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CALCULATIONS OF OPTICAL ABSORPTION AND FLUORESCENCE SPECTRA OF 2,5-DI-(2-BENZOXAZOLYL)PHENOL BY THE MRSF-TDDFT METHOD

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Abstract. The mixed-reference spin-flip time-dependent density functional theory method of calculations of energy, structure and vertical transition of molecules is found to provide relation of energy of the enol and keto structures in the first excited state that is consistent with the low intensity of fluorescence with normal Stokes shift in the spectrum of the compound 2,5-di-(2-benzoxazolyl)phenol in contrast to the results of the calculations with the time-dependent density functional theory methods. The calculated energies of the vertical electronic transitions are in good agreement with the positions of the maxima observed in the fluorescence spectra, but the model overestimates the energies of the expected maxima in the absorption spectrum.

Keywords: absorption spectra, luminescence, molecules, excited-state intramolecular proton transfer, density functional theory
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1. Introduction

2,5-di-(2-benzoxazolyl)phenol (DBP) (Fig. 1) is an organic compound known for several decades as an efficient luminescent substance featured by the photoinduced excited-state intramolecular proton transfer (ESIPT) [1]. Luminescence spectra of DBP in condensed phase consist of two components: weak emission with a normal Stokes shift overlapping with the absorption spectrum and strong band with an anomalously large Stokes shift (Fig. 2). The weak fluorescence is attributed to the enol structures I and III (see Fig. 1), the strong band is caused by transitions in the keto structure formed by ESIPT [1-4]. Cooled molecules of DBP isolated in supersonic jets exhibit only fluorescence with the large Stokes shift originating from the keto species II [3].

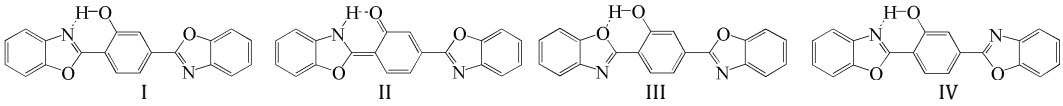

Fig. 1. Structures of the molecule of 2,5-di-(2-benzoxazolyl)phenol (DBP): I – enol structure with the intramolecular hydrogen bond OH…N; II – keto structure; III – enol structure with the intramolecular hydrogen bond OH…O; IV – enol structure with the intramolecular hydrogen bond OH…N and different orientation of the non-hydrogen-bonded benzoxazole moiety.

Time-dependent density functional theory (TDDFT) methods are computationally efficient and widely used to theoretically describe ESIPT in molecules [5]. In the case of DBP, TDDFT calculations with the B3LYP functional demonstrate good correspondence of the

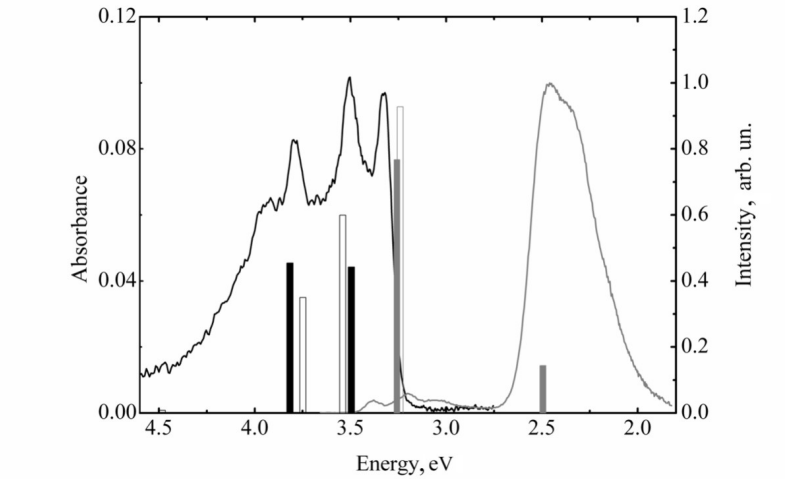

Fig. 2. Calculated vertical transitions (vertical bars) for various ground and excited-state structures of the molecule of DBP in comparison with the experimental absorption (black line) and luminescence spectra (grey line) of the DBP dissolved in CCl_4. Experimental spectra are taken from [4]. The vertical bars indicate the positions of vertical transitions calculated by the MRSF-TDDFT method using the DTCAM-VEE functional; their heights are proportional to the oscillator strengths. Filled bars represent the transitions of structures I and II, empty bars represent structure III. The energy of the transitions from the ground state structures (calculated absorption spectrum) is red-shifted by 0.33 eV.

