

Modeling of Vibronic Structure of Absorption Spectrum of 2-(2'-Hydroxyphenyl)benzoxazole

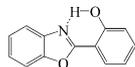
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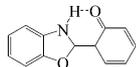
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Introduction

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-(2'-hydroxyphenyl)benzoxazole (HBO) 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 HBO molecule in the ground state is an enol form whereas a keto form has lower energy in the first excited state. In this study we consider application of TDDFT approach and harmonic approximation for vibronic states of the enol form of the molecule of HBO.



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, the B3LYP and ω B97X-D3 functionals. 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. 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] using the time-independent method [4-7]. The spectrum was modeled assuming inhomogeneous broadening by Gaussian function with the half width at half maximum of 0.06 eV and room temperature.

Approximations of the potential energy surface of the molecule in the excited state [8]:

Adiabatic Hessian (AH)

Adiabatic shift (AS)

Adiabatic shift with frequency alteration (ASF)

Vertical Hessian (VH)

Vertical gradient (VG)

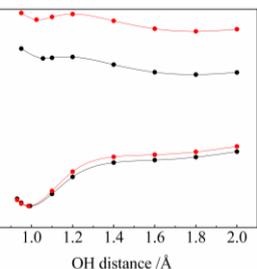
Vertical gradient with frequency alteration (VGF)

Conclusions

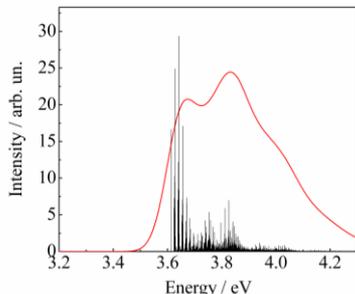
The ω B97X-D3 density functional is found to provide good correspondence of the modeled vibronic structure to the absorption band caused by the transitions to the first electronic excited state in the spectrum measured in solution at room temperature. The B3LYP density functional provides better agreement for the transition energy but substantially worse vibronic structure. The simplest vertical gradient model reproduces relative intensities of the main vibronic components observed in the absorption spectrum. The largest Huang-Rhys factors are found for normal vibrations with the calculated frequencies 123 cm^{-1} and 324 cm^{-1} (in-plane deformation that involves valence angles formed by the C-C bond linking the benzoxazole and phenol moieties and changes the distance between the O and N atoms forming the H-bond); 583 cm^{-1} (in-plane deformation that involves valence angles formed by the C-C bond linking the benzoxazole and phenol moieties); 984 cm^{-1} (in-plane deformation that involves the OCN angle in the oxazole ring) and 1652 cm^{-1} (a mode involving C=N stretch).

Acknowledgements

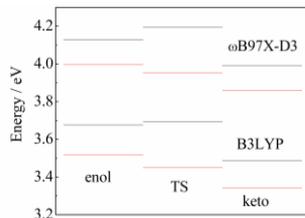
The authors are very grateful to Prof. Fabrizio Santoro and Dr. Javier Cerezo for providing a development version of the FCclasses3 code.



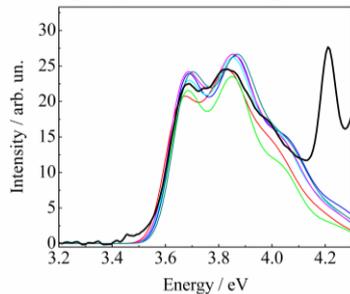
Calculated minimum potential energy curves along OH stretching coordinate of the HBO molecule in the ground (lower curves) and the first excited (upper curves) states. The black curves obtained with the B3LYP functional, the red curves – with the ω B97X-D3 functional.



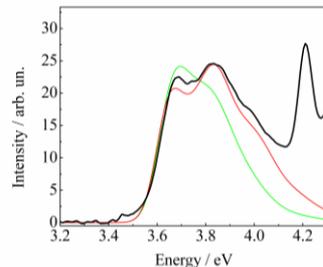
Vibronic transitions (stick spectrum) and absorption spectrum modeled with Gaussian profiles (red line). The spectra are calculated with the use of the AH approximation. Energy is red-shifted by 0.37 eV.



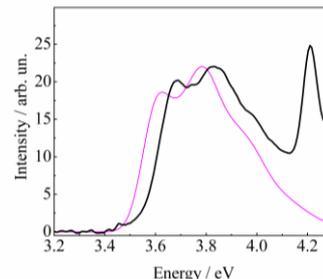
Calculated values of energy corresponding to the enol, keto forms and transition state (TS) in the first excited state of a molecule of HBO. Black lines denote potential energy, red lines denote energy including zero-point vibrational energy.



Absorption spectrum of HBO measured in CCl_4 solution at room temperature (black line) and modeled spectra obtained with the ω B97X-D3 functional using various approximations: AH, red-shifted by 0.37 eV (red line); AS, red-shifted by 0.48 eV (blue); ASF, red-shifted by 0.37 eV (cyan); VH, red-shifted by 0.38 eV (green); VG, red-shifted by 0.49 eV (magenta); VGF, red-shifted by 0.475 eV (dark cyan).



Absorption spectrum of HBO measured in CCl_4 solution at room temperature (black line) and modeled spectra obtained with the use of the AH approximation: calculated for an isolated molecule with the ω B97X-D3 functional (red line, red-shifted by 0.37 eV) and with the B3LYP functional (green line, blue-shifted by 0.16 eV).



Absorption spectrum of HBO measured in CCl_4 solution at room temperature (black line) and modeled spectra obtained with the ω B97X-D3 functional using the AH approximation and the value of adiabatic energy E_{ad} calculated with the B3LYP functional at the ω B97X-D3 geometry of the molecule (magenta, without energy shift).

References

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