The methods of optical physics as a mean of the objects' molecular structure identification (on the base of the research of dophamine and adrenaline molecules)

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Abstract. Structural and dynamic models of dopamine and adrenaline are proposed on the basis of ab initio quantum calculations of the geometric and electronic structure. The parameters of the adiabatic potential are determined, a vibrational states interpretation of the test compound is proposed in this work. The analysis of the molecules conformational structure of the substance is made. A method for calculating the shifts of vibrational excitation frequencies in 1,2,4-threesubstituted of benzole is presented. It is based on second order perturbation theory. A choice of method and basis for calculation of a fundamental vibrations frequencies and intensities of the bands in the IR and Raman spectra is justified. The technique for evaluation of anharmonicity with cubic and quartic force constants is described. The paper presents the results of numerical experiments, geometric parameters of molecules, such as the valence bond lengths and angles between them. We obtain the frequency of the vibrational states and values of their integrated intensities. The interpretation of vibration of conformers is given. The results are in good agreement with experimental values. Proposed frequency can be used to identify the compounds of the vibrational spectra of molecules. The calculation was performed quantum density functional method DFT/B3LYP. It is shown that this method can be used to modeling the geometrical parameters molecular and electronic structure of various substituted of benzole. It allows us to construct the structural-dynamic models of this class of compounds by numerical calculations.

1. Introdution

Detecting the features of compounds spectral identification, their interpretation or their relation to a certain molecular fragment are both fundamental target of mathematical modeling in the theory of molecular system and applied one according to the quantitative and qualitative composition of bioobjects i.e. relations "State-Structure- Spectrum". The achievement of the given problem poccesses its own special features for each composition. The present work demonstrates the possibility of the use of the up-to-date programming software to create structural and dynamical models of the substance and accomplishment on the base of the spectrum identification of the substance. Optical physics methods are the most informative in the studied structures of the discussed types of the molecular objects.

Solving problems of the discussed types is possible due to the high techs of the molecular modeling i.e. the use of quantum method of analyses of parameters of adiabetic potential. These methods in the beginning of the 21 century completely replaced the classical methods of molecular dynamics which are based on the soluteon of inverse problems in theoretical physics.The applied methods are imple-

mented as applied programming lay-outs. Dominating one is "Gaussian" according to the frequence use. Its particular feature is the implementation of the method of functional density DFT/B3LYP allowing to model effectively the problems discussed in article.

The interest to the study of the structure and spectrum of molecule of dofamine and adrenaline is understandable (Figure 1). As an example we refer to the works [1,2,3] where just one of the possible conformers' combinations. Интерес к изучению структуры и спектра молекул дофамина и адреналина (рис.1) понятен. Сошлемся, к примеру, на работы [1,2,3], где рассмотрен лишь один (А) из возможных конформеров соединений. In the work [3] such interpretation for high frequency range is differ from data given in study [4]. In the work [1] there used a classical approach to evaluate the parameters of harmonic force field . In the work [2] the authors researched the range of 570-1880 sm-1. The spectrum modeling calculation are limited by harmonic approximation of the molecular vibrations theory. To measure anaharmonic displacement there used the procedure of scaling [5].

