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CALCULATIONS OF INFRARED SPECTRA OF BENZOXAZOLES EXHIBITING EXCITED-STATE PROTON TRANSFER BY A COMPOSITE METHOD

Y. SYETOV

Department of Experimental and Theoretical Physics, Oles Honchar Dnipro National University, 72 Nauky Ave., Dnipro, 49045, Ukraine. e-mail: setov2003@yahoo.com

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Abstract. Infrared spectra of 2-(2'-hydroxyphenyl)benzoxazole, 2,5-di-(2-benzoxazolyl)phenol and 2,5-bis(2-benzoxazolyl)hydroquinone are calculated by the composite method B3LYP-3c. The calculated frequencies and intensities are in good agreement with the experimental values, including the region of torsional vibrations of the bonds OH, which is not reproduced well by common density functional theory methods. The bands in the region are assigned to OH torsion modes, CH out-of-plane bending vibrations, and torsions of the aromatic and oxazole rings.

Keywords: infrared spectra, molecules, density functional theory, hydrogen bond.
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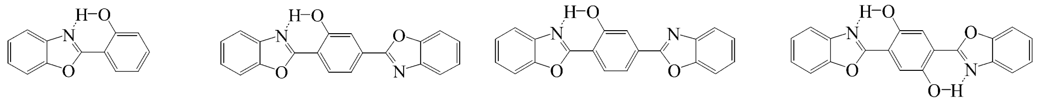
1. Introduction

Some organic molecules with hydrogen bonding OH…N between their fragments can demonstrate photochemical reaction of excited-state intramolecular proton transfer. Such substances are considered to be suitable for optoelectronic applications [1]. In molecules of 2-(2'-hydroxyphenyl)benzoxazole (HBO), 2,5-di-(2-benzoxazolyl)phenol (DBP), and 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ), the nitrogen atom belongs to the benzoxazole moiety. The molecules of the benzoxazoles form enol structures in the ground state (Fig. 1). In the case of DBP, there are two possible enol structures with close values of energy (structure I and structure II in Fig. 1b) [2].



a) b) c)

Fig. 1. Enol structures of 2-(2'-hydroxyphenyl)benzoxazole (HBO) (a), 2,5-di-(2-benzoxazolyl)phenol (DBP) (b) and 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) (c).

Density functional theory (DFT) calculations of infrared absorption spectra of HBO, DBP, and BBHQ performed with the B3LYP functional demonstrate good correspondence to the experimental spectrum in the range 400-1700 cm^{-1}, except the region 670-780 cm^{-1}, which comprises OH torsion modes, CH out-of-plane bending vibrations, and torsions of the aromatic and oxazole rings. Calculated frequencies and eigenvectors of the vibrations in this region are found to be dependent on the basis set and density functional used [2]. The hybrid

B3LYP functional, like many others, does not include dispersion interaction caused by the long-range correlation effect, which is significant in non-covalent bonding. Using a finite basis set introduces additional errors into DFT calculations; however, basis-set-dependent errors can compensate for functional inaccuracies [3].

A "composite" method B3LYP-3c, well-suited for general IR spectra calculations, has been proposed in [4], which includes three corrections: empirical atom-pairwise and triplewise dispersion correction (D3) [5,6], geometrical counterpoise correction scheme (gCP) [7], and a specific basis set [3]. The basis set is a relatively small double-zeta set with adjusted parameters that, in combination with the additive parameterized corrections, provide computational efficiency of the composite method.

In this paper, we assess the performance of the composite B3LYP-3c method for calculating the IR spectra of H-bonded molecules that exhibit excited-state intramolecular proton transfer.

2. Calculations details

The calculations of structure, energy, and vibrations were performed for isolated molecules using the ORCA software package [8-10] with the B3LYP functional [11], triple-zeta def2-TZVP and def2-TZVPD basis sets [12], and with the composite B3LYP-3c method [3-7].

The vibrations were calculated in the harmonic approximation using molecular symmetry, and scaling factors were applied to the frequencies to compare the modeled spectra with experimental data. The scaling factors are 0.975 for the B3LYP-3c and 0.98 for the B3LYP/triple-zeta basis set calculations. The spectra were modeled assuming the Gaussian bandshape with FWHM of 7 cm^{-1} for the transitions.