vertical transitions to the bands observed in the spectra, but the theoretical consideration predicts the energy of the enol structure I to be about 0.11 eV lower than that of the keto structure II for an isolated molecule in the first excited state S_1 [4,6]. A similar relation has been found as a result of TDDFT calculations for the compound 2,5-bis(6-methyl-2-benzoxazolyl)phenol [7]. This energy relationship between the enol and keto structures implies that fluorescence with the normal Stokes shift should predominate, especially for cooled, isolated molecules where environmental effects are excluded. Such a theoretical expectation contradicts the experimental findings. Single-point evaluation of the energy with the B2PLYP functional, which includes double excitations, yields an opposite energy relation between the enol and keto structures for the geometry of molecular structures obtained by B3LYP calculations in the excited state [4], which is consistent with the experiment.

The mixed-reference spin-flip time-dependent density functional theory (MRSF-TDDFT) method introduced in 2018 [8] is a computationally efficient approach that partially includes doubly-excited configurations with analytical gradients implemented [9] and considered as a promising tool for modeling of excited states of molecules [10,11], although some limitations are reported [12]. In the present paper, we assess the relevance of the MRSF-TDDFT calculations for modeling absorption and luminescence spectra of DBP.

2. Calculations details

The calculations of structure, energy, and oscillator strength for vertical transitions were performed for isolated molecules using the MRSF-TDDFT method, with the DTCAM-VEE functional parameterized to reproduce vertical excitation energies for a set of medium-sized molecules, yielding a mean-averaged error of 0.218 eV within the MRSF-TDDFT approach [13,14]. The calculations were also performed using the DFT/TDDFT methods for the ground and excited states, employing the DTCAM-VEE and B3LYP functionals. All calculations were accomplished with the OpenQP software [15] using the 6-31G(d,p) basis set.

3. Results and discussion

In the ground state MRSF-TDDFT like conventional DFT methods does not yield a local minimum for the keto structure II, the lowest energy corresponds to the enol structure I with an intramolecular hydrogen bonding OH...N. There is another structure IV (see Fig. 1) formed by rotation of the non-hydrogen-bonded benzoxazole moiety, but the calculations shows that energy of this structure differs only by about 0.01 eV, some vibronic components attributed to the structure IV are observed only in high-resolution fluorescence excitation spectrum of jet-cooled molecules described in [3]. The structure II, which does not undergo the ESIPT, is predicted to be by 0.28 eV less stable than the structure I (Table 1). The DFT calculations with the B3LYP and DTCAM-VEE yield a close value of 0.27 eV.

Table 1. Calculated values of relative energy (E), energy of vertical transitions (ΔE), oscillator strength (f) for different structures of a DBP molecule in the ground (S_0) and first excited (S_1) states.

Structure	State	MRSF-TDDFT			B3LYP			DTCAM-VEE		
		E, eV	ΔE, eV	f	E, eV	ΔE, eV	f	E, eV	ΔE, eV	f
I(S_0)	S_0	0			0			0		
	S_1	3.83	3.83	0.88	3.44	3.44	1.14	3.75	3.75	1.11
	S_2	4.15	4.15	0.91	3.86	3.86	0.29	4.25	4.25	0.44
	S_3	4.90	4.90	0.00	4.16	4.16	0.01	4.82	4.82	0.02
I(S_1)	S_0	0.29			0.18			0.23		
	S_1	3.54	3.26	1.53	3.25	3.07	1.33	3.52	3.29	1.33
II(S_1)	S_0	0.88			0.71			0.76		
	S_1	3.37	2.49	0.29	3.36	2.66	0.28	3.61	2.85	0.35
III(S_0)	S_0	0.28			0.27			0.27		
	S_1	4.18	3.90	1.07	3.75	3.48	1.28	4.08	3.81	1.28
	S_2	4.41	4.13	0.78	4.19	3.92	0.18	4.56	4.30	0.29
	S_3	5.15	4.87	0.02	4.43	4.16	0.01	5.07	4.80	0.01
III(S_1)	S_0	0.61			0.47			0.53		
	S_1	3.85	3.24	3.24	3.54	3.07	1.48	3.82	3.29	1.51

In the first excited states S_1, the MRSF-TDDFT predicts the energy of the enol structure I to be larger than the energy of the structure II by about 0.17 eV (see Table 1), which qualitatively rationalizes the relation of the intensity of fluorescence bands with normal and anomalously large Stokes shifts. The TDDFT calculations yield an inverse relationship between the energy values for structures I and II; the differences are 0.11 eV for the B3LYP and 0.09 eV for the DTCAM-VEE functionals.

