

## VIBRONIC SPECTRUM OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE

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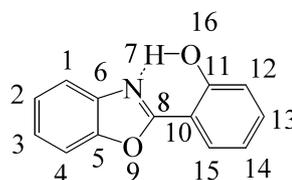
UV-vis absorption spectrum of 2-(2'-hydroxyphenyl)benzoxazole is calculated for the transitions to the first and second excited states using the Franck-Condon approximation and harmonic model for vibrations. The largest intensity of vibronic transitions to the first electronic state is found for an in-plane deformation mode that changes mutual position of the benzoxazole and phenyl fragments; for the stretching vibration involving the aromatic rings and the bond linking the benzoxazole and phenyl moieties. For the second electronic state the vibrations are the deformation modes of oxazole and phenyl rings, stretching vibrations involving the bonds of the nitrogen atom and the bond linking the benzoxazole and phenyl moieties.

**Keywords:** excited state intramolecular proton transfer, absorption, density functional theory, electronic and vibrational states.

Received 05.11.2021; Received in revised form 06.12.2021; Accepted 10.12.2021

### 1. Introduction

2-(2'-hydroxyphenyl)benzoxazole (HBO) is an organic substance that demonstrates excited state intramolecular proton transfer (ESIPT). HBO has been studied for several decades to clarify microscopic mechanism of this photochemical reaction especially when introducing the femtosecond time-resolved spectroscopy [1, 2]. Compounds with ESIPT are considered to be utilized for various applications including media for lasers [3]. In the ground state  $S_0$  the most stable structure of the molecule of HBO is an enol form with an intramolecular hydrogen bond OH...N (Fig. 1). In the first excited state  $S_1$  a keto form with an O...HN hydrogen bond has lower energy than the enol form. Upon absorption of a photon an excited enol structure is formed and ESIPT leads to formation of the keto structure. Absorption spectrum of HBO comprises broad structured bands caused by transitions between various vibrational energy levels of the ground and excited states [1, 2].



**Fig. 1. Enol structure of a molecule of HBO with atomic numbering scheme.**

In the present paper we model vibronic spectrum that is formed by transitions to the first and second excited electronic states. The aim of the study is assignment of the observed vibronic bands to the vibrations of the molecule.

### 2. Calculations and experimental details

The calculations of structure and vibrations were performed for an isolated molecule using the ORCA software package [4, 5],  $\omega$ B97X-D3 functional [6], and def2-SVP basis set [7]. The vibrations were calculated in harmonic approximation. Vibronic structure of the absorption spectra was calculated with the FCclasses3 code [8] using the time-dependent [9] and time-independent methods [10-13] in the Franck-Condon approximation. The time-dependent method allows calculating the spectrum but does not allow considering each vibronic transition separately. Normal coordinates in the ground and excited states were supposed to be related by the Duschinsky transformation [14]. The experimental absorption spectrum of HBO was obtained by the Shimadzu UV-3100 spectrophotometer in  $CCl_4$  solution at room temperature with resolution 1 nm.

### 3. Results and discussion

The calculations of the structures corresponding to the energy minima in the  $S_0$ ,  $S_1$ , and  $S_2$  demonstrate that the enol form of the molecule remains planar in the excited states. Geometrical parameters of the aromatic ring in the benzoxazole fragment change slightly in the excited states (Table 1). Significant changes are found for the bonds of the nitrogen atom, for the bond  $C_8-C_{10}$  linking the benzoxazole and phenol moieties in both excited states,  $C_{10}-C_{11}$  in  $S_1$ , and  $C_{12}-C_{13}$  in the  $S_2$  states. The changes in angles mostly involve hydroxyphehyl fragment.