Structurally dopamine and adrenaline are related to 1,2,4 – benzol substituents(C_6H_3XYZ).According to the study[6] the number of fundamental vibrations of benzol trisubstitution could be divided into following groups: characterized by frequency,mode and intensity,characterized by frequency and mode , characterized by mode. Theoretical interpretation of fundamental vibrations of spectrum suggested in the work [6] completely agrees with experimental fundamental vibrations spectrum allocation 1,2,4 – benzol substituted (X=F, CH_3), suggested in the work [7]. This gives the possibility to assume that the given interpretation of spectrum skeleton will possess a space for both dopamine molecules and (X,Y=OH, Z=CH_2–NH_2)and adrenaline (X,Y=OH, Z=CHOH–$NHCH_3$). The accuracy of such idea could be confirmed by quantum calculations.
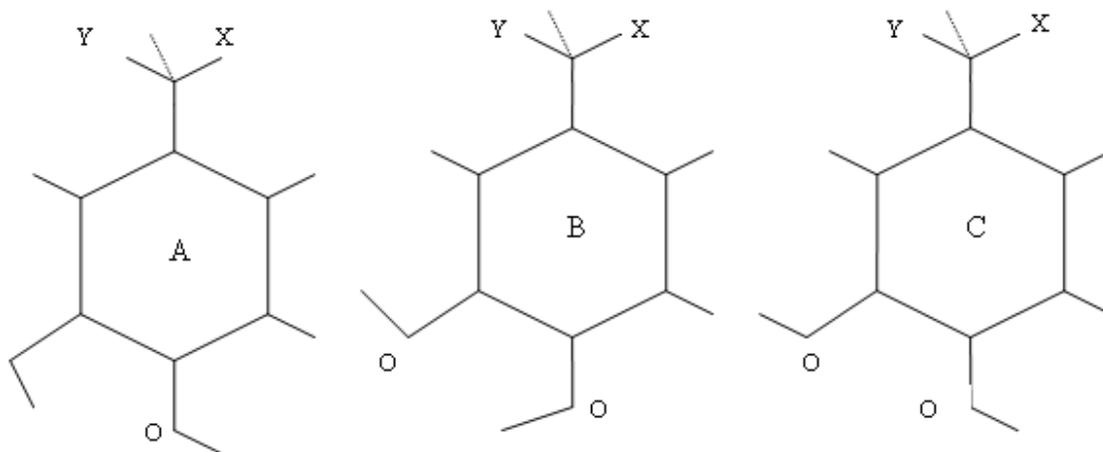

Figure 1. Dopamine molecular diagramms (Y=H, X= CH_2NH_2) and adrenaline (Y=OH, X= CH_2NHCH_3)

The given work suggests structural and dynamical models of possible dopamine and adrenaline conformers on the base of model quantum calculations.All calculations are carried out according to the density functional method DFT/B3LYP [8] with the use of the basis 6-311G*, 6-311G**, 6-311+G**.

2. Methods

The evaluation of the bands' state was carried out by means of the following ratio [9]

$$E_\nu = v_s(n_s + 1/2) + \chi_{sr}(n_s + 1/2)(n_r + 1/2).$$ (1)

There used the equation from the work [10] for anaharmonic constants χ_{sr}.

$$\chi_{ss} = \frac{1}{16}F_{ssss} - \frac{5}{48}\frac{(F_{sss})^2}{\nu_s} + \frac{1}{32}(F_{ssr})^2 (\Omega(s;s;-r) - \Omega(s;s;r) - 12\Omega(r;r;r))(1-\delta_{sr}) \tag{2}$$

$$\chi_{sr} = \frac{1}{16}F_{ssrr} - \frac{1}{8}(F_{ssr})^2 (\Omega(s;s;-r) + \Omega(s;s;r)(1-\delta_{sr})) + \frac{3}{8}(F_{srt})^2 (\Omega(s;r;t) - \Omega(s;r;-t) + \Omega(s;-r;t) - \Omega(s;-r;-t)) \times$$

$$\times (1-\delta_{sr})(1-\delta_{st})(1-\delta_{rt}) + L(a;sr)^2 \frac{\Omega(s;r;0) + \Omega(s;-r;0)}{2} \tag{3}$$

Here $P_\alpha = L(\alpha;sr)Q^s \cdot P_r$; $L(\alpha;sr)$ – constants Coriolis , ν_s –harmonic vibrations frequency(in sm^{-1}); Q^s – dimentionless normal vibration coordinates ; F_{srt} и F_{srtu} – cubic and quatric force constants ,$\Omega(s;\pm r;\pm t) = (\nu_s \pm \nu_r \pm \nu_t)^{-1}$ – resonance functions , n_s —*the quantum number of vibration state* .

