.1	105.3	105.2	**C_4-C_2-O_3**	**123.4**	**120.7**	122.5
C_9-C_{10}	1.407	1.405	1.41	N_6-C_7-C_{12}	107.8	107.9	108.4	**C_2-C_4-$C_{1'}$**	**120.7**	**118.4**	**119.1**
C_{10}-C_{11}	1.393	1.397	1.397	C_7-C_{12}-O_{13}	107.5	107.8	107.7	**C_4-$C_{1'}$-$C_{2'}$**	**121.4**	121.1	**122.6**
C_{11}-C_{12}	1.388	1.384	1.384	C_{12}-O_{13}-C_5	105.0	104.9	105.0	-	-	-	-

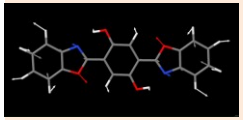


Absorption spectrum of BBHQ dissolved in CCl_4 measured at room temperature (Exp) and spectrum modeled with the time-dependent method (Calc). Calculated energy of the S_0-S_1 transition is red-shifted by 0.2 eV, S_0-S_2 transition is red-shifted by 0.455 eV.

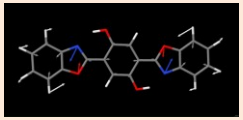
Absorption spectrum for the S_0-S_1 transitions modeled with the time-dependent method at room temperature (red line) and time-independent method at temperature 0 K (black line). The stick spectrum represents vibronic transitions at 0 K. The spectra are red-shifted by 0.2 eV in energy.



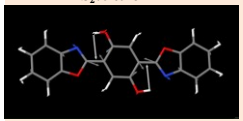
Absorption spectrum for the S_0-S_2 transitions modeled with the time-dependent method at room temperature (blue line) and time-independent method at temperature 0 K (black line). The stick spectrum represents vibronic transitions at 0 K. The spectra are red-shifted by 0.455 eV in energy.



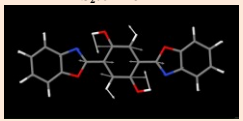
S_2: 909 cm^{-1}



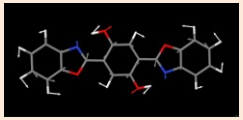
S_2: 942 cm^{-1}



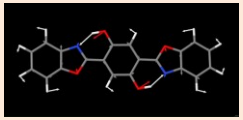
S_2: 1636 cm^{-1}



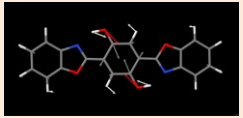
S_2: 1808 cm^{-1}



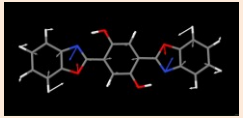
S_1: 123 cm^{-1}



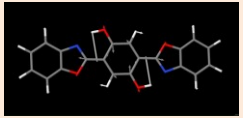
S_1: 334 cm^{-1}



S_1: 474 cm^{-1}



S_1: 958 cm^{-1}



S_1: 1598 cm^{-1}

Conclusions

The calculations performed with the ωB97X-D3 density functional for molecular vibrations and electronic transitions are found to reproduce well the vibronic structure of the S_0-S_1 and S_0-S_2 absorption bands in the spectrum of 2,5-bis(2-benzoxazolyl)hydroquinone measured in solution at room temperature. It allows to determine normal modes that contribute significantly to the absorption spectrum. At the same time energy of the electronic transitions is overestimated by the calculations and the overestimation is different for the S_0-S_1 and S_0-S_2 transitions.

References

1. F. Neese, WIREs Comput. Mol. Sci., 2012, 2, 73.
2. F. Neese, WIREs Comput. Mol. Sci., 2017, 8, e1327.
3. F. Santoro, J. Cerezo, FCclasses3, A code for vibronic calculations. Version 3.0.3. 2023. http://www.iccom.cnr.it/en/fcclasses.
4. J. Cerezo, F. Santoro, J. Comput. Chem., 2023, 44, 626, doi:10.1002/jcc.27027.