Comparison of the eigenvectors of normal modes calculated with different methods was done with the linear Duschinsky transformation using the FCclasses program [13,14].

3. Results and discussion

In the region above 1700 cm^{-1}, IR spectra of the benzoxazoles demonstrate a broad band in the range 3000–3600 cm^{-1} [2] which overlapped with the bands of stretching vibrations of CH bonds. The broad band is specific for infrared spectra of H-bonded systems [15]. Molecules of HBO, DBP, and BBHQ are planar; the symmetry of the structure of HBO and DBP is C_s, whereas a molecule of BBHQ belongs to the C_{2h} symmetry group. An isolated molecule of HBO demonstrates 69 normal modes classified as 47A' + 22A'', 105 modes of DBP are 71A' + 34A'', and 108 modes of BBHQ are $37A_g + 17B_g + 18A_u + 36B_u$. In the region below 1700 cm^{-1}, there are 60 fundamental vibrations in the HBO molecule (Table 1), 93 in the DBP molecule, and 96 in the BBHQ molecule.

As the Duschinsky transformation reveals, the normal vibration eigenvectors obtained with the BLYP-3c approach for a molecule of HBO are similar to the eigenvectors calculated with the B3LYP/def2-TZVP method, which exploits a more extended triple-zeta basis set (see Table 1). Only two modes with scaled frequencies 928 and 933 cm^{-1} change their order, when the frequencies of the similar vibrations yielded by the B3LYP/def2-TZVP method are 934 and 933 cm^{-1}. For the triple–zeta basis set with diffuse functions def2-TZVPD, the modes 919 and 926 cm^{-1} relate to the modes 935 and 934 cm^{-1}, and a noticeable difference of eigenvectors appears in the range 690-760 cm^{-1} (see Table 1). Changes in the order of frequencies are found upon addition of the diffuse function as well (comparison of the results obtained with the use of the def2-TZVP and def2-TZVPD basis sets) for these modes: the vibrations 916, 933, and 934 cm^{-1} (def2-TZVP) correspond to the vibrations 935, 955, and 934 cm^{-1} (def2-TZVPD). In the region below 1700 cm^{-1}, which does not include CH and OH stretching vibrations, the difference in scaled frequency for B3LYP-3c and B3LYP/def2-TZVP methods does not exceed 15 cm^{-1} except for the OH torsion mode 704 cm^{-1}, when the difference is about 33 cm^{-1}. These values are less than the maximum difference of the scaled frequencies obtained by B3LYP/def2-TZVP and B3LYP/def2-TZVPD calculations when the value is about 36 cm^{-1}.

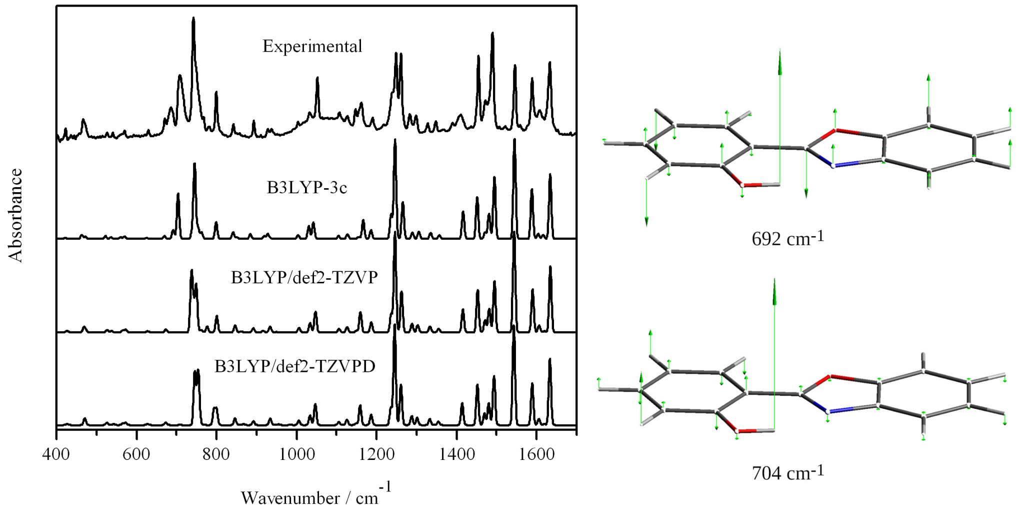
Table 1. Calculated scaled frequencies (ν, cm^{-1}), IR intensity (I, arb. un.), frequencies derived from the experimental IR spectrum [2] (Exp., cm^{-1}) of the vibrations of a molecule of HBO in the region below 1700 cm^{-1} along with the largest squared elements of the Duschinsky rotation matrix J^2_{nm} for the normal mode *n* calculated by the B3LYP-3c method and normal mode *m* calculated by the B3LYP/def2-TZVP or B3LYP/def2-TZVPD methods.

