

MODELING OF ABSORPTION SPECTRUM OF 2,5-BIS(2-BENZOXAZOLYL)HYDROQUINONE

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Vibronic structure of the absorption band of 2,5-bis(2-benzoxazolyl)hydroquinone is calculated for the transitions to the first excited state using the Franck-Condon approximation and harmonic model for vibrations. 2,5-bis(2-benzoxazolyl)hydroquinone is an organic compound that undergoes the excited state intramolecular proton transfer. It is found that the use of normal modes and values of energy of the electronic states calculated with the ω B97X-D3 density functional provides good agreement with the experimental spectrum, overestimating energy of the 0-0 transition by 0.13 eV. The largest intensity of vibronic transitions is demonstrated by deformation vibrations changing the distance between the oxygen and nitrogen atoms of the hydrogen bonds, a deformation vibration of the oxazole rings, deformation and stretching vibrations of the hydroquinone moiety.

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

Received 15.10.2023; Received in revised form 09.11.2023; Accepted 15.11.2023

1. Introduction

An organic compound 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) is extensively studied both experimentally and theoretically for several decades as a molecular system that undergoes the excited state intramolecular proton transfer (ESIPT) [1-4].

The most stable molecular structure in the ground state is the enol form with two hydrogen bonds OH...N (Fig. 1); in the first excited state the enol and keto structures coexist causing dual fluorescence. Dual fluorescence comprises two bands: the first with a Stokes shift that is common for the aromatic compounds (“blue”) and the second with an anomalously large Stokes shift (“red”). The red fluorescence is attributed to the transitions in the mono-keto structure formed by the single proton transfer (see Fig. 1). Besides studies performed for BBHQ in condensed state and different solvents or matrix, photophysical properties are studied for molecules isolated in supersonic jets [1-4]. The enol and keto structures in the excited state are separated by a barrier which value is estimated experimentally to be about 340 cm^{-1} in supersonic jets [1] and 121 cm^{-1} [4] in organic glasses. The absorption spectra or fluorescence excitation spectra in condensed media demonstrate diffuse vibronic structure, at low temperature progression formed by the vibration with frequency 120 cm^{-1} is distinguished [2]. The similar progression by 114 cm^{-1} formed by sharp lines is observed in the fluorescence excitation spectra for the molecules isolated in jets, however, excitation of the fluorescence with the light energy of about 1190 cm^{-1} above the 0-0 transition lead to broadening of the spectra and decrease in the fluorescence intensity [1, 3].

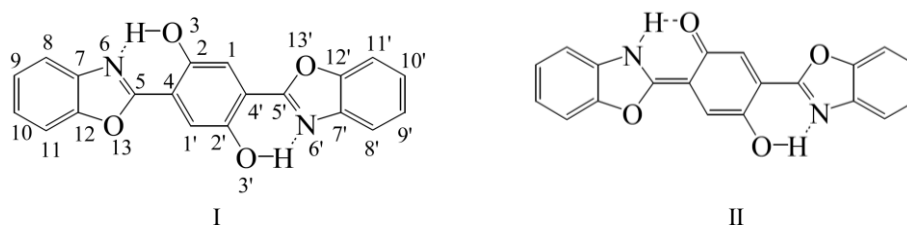


Fig. 1. Enol (I) and keto (II) structures of a molecule of BBHQ with atomic numbering scheme.

It was found that the calculation of the vibronic structure of the absorption spectrum for the related benzoxazole, 2-(2'-hydroxyphenyl)benzoxazole (HBO) with the TDDFT method

using the ω B97X-D3 density functional provides good agreement with the observed bandshape [5].

In this work we apply this approach to calculations of the absorption spectrum of BBHQ. The aim of the study is to model vibronic profile of the absorption band of BBHQ and determine the vibrations contributing to the transitions.