Calculated energy of the vertical transitions in the enol structure I and keto structure II as well as structure III demonstrates good correspondence to the maxima of fluorescence bands observed in the spectrum of DBP dissolved in CCl_4 while the energy of the vertical transition corresponding to the absorption is systematically overestimated by about 0.33 eV (see Fig. 2). The experimental absorption and fluorescence spectra of the solution demonstrate clear vibrational structure of the bands. The absorption spectrum comprises maxima at 3.33, 3.51, 3.79, and 3.94 eV. The weak fluorescence band with the normal Stokes shift demonstrates maxima at 3.02, 3.20, and 3.38 eV; the strong band assigned to the keto structure II exhibits vibronic components located at 2.46 and 2.36 eV. Attributing the vertical transitions to the largest

maxima in the spectra, the differences in energy calculated by the MRSF-TDDFT method and experimental values are 0.32 eV for the S_0-S_1 and 0.36 eV for the S_0-S_2 transitions in the enol structure I. For the luminescence spectrum, the differences are 0.06 eV for the transitions in the enol structure I and 0.03 eV for the keto structure II. The calculations do not take into account interaction with the solvent. Absorption spectrum of DPB in vapor at 490 K is reported in [3], where the energy of the corresponding maxima is about 3.64 and 3.94 eV; overestimations for these values are 0.19 and 0.21 eV. Adiabatic excitation energy (energy difference between minima in the ground and excited states) is calculated to be 3.54 eV for the enol structure I; the value is quite close to the energy of the 0-0 transition at 3.45 eV for jet-cooled molecules [3].

The TDDFT/B3LYP method underestimates the energy of the S_0-S_1 transition (-0.07 eV) while overestimates the energy of the S_0-S_2 transition (0.07 eV) in the absorption spectrum. For the fluorescence, the differences are -0.13 eV for structure I and 0.2 eV for structure II. The TDDFT calculations with the DTCAM-VEE functional predict energy deviations of 0.24 eV for the S_0-S_1 and 0.46 eV for the S_0-S_2 transitions in structure I. For the fluorescence spectrum overestimation, the values are 0.39 eV for the intense band and 0.09 eV for the weak band.

The energy of interaction between a molecule and solvent depends on the molecule's electronic state and varies with structure, causing shifts in energy levels. Evaluation of the solvent effects performed by DFT/TDDFT methods with the B3LYP functional and polarizable continuum model (PCM) for description of the solvent implemented in the GAMESS program [16] demonstrate that in CCl_4 the energy difference between structures I and II decreases from 0.27 to 0.25 eV in the ground state S_0 in comparison with the isolated molecule, the energy difference between the enol I and keto II structures changes by less than 0.01 eV in the first excited state S_1, considered absorption transitions are red-shifted by 0.10 eV for the S_0-S_1 and 0.03 eV for S_0-S_2. Estimation for fluorescence predicts shifts to lower energy by 0.07 eV for the transition in the keto structure II and 0.18 eV in the enol structure I.

In the ground state S_0, the maximum absolute differences in bond lengths between the structures I obtained by MRSF-TDDFT/DTCAM-VEE and DFT calculations are 0.011 Å for the B3LYP functional and 0.006 Å for the DTCAM-VEE functional; the maximum absolute differences in valence angles are 0.40° and 0.36°, respectively. The hydrogen bonding distance OH...N is shorter in the case of MRSF-TDDFT and equals 1.768 Å against 1.784 Å for DFT calculations with both functionals. In contrast to DFT methods, the MRSF-TDDFT method treats a ground state in the same way as excited states.