Mode	B3LYP-3c		B3LYP/ def2-TZVP		B3LYP/ def2-TZVPD		Exp.	B3LYP/ def2-TZVP		B3LYP/ def2-TZVPD	
n	ν	I	ν	I	ν	I	ν	*m*	J^2_{nm}	*m*	J^2_{nm}
1	2	3	4	5	6	7	8	9	10	11	12
1	58	0.25	59	0.12	60	0.15	-	1	0.97	1	0.99
2	64	0.65	64	0.79	65	0.77	-	2	0.97	2	0.99
3	117	0.69	117	0.82	116	0.84	-	3	1.00	3	1.00
4	156	0.07	158	0.04	159	0.02	-	4	1.00	4	1.00
5	241	0.02	242	0.04	242	0.04	-	5	1.00	5	1.00
6	258	0	260	0	261	0	-	6	1.00	6	1.00
7	274	1.03	273	1.14	273	1.22	-	7	1.00	7	1.00
8	311	2.69	311	2.69	311	2.72	-	8	1.00	8	1.00
9	330	0.04	333	0.11	334	0.09	-	9	1.00	9	1.00
10	421	1.69	426	2.38	426	2.31	423	10	1.00	10	1.00
11	463	6.38	468	7.78	470	7.89	457	11	1.00	11	1.00
12	472	3.33	473	3.4	472	3.37	467	12	1.00	12	1.00
13	522	4.47	526	3.77	526	3.91	527	13	1.00	13	1.00
14	536	2.67	537	2.04	543	1.76	540	14	1.00	14	1.00
15	560	2.78	565	2.69	565	2.65	563	15	1.00	15	1.00
16	570	3.84	573	4.33	573	4.17	570	16	1.00	16	1.00
17	573	0.00	577	0.01	581	0.00	-	17	1.00	17	1.00
18	625	1.76	627	1.74	627	1.82	630	18	1.00	18	1.00
19	670	4.37	673	4.59	673	4.48	671	19	0.86	19	0.85
20	692	14.51	702	0.34	708	0.08	685	20	0.82	20	0.49
21	704	72.36	737	92.37	746	85.43	708	21	0.95	22	0.80
22	739	12.03	743	36.91	754	79.71	-	22	0.90	21	0.64
23	745	119.28	750	73.99	757	14.14	743	23	0.93	23	0.83
24	754	17.7	762	3.77	767	0.68	748	24	0.93	24	0.75
25	763	10.52	776	9.06	794	25.28	761	25	1.00	25	1.00
26	799	27.06	801	26.35	800	25.43	799	26	1.00	26	1.00