When testing the method DFT/B3LYP resources , during the primarily calculations of geometrical and electronic structures 1,2,4- trisubstituted benzol , there used relevant difluoro and dihydroxytoluene .The given approach was used in the works [11-12] when constructing structural and dynamical models of a number of trisubstituted benzol.

3. Results

According to the calculations the geometrical structure of benzol ring when being replaced is not changed greatly. The length of the valence bonds are distinguished by the amount of ∼ 0.008 Å, values of the bond angles ∼ 1.6°.

The results of model calculations of the vibrational state of the benzol skeleton of the possible conformers of the given test compositions completely agree with the experimental fundamental frequency assignement suggested in the works [1,6,7].

In studied conformers of 1,2-digydro-4-methyl benzol, the great interest is in the band position which are interpreted as valent (q_{OH}) and non- plane deformational vibrations (χ_{OH}) of hydroxyl sections. These are the doublets ∼ 3710 and 3650 sm^{-1} in highly frequency range of vibrational spectrum for conformers A and B . The bands are identical for the third conformer (∼ 3700 sm^{-1}). We can notice that in the works [1,3] the value of frequency being interpreted as valent frequency bonds OH (q_{OH}) is transformed into long waved area of the frequency spectrum for ∼ 300 sm^{-1} in comparison with data given above and suggested assignment for the mentioned frequency from the work [8]. Due to the fact that the relevant experiment introduced in the works [1,3] corresponds to the condensing state of dopamine and adrenaline.

The band state interpreted as torsion vibrations χ_{OH}, is characterized by the following doublets : 410 и 210 sm^{-1}, 420 и 170 sm^{-1}, 360 и 310 sm^{-1}. According to the model calculations the bands are the most intensive in a low frequency range of vibrational spectrum .

The most important fact is the vibrational characteristics of the benzol skeleton according to the frequency. There can be observed characteristics according to the intensity for the given type of benzol trisodium while interfusing according to the form for deformational vibrations of hydroxide fragments. При отсутствии смешивания по форме с деформационными колебаниями гидроксильных фрагментов, наблюдается характеристичность по интенсивности для данного типа тризамещенных бензола.The testing results confirm the suggested theory.The intensity band changing values is connected either with the varied electronic substitutes' properties or with the interfusion of ordinary vibrations forms interpreted as deformational vibrations of the relations CH (H=H, F, O) in the model calculations. It can be seen in 1,2 dihydro- 4 methyl benzol in the range of e 1550-1100 sm^{-1}.

The interpretation of vibrational spectrum of dopamine is introduced in the table 1. It was supposed that a molecule belongs to the symmetry group C_s (the carboatomic plane is the molecule symmetry plane). Torsional vibrations were produced when the fragments CH_2C и CH_2NH_2 of substitutes are in the transconfiguration relatively each other .