In the first excited state S_1, the maximum absolute differences in bond lengths between structures I obtained by the MRSF-TDDFT/DTCAM-VEE and TDDFT calculations are 0.011 Å for the B3LYP functional and 0.007 Å for the DTCAM-VEE functional; the maximum absolute differences in valence angles are 0.44° and 0.28°, respectively. The hydrogen bonding distance OH...N is shorter in the case of MRSF-TDDFT and equals 1.710 Å against 1.734 Å (B3LYP) and 1.722 Å (DTCAM-VEE) for TDDFT. For the keto structure II, the maximum absolute values are larger and reach 0.034 and 0.029 Å for the bond length, and 2.61° and 2.46° for the valence angles. The hydrogen bonding distance NH...O is calculated by MRSF-TDDFT to be 1.908 Å, while the values for the TDDFT methods are 1.780 Å (B3LYP) and 1.784 Å (DTCAM-VEE).

Single-point energy evaluations were performed using the MRSF-TDDFT method for the structures obtained by the DFT/TDDFT methods to clarify the significance of the differences in

geometric parameters obtained by the considered methods. In this case, the energy of structure I is larger than the energy of structure II by about 0.12 eV in the first excited state S_1. The value is about 30% lower than that obtained with the strict calculations, in which energy minima are found using the MRSF-TDDFT method. The values are close for structures calculated using TDDFT with the B3LYP and DTCAM-VEE functionals. A relatively small difference between the results of the accurate calculations and the energy evaluation for the structures obtained by the TDDFT method is due to the weak dependence of energy on the atomic coordinates in the vicinity of the excited-state minimum in the direction of the difference.

Calculations of vertical transitions performed with MRSF-TDDFT on the geometry obtained by the DFT/TDFT calculations yield differences less than 0.1 eV for fluorescence of the enol structure I and above 0.2 eV for the keto structure II, as expected for larger changes in geometrical parameters of the structures. The difference for the transitions corresponding to the absorption is less than 0.1 eV for DTCAM-VEE and less than 0.15 eV for B3LYP.

4. Conclusions

The mixed-reference spin-flip time-dependent density functional theory method is applied to the calculation of the structure and vertical electronic transitions of the molecular species of 2,5-di-(2-benzoxazolyl)phenol, responsible for the emission bands observed in the fluorescence spectrum. The MRSF-TDDFT method predicts the energy relationship between the enol and keto structures in the excited state, which is consistent with the low intensity of the fluorescence band with the normal Stokes shift in the high-frequency region of the spectrum. The calculated energies of the vertical electronic transitions are in good agreement with the positions of the maxima observed in the fluorescence spectra, but the model overestimates the energies of the expected maxima in the absorption spectrum. Energy of motion of nuclei should be taken into account for more accurate modeling of the absorption and fluorescence spectra; however, in the case of the considered molecule exhibiting the excited-state intramolecular proton transfer, the relevance of the simple model of harmonic vibrations is uncertain, and for the keto structure, there is no local energy minimum in the ground state. The MRSF-TDDFT method, which provides the correct energy relationship between the enol and keto structures in the excited state for a DBP molecule, is expected to improve the description of potential energy surfaces and emission spectra for ESIPT-based fluorescent compounds at a reasonable computational cost.

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References

1. Kauffman, J. M., & Bajwa, G. S. (1993). Synthesis and photophysical properties of fluorescent 2,5-dibenzoxazolylphenoles and related compounds with excited state proton transfer. *J. Heterocyclic Chem., 30,* 1613-1622.
2. Tarkka, R. M., & Jenekhe, S. A. (1996). Effects of electron delocalization on intramolecular proton transfer. *Chem. Phys. Lett.*, 260, 533-538.
3. Vdovin, A., Sepioł, J., Jasny, J., Kauffman, J. M., & Mordziński, A. (1998). Excited state proton transfer in jet-cooled 2,5-di-(2-benzoxazolyl)phenol. *Chem. Phys. Lett., 296*, 557-565.
4. Syetov, Y. (2017). Optical absorption and luminescence spectra of 2,5-di-(2-benzoxazolyl) phenol in the solid state. *Ukr. J. Phys. Opt., 18*(3), 139-142.
5. Jankowska, J., & Sobolewski, A. L. (2021). Modern Theoretical Approaches to Modeling the Excited-State Intramolecular Proton Transfer: An Overview. *Molecules, 26*(17), 5140.
6. Syetov, Y. (2013). TDDFT Calculations of Electronic Spectra of Benzoxazoles Undergoing Excited State Proton Transfer. *J. Fluoresc., 23,* 689-696.

