

COMPUTATIONAL STUDY OF ELECTRONIC-VIBRATIONAL SPECTRUM OF ROTAMERS OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE

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UV-vis absorption spectrum of internally hydrogen-bonded enol structures of 2-(2'-hydroxyphenyl)benzoxazole is calculated for the transitions to the first excited state using the Franck-Condon approximation and harmonic model for vibrations. It is shown that the absorption spectrum of the structure with the hydrogen bond OH...O is shifted to larger energy by about 0.13 eV compared to the spectrum of the most stable structure with the hydrogen bond OH...N. The largest intensity of vibronic transitions to the first electronic state of the OH...O structure demonstrates high-frequency vibrations involving deformation mode of the oxazole ring, stretching of the both aromatic rings, and stretching of the bond linking the benzoxazole and phenyl moieties.

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

Received 09.11.2022; Received in revised form 19.12.2022; Accepted 23.12.2022

1. Introduction

2-(2'-hydroxyphenyl)benzoxazole (HBO) is an organic compound that demonstrates excited state intramolecular proton transfer (ESIPT). HBO has been extensively studied for decades as photoreactive molecule and possible material for several applications. Various HBO derivatives with ESIPT are synthesized and studied nowadays. [1]. There are two rotameric enol structures with the intermolecular hydrogen bonds OH...N and OH...O in the ground state S_0 (Fig. 1). The structures are in dynamic equilibrium in liquid solutions, the most stable is structure I. Structure II does not undergo ESIPT and demonstrates fluorescence band with usual Stokes shift. The fluorescence spectrum of HBO is dominated by the prominent band with abnormal large Stokes shift caused by transition in the keto structure formed by ESIPT in structure I in the excited state S_1 . The weak fluorescence band with normal Stokes shift could be caused by transitions from the excited enol structure I but it is assigned to transitions in structure II based on the different excitation spectrum and lifetime [2, 3]. Measured absorption spectrum of HBO is dominated by the spectrum of structure I and comprises broad structured bands caused by transitions between various vibrational energy levels of the ground and excited states [2-4]. Vibrations of structures I and II is calculated to differ in frequency and eigenvectors for a number of modes in the ground state [5].



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

In the present paper we calculate electronic-vibrational spectra of structure I and II of the molecule of HBO. The aim of the study is clarifying the difference of the absorption spectra of the rotameric species.

2. Calculations details

The calculations of structure and vibrations were performed for an isolated molecule using the ORCA software package [6, 7], ω B97X-D3 functional, and def2-SVP basis set as described in [4]. The vibrations were calculated in the harmonic approximation, the frequencies are unscaled. Vibronic structure of the absorption spectra was calculated with the

FCclasses3 code [8, 9] using the time-dependent [10] and time-independent methods [11-14] 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 [15]. The spectra were modeled assuming the Gaussian bandshape with HWHM of 0.045 eV for the transitions. This approach is found to overestimate electronic energy of the state S_1 by about 0.37 eV but reproduce intensity of the vibronic components observed in the experiments for the band corresponding to the S_0 - S_1 transition [4].

3. Results and discussion

Structure II is predicted by the calculations to be planar in the first excited state S_1 . Like the structure I, the largest changes between structures II in the ground and excited state are found for the bonds of the nitrogen atom, for the bond C_8 - C_{10} linking the benzoxazole and phenol moieties in both the excited states, C_{10} - C_{11} (Table 1). The changes in the angles C_8 - C_{10} - C_{11} and N - C_8 - C_{10} defining mutual position of the benzoxazole and phenol moieties are less in structure II than in structure I (0.2° and 0.9° , 0.0° and 0.4°).

Table 1

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

State	S_0		S_1		State	S_0		S_1	
Parameter	I	II	I	II	Parameter	I	II	I	II
C_1 - C_2	1.392	1.392	1.391	1.387	C_1 - C_2 - C_3	121.7	121.7	122.0	122.2
C_2 - C_3	1.406	1.407	1.407	1.411	C_2 - C_3 - C_4	121.6	121.6	121.4	121.5
C_3 - C_4	1.394	1.394	1.400	1.403	C_3 - C_4 - C_5	115.7	115.5	116.1	115.8
C_4 - C_5	1.387	1.386	1.383	1.380	C_4 - C_5 - C_6	123.8	124.2	123.6	124.4
C_5 - C_6	1.397	1.397	1.417	1.425	C_5 - C_6 - C_1	120.1	119.6	119.4	118.5
C_6 - C_1	1.396	1.396	1.407	1.418	C_6 - C_1 - C_2	117.2	117.4	117.4	117.4
C_5 - O_9	1.364	1.366	1.358	1.358	C_5 - O_9 - C_8	105.1	105.0	105.0	104.9
O_9 - C_8	1.353	1.375	1.371	1.404	C_6 - N - C_8	105.2	105.1	105.7	105.5
C_6 - N	1.389	1.389	1.357	1.345	N - C_8 - O_9	114.5	114.3	113.0	112.6
N - C_8	1.301	1.289	1.345	1.341	C_8 - C_{10} - C_{11}	118.8	123.3	117.9	123.1
C_8 - C_{10}	1.453	1.463	1.405	1.402	C_{10} - C_{11} - O_{16}	123.0	124.4	120.0	121.4
C_{10} - C_{11}	1.417	1.413	1.476	1.466	N - C_8 - C_{10}	126.0	127.9	125.6	127.9
C_{11} - C_{12}	1.405	1.405	1.404	1.395	C_{10} - C_{11} - C_{12}	118.6	118.9	120.2	120.4
C_{12} - C_{13}	1.385	1.385	1.379	1.395	C_{11} - C_{12} - C_{13}	120.5	120.8	120.3	120.4
C_{13} - C_{14}	1.402	1.402	1.413	1.415	C_{12} - C_{13} - C_{14}	121.0	120.6	119.7	120.0
C_{14} - C_{15}	1.384	1.384	1.396	1.382	C_{13} - C_{14} - C_{15}	119.1	119.1	121.8	121.3
C_{15} - C_{10}	1.406	1.407	1.413	1.430	C_{14} - C_{15} - C_{10}	120.8	121.3	120.3	120.5
C_{11} - O_{16}	1.330	1.341	1.306	1.325	C_{15} - C_{10} - C_{11}	120.0	119.3	117.7	117.5