1	2	3	4	5	6	7	8	9	10	11	12
27	841	10.44	846	11.03	846	10.97	842	27	0.99	27	0.98
28	848	0.3	852	0.17	856	0.2	-	28	0.98	28	0.98
29	851	2.44	862	1.52	867	1.64	857	29	1.00	29	1.00
30	884	7.68	892	6.5	892	6.2	893	30	1.00	30	1.00
31	919	4.22	916	2.58	934	8.3	910	31	1.00	32	1.00
32	928	7.54	933	1.25	935	2.93	928	33	0.81	31	1.00
33	933	1.95	934	8.18	955	1.29	937	32	0.99	33	1.00
34	958	0.02	944	0.02	978	0	943	34	0.81	34	1.00
35	960	0.07	949	0.42	985	0.16	951	35	1.00	35	1.00
36	1004	6.13	1006	7.04	1006	7.06	1004	36	0.94	36	0.94
37	1031	20.59	1034	14.86	1034	15.74	1033	37	0.94	37	0.94
38	1042	26.05	1047	33.62	1047	33.9	1052	38	1.00	38	1.00
39	1105	4.81	1106	5.53	1106	5.38	1107	39	1.00	39	1.00
40	1127	7.62	1126	8.18	1126	8.94	1127	40	1.00	40	1.00
41	1155	2.96	1150	2.65	1149	2.75	1147	41	1.00	41	0.99
42	1167	29.83	1160	32.58	1159	31.78	1161	42	0.99	42	0.99
43	1186	14.27	1187	16.35	1186	16.88	1190	43	1.00	43	1.00
44	1236	39.34	1236	29.67	1236	28.02	1239	44	1.00	44	1.00
45	1246	159.91	1246	160.88	1245	161.5	1249	45	0.99	45	0.99
46	1266	58.26	1262	65.43	1261	65.06	1261	46	0.98	46	0.97
47	1290	10.45	1289	14.1	1288	14.92	1283	47	0.98	47	0.97
48	1305	11.38	1303	11.75	1301	11.64	1299	48	0.99	48	0.99
49	1335	9.75	1333	9.53	1333	9.61	1328	49	1.00	49	1.00
50	1357	5.73	1355	5.84	1354	5.78	1348	50	1.00	50	1.00
51	1416	43.85	1416	36.93	1414	35.07	1410	51	1.00	51	1.00
52	1451	66.51	1453	67.8	1452	64.43	1455	52	0.97	52	0.97
53	1471	10.89	1471	19.43	1470	18.99	1472	53	0.97	53	0.97
54	1481	40.2	1481	38.27	1480	34.8	-	54	0.99	54	0.99
55	1495	99.33	1495	81.81	1494	79.12	1490	55	1.00	55	1.00
56	1545	160.85	1544	160.95	1543	160.47	1546	56	0.99	56	0.99
57	1588	80.09	1590	68.92	1589	67.25	1589	57	0.98	57	0.98
58	1604	8.37	1606	10.82	1605	10.23	1607	58	0.98	58	0.98
59	1616	6.24	1619	1.93	1619	2.03	1617	59	0.99	59	0.99
60	1634	103.49	1634	105.67	1633	106.48	1633	60	1.00	60	1.00

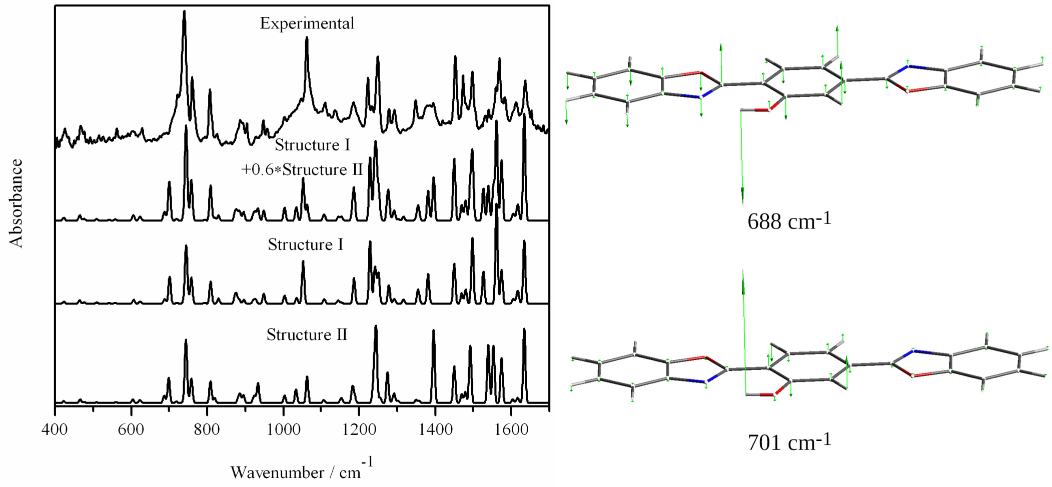
In the range 670-780 cm^{-1}, the B3LYP-3c method predicts the vibrations with frequencies 670, 692, 704, 739, 745, 754, and 763 cm^{-1} for the molecule of HBO. The modes with similar eigenvectors, calculated with the B3LYP/def2-TZVP method, exhibit frequencies of 673, 702, 737, 743, 750, 761, and 776 cm^{-1}. Comparison with the experimental spectrum demonstrates that the spectral pattern predicted by the B3LYP-3c method agrees better with the bands observed at 671, 685, 708, 743, 768, and 780 cm^{-1} (Fig. 2a), reproducing the bands at 685 and 708 cm^{-1} in particular. The vibrations with calculated frequencies 692 and 704 cm^{-1} (B3LYP-3c) are modes with significant contribution of the torsion motion of the bond OH (Fig. 2b) and can be approximately described as combination of the OH bond torsion, out-of-plane motion of the phenol aromatic ring that can be considered as vibration