7. Dobkowski, J., Kijak, M., Gawinkowski, S., Karpiuk, E., Pietrzak, M., Sazanovich, I. V., & Waluk, J. (2022). Solving the Puzzle of Unusual Excited-State Proton Transfer in 2,5-Bis(6-methyl-2-benzoxazolyl)phenol. *J. Phys. Chem. A, 126,* 1823−1836.
8. Lee, S., Filatov, M., Lee, S., & Choi, C. H. (2018). Eliminating Spin-Contamination of Spin-Flip Time-Dependent Density Functional Theory Within Linear Response Formalism by the Use of Zeroth-Order Mixed-Reference (MR) Reduced Density Matrix. *J. Chem. Phys., 149*(10), Article 104101.
9. Lee S., Kim E. E., Nakata H., Lee S., & Choi C. H. (2019). Efficient Implementations of Analytic Energy Gradient for Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT). *J. Chem. Phys., 150*(18), 184111.
10. Park, W., Komarov, K., Lee, S., & Choi, C. H. (2023). Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory: Multireference Advantages with the Practicality of Linear Response Theory. *J. Phys. Chem. Lett., 14*(39), 8896-8908.
11. Lee, S., Park, W., & Choi, C.H. (2025). Expanding Horizons in Quantum Chemical Studies: The Versatile Power of MRSF-TDDFT. *Acc. Chem. Res., 58*(2), 208−217.
12. Janoš, J., Orr-Ewing, A. J., & Curchod, B. F. E., & Slavíček, P. (2026). *Limitations of MRSF-TDDFT for Applications in Photochemistry.* arXiv:2604.09230. https://doi.org/10.48550/arXiv.2604.09230
13. Okuno, K., Shigeta, Y., Kishi, R., Miyasaka, H., & Nakano, M. (2012). Tuned CAM-B3LYP functional in the time-dependent density functional theory scheme for excitation energies and properties of diarylethene derivatives. *J. Photochem. Photobiol. A, 235*(29), 29-34.
14. Komarov, K., Park, W., Lee, S., Huix-Rotllant, M., & Choi, C. H. (2023). Doubly Tuned Exchange–Correlation Functionals for Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory. *J. Chem. Theory Comput. 19,* 7671-7684.
15. Mironov, V., Komarov, K., Li J, Gerasimov, I., Mazaheri, M., Park, W., Lashkaripour, A., Oh, M., Nakata, H., Ishimura, K., Huix-Rotllant, M., Lee, S., & Choi C. H. (2024). OpenQP: A Quantum Chemical Platform Featuring MRSF-TDDFT with an Emphasis on Open-source Ecosystem. *J. Chemical Theory Comput., 20*(21), 9464−9477.
16. Barca, G. M. J., Bertoni, C., Carrington, L., Datta, D., De Silva, N., Deustua, J. E., Fedorov, D. G., Gour, J. R., Gunina, A. O., Guidez, E., Harville, T., Irle, S., Ivanic, J., Kowalski, K., Leang, S. S., Li, H., Li, W., Lutz, J. J., Magoulas, I., Mato, J., Mironov, V., Nakata, H., Pham, B. Q., Piecuch, P., Poole, D., Pruitt, S. R., Rendell, A. P., Roskop, L. B., Ruedenberg, K., Sattasathuchana, T., Schmidt, M. W., Shen, J., Slipchenko, L., Sosonkina, M., Sundriyal, V., Tiwari, A., Galvez Vallejo, J. L., Westheimer, B., Wloch, M., Xu, P., Zahariev, F., & Gordon, M. S. (2020). Recent developments in the general atomic and molecular electronic structure system. *The Journal of Chemical Physics, 152*(15), 154102.

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Анотація. Виявлено, що результати обчислення енергії, структури та вертикальних переходів молекул на основі змішано-референтної спін-фліп часово-залежної теорії функціоналу густини передбачають співвідношення енергій енольної та кето-структур у першому збудженому стані, яке відповідає низькій інтенсивності флуоресценції з нормальним стоксовим зсувом у спектрі сполуки 2,5-ді-(2-бензоксазоліл)фенолу, на відміну від результатів розрахунків із використанням методів часово-залежної теорії функціоналу густини. Обчислені енергії вертикальних електронних переходів добре узгоджуються з положеннями максимумів, що спостерігаються в спектрах флуоресценції, проте модель переоцінює енергію очікуваних максимумів у спектрі поглинання.

Ключові слова: спектри поглинання, люмінесценція, молекули, внутрішньомолекулярне фотоперенесення протона, теорія функціоналу густини