The modeled absorption spectrum of structure II demonstrates shift to the larger energies compared to the spectrum of structure I and more pronounced vibronic structure (Fig. 2). The difference in the position of the main maxima and the 0-0 transitions is about 0.13 eV. The electronic-vibrational transitions in structure I and II calculated under low-temperature conditions, when thermal excitation of vibrations is negligible, are shown in Fig. 3. The calculated spectra demonstrate correspondence to the experimental excitation spectra reported in [2], however, the measurements are conducted in ethanol solution where the molecules with intermolecular hydrogen bonds to solvent are present [2, 3].

The spectrum of structure I comprises progressions corresponding to transitions to vibrational levels of the mode 116 cm^{-1} . This mode is an in-plane deformation vibration that changes mostly the $\text{N-C}_8\text{-C}_{10}$ angle modulating the distance between the oxygen and nitrogen atoms of the hydrogen bond. High-frequency vibration that demonstrates large intensity of the transitions is the mode 1492 cm^{-1} which is a stretching vibration that involves both the aromatic rings, $\text{C}_{11}\text{-O}_{16}$ and $\text{C}_8\text{-C}_{10}$ bonds [4].

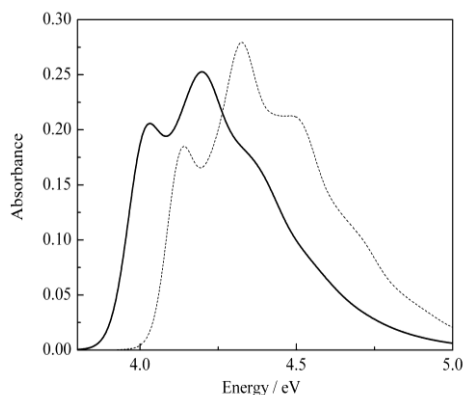


Fig. 2. Absorption spectra of rotameric species of the molecule of HBO calculated with the time-dependent method (solid line – structure I; dashed line – structure II) at room temperature.

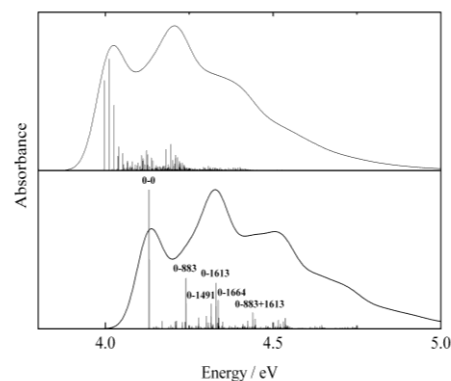


Fig. 3. Absorption spectra and $\text{S}_0\text{-S}_1$ transitions modeled with the time-independent method assuming transitions only from the vibrationless energy level in the ground state for structure I (upper graph) and structure II (lower graph).

The spectrum of structure II exhibits intense 0-0 transition and transitions to high-frequency vibrational levels without prominent low-frequency progressions. The low frequency mode that modulates the distance between the oxygen atoms of the hydrogen bonds has frequency 115 cm^{-1} in the excited state that is close to the value for structure I. In the ground state the frequencies are 122 and 123 cm^{-1} . This demonstrates that the frequency of this mode depends very weakly on the changes in hydrogen bonding strength from $\text{OH}\dots\text{N}$ to $\text{OH}\dots\text{O}$. At the same time, the shift in position of the energy minimum along this mode is less in structure II than in structure I that leads to the absence of corresponding prominent low-frequency progressions in the spectrum.

Large intensity of transitions is found for vibrations at 883 , 1491 , 1613 and 1664 cm^{-1} (see Fig. 3). Despite the Duschinsky rotation these modes can be related to the vibrations in the ground state by the largest elements of the matrix. The frequencies in the ground state are 968 , 1513 , 1686 and 1730 cm^{-1} . The mode 883 cm^{-1} is mostly an in-plane deformation mode of the oxazole ring; 1491 cm^{-1} – stretching vibration of the both aromatic rings; 1613 and 1664 cm^{-1} – stretching vibration of the both aromatic rings involving $\text{C}_8\text{-C}_{10}$ bonds.

4. Conclusions

Calculations of the absorption spectrum of rotameric species of 2-(2'-hydroxyphenyl)benzoxazole are performed in the Franck-Condon approximation assuming harmonic molecular vibrations in the ground and excited states. In contrast to the absorption spectrum of the most stable structure with the hydrogen bond $\text{OH}\dots\text{N}$, the electronic-vibrational spectrum of the structure with the hydrogen bond $\text{OH}\dots\text{O}$ does not demonstrate low-frequency progressions caused by the mode that modulates the distance between the oxygen atoms of the hydrogen bond.

Acknowledgements

The authors are 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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