4 according to Varsanyi’s notation for vibrations of benzene derivatives [16], and a vibration of the benzoxazole moiety which can be attributed to Varsanyi’s mode 11. The two vibrations with frequencies 692 and 704 cm^{-1} differ in relation to the phases between the OH torsion and aromatic rings vibrations (see Fig. 2b). The mode 670 cm^{-1} is an in-plane bending vibration of both the aromatic rings that can be described as Varsanyi’s mode 6a. The modes with calculated frequencies 739, 745, 754, and 763 cm^{-1} involve out-of-plane bending vibrations of CH bonds, torsion of the benzoxazole and phenol moieties, with a smaller contribution of the OH torsion.



a) b)

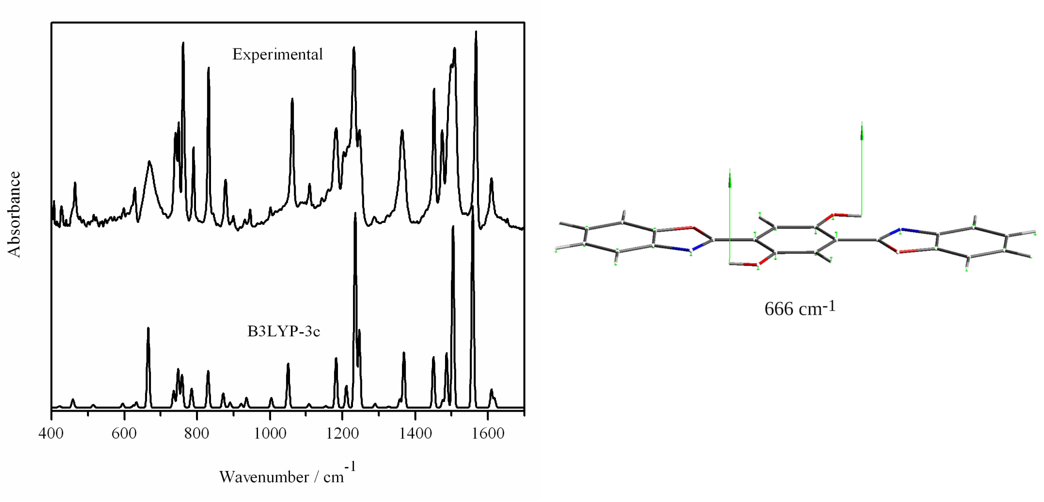
Fig. 2. (a) The IR spectrum in the range 400-1700 cm^{-1} of an isolated molecule of HBO modelled with the B3LYP-3c, B3LYP/def2-TZVP, and B3LYP/def2-TZVPD methods, along with the experimental spectrum of HBO measured in KBr pellets [2]. (b) Atom displacement in the calculated normal vibrations with a significant contribution of the OH bond torsion.



a) b)

Fig. 3. (a) The IR spectrum in the range 400-1700 cm^{-1} of an isolated molecule of DBP modelled with the composite B3LYP-3c method for structure I and structure II, along with the total spectrum. The experimental spectrum [2] is measured in KBr pellets. (b) Atom displacement in the calculated normal vibrations with a significant contribution of the OH bond torsion.