2. Calculations details

The calculations of structure and vibrations were performed for an isolated molecule by the DFT and TDDFT methods with the ω B97X-D3 functional and def2-SVP basis set using the ORCA software package [6, 7]. The vibrations were calculated in harmonic approximation. 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 are simulated using Gaussian lines with HWHM of 0.03 eV for the transitions. The experimental absorption spectrum of BBHQ was obtained by the Shimadzu UV-3100 spectrophotometer in CCl_4 solution at room temperature with resolution 1 nm.

3. Results and discussion

The enol structure molecule of BBHQ possesses C_{2h} symmetry both in the ground S_0 and first excited S_1 states. The largest changes in lengths between the ground and excited state are found for the bonds C_2-C_4 , C_2-O_3 of the hydroquinone moiety, for the bond C_4-C_5 linking the benzoxazole and hydroquinone moieties, and for the bond C_5-N_6 (Table 1). The largest changes are demonstrated by the angles $C_1-C_2-C_4$, $C_4-C_2-O_3$ and $C_2-C_4-C_{1'}$ of the hydroquinone moiety. Energy of the transition state separating the enol and keto structures in the state S_1 is calculated to be 270 cm^{-1} (relatively to the energy of the enol structure with zero-point vibrational energy) that is in good correspondence with the experimental estimation of 310 cm^{-1} for jet-cooled molecules reported in [1].

Table 1

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

Parameter	S_0	S_1	Parameter	S_0	S_1	Parameter	S_0	S_1
C_1-C_2	1.393	1.403	$C_{12}-C_7$	1.398	1.404	$O_{13}-C_5-N_6$	114.6	114.0
C_2-C_4	1.418	1.457	$C_{12}-O_{13}$	1.363	1.365	$C_7-C_8-C_9$	117.1	117.3
$C_4-C_{1'}$	1.399	1.401	$O_{13}-C_5$	1.352	1.358	$C_8-C_9-C_{10}$	121.7	121.8
C_4-C_5	1.457	1.422	C_2-O_3	1.336	1.310	$C_9-C_{10}-C_{11}$	121.7	121.5
C_5-N_6	1.300	1.321	$C_1-C_2-C_4$	117.9	120.5	$C_{10}-C_{11}-C_{12}$	115.6	115.9
N_6-C_7	1.389	1.377	$C_2-C_4-C_5$	118.7	118.2	$C_{11}-C_{12}-C_7$	123.8	123.7
C_7-C_8	1.397	1.398	$C_4-C_5-N_6$	126.0	125.3	$C_{12}-C_7-C_8$	120.1	119.8
C_8-C_9	1.391	1.393	$C_5-N_6-C_7$	105.1	105.3	$C_4-C_2-O_3$	123.4	120.7
C_9-C_{10}	1.407	1.405	$N_6-C_7-C_{12}$	107.8	107.9	$C_2-C_4-C_{1'}$	120.7	118.4
$C_{10}-C_{11}$	1.393	1.397	$C_7-C_{12}-O_{13}$	107.5	107.8	$C_4-C_{1'}-C_{2'}$	121.4	121.1
$C_{11}-C_{12}$	1.388	1.384	$C_{12}-O_{13}-C_5$	105.0	104.9	-	-	-

The calculated value of energy of the 0-0 transition is 3.10 eV, which is larger by 0.13 eV than experimental value 2.97 eV obtained from the measurements of excitation spectra for molecules isolated in supersonic jets [1-3]. The modeled absorption spectrum demonstrates

good correspondence of the vibronic bandshape to experimental spectrum of BBHQ dissolved in non-polar solvent at room temperature (Fig. 2).

