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MODELING OF INFRARED SPECTRUM OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE WITH A COMPOSITE DFT METHOD

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Infrared spectrum of a molecule of 2-(2'-hydroxyphenyl)benzoxazole is modeled with composite calculations including density functional theory method, dispersion correction, geometrical counterpoise correction and adjustment of the basis set. It is found that the composite method noticeably improves agreement with the experimental spectrum in comparison with the results obtained with the density functional method using a relatively small basis set. The composite method reproduces the bands observed in the spectrum at 685 and 708 cm^{-1} which are assigned to the vibrations involving out-of-plane motion of the bond OH.

Keywords: modeling, hydrogen bond, infrared spectra, density functional theory, molecular vibration.

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1. Introduction

Density functional theory (DFT) methods are widely used nowadays for calculations of properties of molecules and solids [1]. One of the most popular density functional used for the calculations of vibrations of organic molecules is a hybrid functional B3LYP [2]. Any semi-local (hybrid) density functional does not include dispersion interaction (London dispersion forces) caused by long-range correlation effect. The London dispersion forces are significant in non-covalent bonding. The DFT calculations are also affected by using a finite basis set [3]. A composite method B3LYP-3c proposed in [4] includes empirical atom-pairwise and atom-triplewise dispersion corrections (D3) [5,6], geometrical counterpoise correction scheme (gCP) [7] and basis set modification [3]. The composite method is found to be well suited for general IR spectra calculations [4].

2-(2'-hydroxyphenyl)benzoxazole (HBO, Fig. 1) is an organic compound with an intramolecular hydrogen bond and demonstrates excited state proton transfer [8]. DFT calculations of infrared absorption spectra of HBO performed with the B3LYP functional demonstrate good correspondence to the experimental spectrum except the bands attributed to the out-of-plane vibrations that involve the OH bond. Calculated frequencies and eigenvectors of these vibrations are found to be dependent on the used basis set [9].

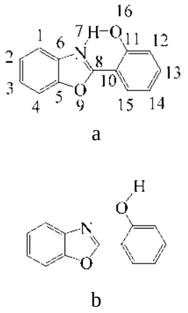
In the present paper we analyze the performance of the combined B3LYP-3c method in modeling of IR spectra of the H-bonded molecule.

2. Calculations details

The calculations of structure, energy and vibrations were performed for an isolated molecule using the ORCA software package [10,11,13] with the B3LYP functional [2], def2-SVP basis set [12] and with the composite B3LYP-3c method [3-7]. The vibrations were calculated in harmonic approximation, scaling factor of 0.975 was used for the frequencies to compare the modeled spectra with experimental data. The spectra were modeled assuming the Gaussian bandshape with FWHM of 7 cm^{-1} for the transitions.

3. Results and discussion

Geometrical parameters of the molecular structure around the hydrogen bond are presented in Table 1. Energy of the hydrogen bond is estimated as energy difference between the hydrogen-bonded enol structure (Fig. 1a) and non-hydrogen-bonded enol structure (Fig. 1b). The lowest energy of the molecule in the ground state corresponds to the H-bonded enol structure. The composite B3LYP-3c method predicts larger distance and lower energy for the OH…N hydrogen bond in comparison with the results obtained with the B3LYP/def2-SVP calculations (1.816 and 1.754 Å, 0.50 and 0.56 eV). Calculations performed with the separated corrections demonstrate that the empirical dispersion correction D3 leads to shortening of the N…H distance and increasing of the energy, while the basis set modification and geometrical counterpoise correction (gCP) oppositely increase the distance and decrease the energy.



a

b

Fig. 1. Enol structures of an HBO molecule: (a) a structure with an intramolecular hydrogen bond, numbers denote positions of the atoms; (b) a structure without a hydrogen bond.

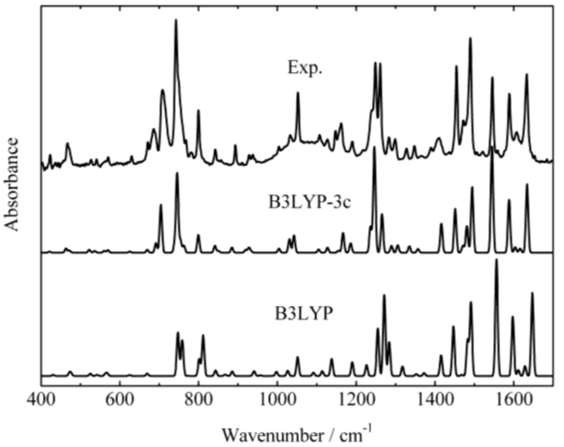


Fig. 2. Experimental IR spectrum in the range 400-1700 cm^{-1} of HBO (Exp.) measured in KBr pellet [9] and the spectra modeled with the composite B3LYP-3c and B3LYP/def2-SVP methods.

The composite B3LYP-3c method noticeably improves agreement of the modeled IR absorption spectrum with the experimental data in the regions 670-790 and 1270-1370 cm^{-1} against the B3LYP/def2-SVP approach (Fig. 2). In the range 670-790 cm^{-1} the composite method reproduces medium broad band at 685 cm^{-1} (scaled calculated value is 692 cm^{-1}) and strong broad band at 708 cm^{-1} (calculated value is 704 cm^{-1}). In the range 1270-1370 cm^{-1} B3LYP-3c method provides better agreement in intensity and position of the bands at 1283, 1298, 1328, 1348 cm^{-1}. The calculated frequencies are 1290, 1305, 1335, 1357 cm^{-1} for the B3LYP-3c method and 1284, 1318, 1353, 1372 cm^{-1} for the B3LYP/def2-SVP approach.