A molecule of DBP comprises a non-hydrogen-bonded benzoxazole moiety, and there are two enol structures I and II that differ in energy by about 0.01 eV according to the B3LYP-3c calculations; the value is close to the number reported in [2]. The energy difference implies that the equilibrium relative number of structures is about 0.6 and the total modeled IR spectrum obtained by adding the spectra of the structure I and structure II with the corresponding weight demonstrates good agreement with the experimental spectrum (Fig. 3a). The calculations predict the vibrations with frequencies 688, 692, 701, 720, 739, 744, 749, 758, 760 cm^{-1} for structure I of DBP in the range 670–780 cm^{-1}. The bands at 689, 707, 722, 740, and 760 cm^{-1} can be distinguished in the experimental spectrum. The normal modes 688 and 701 cm^{-1} are vibrations where the OH torsion is significant (Fig. 3b). These two modes involve CH bending 11, torsion of the phenol ring 4 (Varsanyi's notation [16]), and torsion of the oxazole ring as well. The vibrations of structure II in this range differ in frequency within 3 cm^{-1}. The mode 692 cm^{-1} is the in-plane bending vibration 6a of the aromatic rings, mostly the phenol one. This in-plane vibration is calculated to yield a low band intensity in the IR spectrum. The remaining modes in the range 670–780 cm^{-1} are out-of-plane vibrations involving CH bending 11, torsion of the aromatic rings 4, torsion of the oxazole rings, and a small contribution by the OH torsion.



a) b)

Fig. 4. (a) The IR spectrum in the range 400-1700 cm^{-1} of an isolated molecule of BBHQ modelled with the composite B3LYP-3c method and experimental spectrum [2] in a KBr pellet. (b) Atom displacement in the calculated normal vibrations with a significant contribution of the OH bond torsion.

The IR spectrum of BBHQ is simplified because its structure possesses a center of symmetry, and only normal modes with the A_u and B_u symmetry exhibit IR absorption bands in the dipole approximation. The B3LYP-3c calculations predict four normal modes active in the IR spectrum with frequencies of 666, 736, 748, and 759 cm^{-1} (all of the A_u symmetry) in the region 660–780 cm^{-1}; however, the relative IR intensity for the vibration 759 cm^{-1} is calculated to be lower than the intensity for the vibration 748 cm^{-1}. The calculated frequencies are in good correspondence to the four bands at 669, 741, 749 and 761 cm^{-1} observed in the experimental spectrum (Fig. 4a). The mode 666 cm^{-1} is OH torsion (Fig. 4b); the mode 736 cm^{-1} is mostly out-of plane bending vibrations 11 (Varsanyi's nomenclature [16]) of CH bonds of benzoxazole and torsion of the hydroquinione moieties; the modes 748 and 759 cm^{-1} are out-of plane bending vibrations of CH bonds mixed with torsion of the benzoxazole and hydroquinone moieties.

Good correspondence of the modeled spectra to the experimental data allows assignment of the observed broad asymmetric bands in the region 660-780 cm^{-1} to the vibrations with significant contribution of the torsional motion of the bonds OH for all three compounds.

4. Conclusions

Calculations of infrared spectra of molecules of the benzoxazoles with hydrogen bonds exhibiting excited-state intramolecular proton transfer are performed with a composite B3LYP-3c method. The addition of the parameterized corrections to the energy obtained by the B3LYP density functional in combination with a specific, relatively small double-zeta basis set provides good correspondence of the modeled infrared spectrum of benzoxazoles to absorption bands observed in the experiment. The calculations reproduce the broad bands in the spectral region 660-780 cm^{-1} associated with out-of-plane vibrations of the OH bonds involved in hydrogen bonding in the molecules. Using a small basis set enables calculations on large molecules, given the computational resources required; however, the composite method is limited to ground-state infrared spectra because the corrections are not valid for excited states.

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Анотація. *Інфрачервоні спектри 2-(2'-гідроксифеніл)бензоксазолу, 2,5-ді-(2-бензоксазоліл)фенолу та 2,5-біс(2-бензоксазоліл)гідрохінону розраховані методом теорії функціоналу густини з використанням додаткових поправок B3LYP-3c. Розраховані частоти та інтенсивності добре узгоджуються з експериментальними значеннями, включно з областю торсійних коливань зв'язків OH, яка недостатньо добре моделюється найбільш поширеними методами теорії функціоналу густини. Смуги в цій області віднесені до торсійних коливань OH, позаплощинних деформаційних коливань CH та торсійних коливань ароматичних та оксазольних кілець.*

Ключові слова: *інфрачервоні спектри, молекули, теорія функціоналу густини, водневий зв'язок.*