The time-independent calculations are performed assuming temperature 0 K (only vibrationless energy level is populated in the ground state) in order to simplify analysis. The lowest frequencies of molecular vibrations are calculated to be 23 and 47 cm^{-1} , the Boltzmann population ratios at room temperature are 0.9 and 0.8 correspondingly. The high thermal population leads to large number of transitions with significant intensities involving these states. Large intensity of transitions is found for the vibrations with calculated frequencies 123, 334, 474, 958 and 1598 cm^{-1} (Fig. 3). The modes 123, 334, 474 and 958 cm^{-1} in the excited state correspond to the vibrations 126, 330, 485 and 966 cm^{-1} in the ground state. Despite more noticeable Duschinsky rotation the mode 1598 cm^{-1} can be related to the vibration 1639 cm^{-1} in the ground state by the largest element of the matrix.

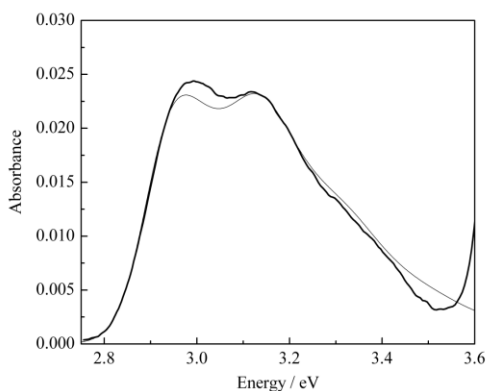


Fig. 2. Experimental absorption spectrum of BBHQ dissolved in CCl_4 (bold line) and spectra calculated with the time-independent method (thin line). The modeled spectrum is red-shifted by 0.2 eV in energy.

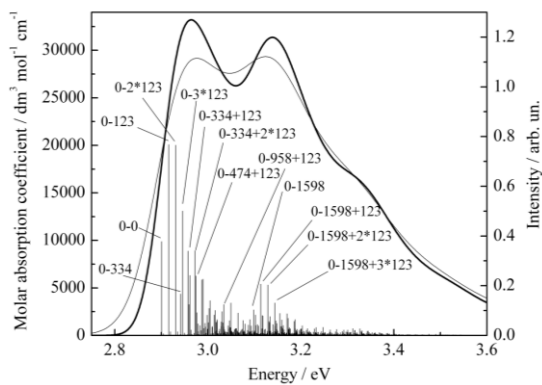


Fig. 3. Absorption spectrum modeled with the time-dependent method at room temperature (thin line) and time-independent method at temperature 0 K (solid line). The stick spectrum represents vibronic transitions. The spectra are red-shifted by 0.2 eV in energy.

The mode 123 cm^{-1} is an in-plane deformation vibration with the A_g symmetry that changes mostly the $C_4-C_5-N_6$ and $C_4-C_5-O_{13}$ angles (and the angles corresponding by the symmetry) modulating the distance between the oxygen and nitrogen atoms of the hydrogen bond, the experimental value of the frequency is 114 cm^{-1} [1,3]. The mode 334 cm^{-1} is an in-plane deformation vibration with the A_g symmetry that changes mostly the $C_2-C_4-C_5$ and $C_5-C_4-C_{1'}$ angles and also modulates the distance between the oxygen and nitrogen atoms of the hydrogen bond. The mode 474 cm^{-1} is an in-plane deformation vibration of the hydroquinone aromatic ring with the A_g symmetry. The mode 958 cm^{-1} is an in-plane deformation vibration of the oxazole rings with the A_g symmetry changing mostly the angle $O_{13}-C_5-N_6$. The mode 1598 cm^{-1} is an in-plane stretching vibration of the hydroquinone moiety with the A_g symmetry involving bonds C_2-C_4 , C_4-C_5 and C_4-O_3 .

4. Conclusions

Calculations of the vibronic structure of the S_0-S_1 absorption band of 2,5-bis(2-benzoxazolyl)hydroquinone assuming the harmonic vibrational movement of the nuclei obtained with the ω B97X-D3 density functional provide good agreement with the experimental spectra as in the case of a related compound 2-(2'-hydroxyphenyl)benzoxazole. Nevertheless, it is necessary to adjust the parameter of homogeneous broadening of the spectral lines of the vibronic transitions for better fit to experiment.

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