Table 1

Calculated geometrical parameters (bond length, Å; angle, degree) and energy of the hydrogen bond of the molecule of HBO obtained with the B3LYP/def2-SVP method involving dispersion correction (D3), geometrical counterpoise correction (gCP) and modified basis set (def2-mSVP) (see Fig. 1 for atom numbers notation)

Parameter	B3LYP/ def2-SVP	B3LYP–D3/def2-SVP	B3LYP–gCP/def2-SVP	B3LYP–D3-gCP/def2-SVP	B3LYP/ def2-mSVP	B3LYP–D3/def2-mSVP	B3LYP–gCP/def2-mSVP	B3LYP–3c
Energy / eV	0.56	0.58	0.51	0.53	0.53	0.55	0.51	0.50
C_8-N_7	1.310	1.313	1.311	1.313	1.310	1.311	1.312	1.312
C_8-C_{10}	1.448	1.452	1.445	1.452	1.446	1.443	1.453	1.450
C_{10}-C_{11}	1.426	1.430	1.425	1.430	1.422	1.421	1.427	1.426
C_{11}-O_{16}	1.335	1.339	1.334	1.339	1.343	1.342	1.349	1.348
O_{16}-H	0.993	0.995	0.993	0.995	0.994	0.995	0.998	0.999
N_7-H	1.754	1.784	1.744	1.784	1.785	1.775	1.827	1.816

N_7-C_8-C_{10}	126.1	126.3	126.1	126.3	126.3	126.4	126.5	126.5
C_8-C_{10}-C_{11}	118.6	118.8	118.5	118.8	119.0	118.9	119.3	119.2
C_{10}-C_{11}-O_{16}	122.7	123.0	122.6	123.0	123.1	123.0	123.3	123.5
C_{11}-O_{16}-H	108.9	109.2	108.8	109.2	108.9	108.8	109.5	109.4

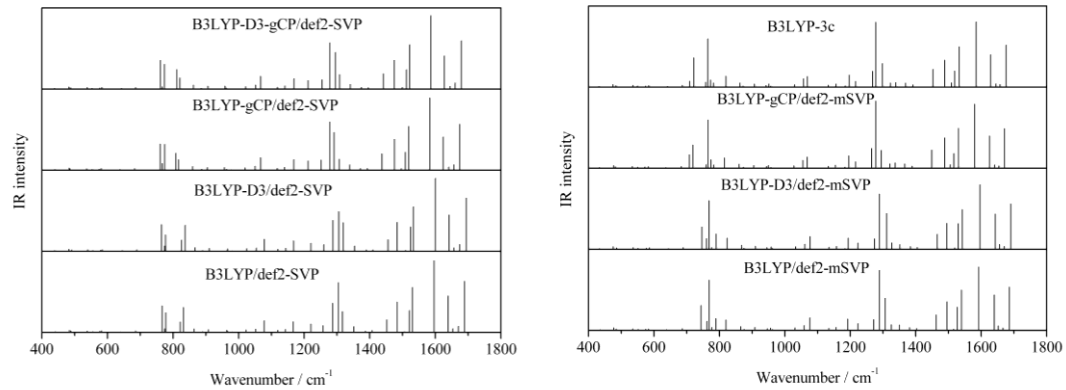


Fig. 3. IR spectrum of a molecule of HBO calculated with the B3LYP/def2-SVP method involving dispersion correction (D3), geometrical counterpoise correction (gCP) and the modified basis set (def2-mSVP).

Separated usage of the corrections reveals that inclusion of the D3 dispersion does not affect the modeled IR spectrum and the overall improvement is provided by both the basis set modification and the gCP basis set superposition error correction (Fig 3).

The vibrations with calculated frequencies 692 cm^{-1} and 704 cm^{-1} (B3LYP-3c) are modes with significant contribution of the torsion motion of the O-H bond and can be approximately described as combination of the OH bond torsion, out-of-plane vibration 4 of the phenol aromatic ring and vibration 11 of the benzoxazole moiety according to Varsanyi's notation [14]. The two modes differ in relation of phases between the OH torsion and aromatic rings vibrations. The B3LYP/def2-SVP method yields modes 704 and 747 cm^{-1} where the OH torsion motion contributes less than in the case of results of the B3LYP-3c calculations.

In the frequency range 1270-1370 cm^{-1} the B3LYP/def2-SVP method yields the mode 1284 cm^{-1} which differs in eigenvector from the closest vibration obtained with the B3LYP-3c calculations, whereas other modes 1318, 1353 and 1372 are similar. The mode with calculated frequency 1290 cm^{-1} is mostly vibration 3 (according to Varsanyi notation for vibrations of benzene derivatives [14]) of benzoxazole moiety with the contribution of the stretching of the C_{11}-O_{16} bond in the phenol. The mode 1305 cm^{-1} is vibration 3 of the phenol ring combined with stretching of the C_{11}-O_{16} bond in the phenol moiety, stretching of bonds in the oxazole ring and stretching of the C_8-C_{10} bond between the benzoxazole and phenol fragments. The modes 1335 and 1357 cm^{-1} can be approximately described as vibration 15 of the aromatic rings mixed with stretching of the bonds in the oxazole ring.

4. Conclusions

Infrared spectrum of 2-(2'-hydroxyphenyl)benzoxazole, a molecule with internal hydrogen bond, is modeled with the combined B3LYP-3c method that adds dispersion correction, geometrical counterpoise correction and adjustment of the basis set to the density functional theory approach. It is shown that the composite method improves agreement with the experimental spectrum for the bands related to the modes involving torsion of the OH bond. Using small basis set in the composite method allows calculations for large molecules regarding required computational resources.

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