Table 1

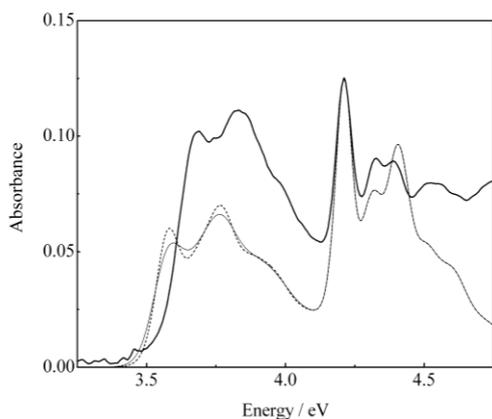
Calculated geometrical parameters (bond length, Å; angle, degree) of the molecule of HBO in the ground  $S_0$ , first  $S_1$ , and second  $S_2$  excited states (see Fig. 1 for the notation of atom numbers)

Parameter	$S_0$	$S_1$	$S_2$	Parameter	$S_0$	$S_1$	$S_2$
$C_1-C_2$	1.392	1.391	1.391	$C_1-C_2-C_3$	121.7	122.0	122.2
$C_2-C_3$	1.406	1.407	1.410	$C_2-C_3-C_4$	121.6	121.4	121.5
$C_3-C_4$	1.394	1.400	1.403	$C_3-C_4-C_5$	115.7	116.1	115.8
$C_4-C_5$	1.387	1.383	1.384	$C_4-C_5-C_6$	123.8	123.6	123.9
$C_5-C_6$	1.397	1.417	1.423	$C_5-C_6-C_3$	120.1	119.4	119.3
$C_6-C_1$	1.396	1.407	1.410	$C_6-C_1-C_2$	117.2	117.4	117.3
$C_5-O_9$	1.364	1.358	1.356	$C_5-O_9-C_8$	105.1	105.0	104.9
$O_9-C_8$	1.353	1.371	1.376	$C_6-N-C_8$	105.2	105.7	105.4
$C_6-N$	1.389	1.357	1.357	$N-C_8-O_9$	114.5	113.0	113.4
$N-C_8$	1.301	1.345	1.340	$C_8-C_{10}-C_{11}$	118.8	117.9	120.1
$C_8-C_{10}$	1.453	1.405	1.407	$C_{10}-C_{11}-O_{16}$	123.0	120.0	121.7
$C_{10}-C_{11}$	1.417	1.476	1.430	$N-C_8-C_{10}$	126.0	125.6	126.2
$C_{11}-C_{12}$	1.405	1.404	1.400	$C_{10}-C_{11}-C_{12}$	118.6	120.2	119.2
$C_{12}-C_{13}$	1.385	1.379	1.427	$C_{11}-C_{12}-C_{13}$	120.5	120.3	122.1
$C_{13}-C_{14}$	1.402	1.413	1.389	$C_{12}-C_{13}-C_{14}$	121.0	119.7	119.0
$C_{14}-C_{15}$	1.384	1.396	1.410	$C_{13}-C_{14}-C_{15}$	119.1	121.8	119.9
$C_{15}-C_{10}$	1.406	1.413	1.430	$C_{14}-C_{15}-C_{10}$	120.8	120.3	121.8
$C_{11}-O_{16}$	1.330	1.306	1.333	$C_{15}-C_{10}-C_{11}$	120.0	117.7	117.9

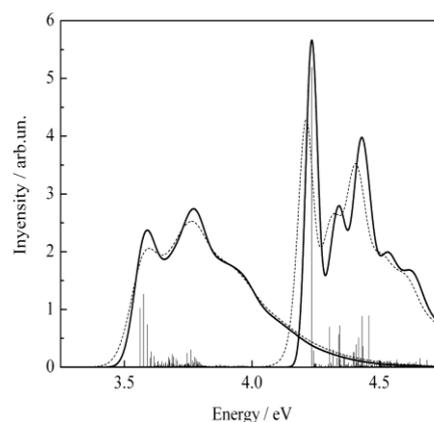
The calculated spectrum demonstrates good correspondence to the bands observed in the experiment (Fig. 2). The calculations overestimate electronic energy by about 0.435 eV, however, the overestimation is similar for the  $S_1$  and  $S_2$  states. The calculated bands caused by the  $S_0-S_1$  and  $S_0-S_2$  transitions are shown separately in Fig. 3. To reduce the number of transitions involved in the spectrum formation, the time-independent calculations are performed for the transitions from the lowest vibrational level in the  $S_0$  state. This implies low-temperature conditions when thermal excitation of vibrations is negligible. The spectra calculated for transitions from the lowest vibrational level are like those obtained by the time-dependent approach at room temperature (Fig. 3).

The calculated intense progression comprising 0-0 transition and transitions to vibrational levels of the mode  $116\text{ cm}^{-1}$  corresponds to the observed component with the maximum at 3.69 eV. This mode is an in-plane deformation vibration that changes mostly the  $N-C_8-C_{10}$  angle modulating the distance between the oxygen and nitrogen atoms of the hydrogen bond. The normal coordinate is similar to one in the ground state.

In the vicinity of the observed maximum at 3.83 eV a progression by  $116\text{ cm}^{-1}$  can be distinguished starting at the state  $1492\text{ cm}^{-1}$ . The mode  $1492\text{ cm}^{-1}$  is mostly a combination of three ground state normal coordinates. This mode is a stretching vibration that involves both the aromatic rings,  $C_{11}-O_{16}$ , and  $C_8-C_{10}$  bonds.



**Fig. 2.** Experimental absorption spectrum of HBO dissolved in  $\text{CCl}_4$  (bold line) and spectra calculated with the time-independent method (thin solid line – the spectrum obtained with the Gaussian HWHM 0.045 eV for  $S_0$ - $S_1$  transition and 0.0275 eV for  $S_0$ - $S_2$  transition; dashed line – with HWHM 0.0275 eV for both transitions). The modeled spectra are red-shifted by 0.435 eV in energy.



**Fig. 3.** Absorption spectrum modeled for the  $S_0$ - $S_1$  and  $S_0$ - $S_2$  transitions with the time-independent method at room temperature (dashed line) and time-dependent method at low temperature (solid line). The stick spectrum represents vibronic transitions. The spectra are red-shifted by 0.435 eV in energy.

The calculated intense 0-0  $S_0$ - $S_2$  transition corresponds to the prominent band observed at about 4.21 eV. In the region of maxima at 4.33 and 4.39 eV the transitions to the excited one quantum vibrational states 572, 861, 891 and 1611, 1822  $\text{cm}^{-1}$  can be distinguished by their intensity. The modes 572 and 861  $\text{cm}^{-1}$  are deformation vibrations of the phenyl ring, 891  $\text{cm}^{-1}$  – deformation of the oxazole ring. The normal coordinates of the modes 572 and 861  $\text{cm}^{-1}$  retain similarity to the normal coordinates in the ground states, while the normal coordinates of the mode 891  $\text{cm}^{-1}$  are mostly combinations of two ground state modes. The mode 1611  $\text{cm}^{-1}$  is a stretching vibration involving N- $\text{C}_8$  and  $\text{C}_8$ - $\text{C}_{10}$  bonds; 1822  $\text{cm}^{-1}$  is a stretching vibration of the phenyl ring also involving N- $\text{C}_8$  and  $\text{C}_8$ - $\text{C}_{10}$  bonds. The normal coordinates of stretching modes 1611 and 1822  $\text{cm}^{-1}$  are combinations of more than 3 ground state modes. In the region of weak band around 4.53 eV there are no predominant components.

#### 4. Conclusions

Modeling of the absorption spectrum of 2-(2'-hydroxyphenyl)benzoxazole with the use of Franck-Condon approximation and harmonic vibration model for movement of the nuclei demonstrates good correspondence to vibronic structure observed in the experiment. However, the calculations using the  $\omega$ B97X-D3 density functional systematically overestimate the value of electronic energy of the excited states, and relative values of transition dipole moment that defines integral intensity of bands are rather semi-quantitative. The calculated intensity of the band corresponding to the transition to the first excited state is lower than observed in the experiment.

#### Acknowledgements

The author is very grateful to Prof. Fabrizio Santoro of the Institute of Chemistry of Organometallic Compounds of the Italian National Research Council and Dr. Javier Cerezo of Autonomous University of Madrid for providing a development version of the FCclasses3 code

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