Table 1. Fundamental dopamine vibration interpretation

Form of vibration	$\nu_{эксп}$ [5]	ν_r	Model_A			Model_B			Model_C		
			$\nu_{анг}$	IR	CR	$\nu_{анг}$	IR	CR	$\nu_{анг}$	IR	CR
Flat vibrations of 1,2,4 trisubstituted benzol fragment фрагмента (symmetryA′)											
Q,γ,β	1621	1663	1621	9.6	37	1622	20	8.7	1618	4.1	32
Q,γ,β	1596	1645	1605	178	6.1	1601	39	8.5	1601	35	12
β,Q	1522	1559	1521	146	2.0	1511	188	1.1	1526	138	1.5
$β_{OH}$,β	1382	1404	1376	38	6.7	1369	6.2	3.7	1364	14	5.1
$β_{OH}$,β	1326	1354	1319	13	1.0	1321	140	1.9	1324	7.6	1.2
Q_{CC},β	1277	1314	1279	114	13	1281	126	13	1286	104	11
Q_{CO},Q	1234	1292	1259	132	1.1	1256	48	0.6	1266	30	2.6
Q_{CO},$β_{OH}$	-	1284	1247	73	3.7	1255	59	0.3	1257	36	5.3
$β_{OH}$,β	1188	1214	1193	54	8.3	1188	31	5.3	1174	309	1.0
$β_{OH}$,β	1176	1185	1149	75	3.4	1153	102	4.1	1169	67	3.2
β,Q	1144	1166	1135	7.2	2.4	1135	7.2	2.6	1144	5.2	3.4
γ,$β_{OH}$	1099	1128	1103	107	1.0	1101	92	4.3	1100	82	1.3
γ	922	958	931	2.7	5.8	937	13	5.0	939	12	4.7
γ	771	794	779	39	18	775	48	18	774	22	18
γ	728	758	741	5.8	8.4	741	10	7.3	742	7.2	8.7
$β_{CO}$,γ	571	588	579	19	2.8	578	9.3	5.4	567	10	3.3
$β_{CC}$,$β_{CC'}$	445	467	456	3.4	1.0	456	5.7	0.9	460	4.2	1.5
$β_{CC}$,$β_{CC'}$	340	337	330	9.5	0.3	330	1.0	0.3	330	0.6	0.6
$β_{CO}$,γ	312	316	310	3.2	3.6	309	6.3	3.3	310	16	2.2
$β_{CO}$,γ	285	297	291	2.2	4.9	292	3.7	4.3	290	1.8	6.1
Non-flat vibrations of 1,2,4 trisubstitute fragment (symmetry A)											
ρ	932	936	914	1,6	0,2	890	3.5	0.1	887	1.0	0.1
ρ	854	849	818	29	0.6	851	11	0.7	820	24	0.8
ρ	804	807	806	13	0.7	780	29	0.4	783	22	0.7
χ,ρCO	688	706	690	0.1	0.1	689	0.2	0.1	691	0.2	0.1
$ρ_{CC}$,χ	603	600	584	9.9	0.3	588	4.4	0.1	588	7.6	0.2
χ,$χ_{OH}$	434	456	445	2.9	0.9	448	11	1.3	446	1.6	0.2
$ρ_{CO}$,χ	330	343	350	7.7	2.2	352	4.3	2.5	306	6.7	4.8
χ	237	223	220	2.5	1.2	224	19	0.3	213	4.9	1.4

χ	152	157	155	4.7	1.0	156	0.1	0.5	152	0.1	0.5
Vibrations of fragment CH_2-CH_2NH_2											
q_{OH}	3615	3844	3712	69	103	3714	79	125	3698	42	152
q_{OH}		3803	3658	101	77	3654	102	78	3696	72	75
q_{NH}	3427	3553	3432	0.1	60	3431	0.1	61	3431	0.1	60
q_{NH}	3360	3478	3361	1.1	110	3360	1.0	111	3360	1.1	110
γ_{HNH}	1623	1666	1622	27	5.2	1624	5.0	24	1622	24	5.6
α_{CNH}	1430	1388	1364	10	6.2	1349	8.0	11	1350	52	16
Q_{CN}	1059	1092	1067	8.2	6.6	1067	3.7	5.4	1066	3.9	6.0
Q_{C-C}	1040	1049	1025	34	1.8	1024	74	2.4	1025	44	2.3
β_{CNH}	780	861	840	223	3.8	844	198	3.1	843	217	3.3
χ_{OH}	-	-	415	70	1.2	424	66	1.0	362	63	2.4
χ_{OH}	303	-	199	141	3.0	190	131	4.3	311	137	0.1
x_{CN}	-	293	287	41	1.9	287	42	1.9	287	49	1.8

Note: Vibrational frequency in sm^{-1},Intensity in IR spectrum in km\mole , in spectrum CR Å^4/ а.е.м.

For the spectrum identification of conformers there can be used IR bands intensity in the range of 1200-1400 см$^{-1}$ and the bands interpreted as deformational non-flat vibrations of the bonds OH (χ_{OH}).The use of the basis 6-311G+** [7] leads to the displacement of calculated values of vibrations ($\Delta\sim$ 50 см$^{-1}$). But the significant intensity of the given bands in IR spectrum in the range of lower than 400 sm^{-1} does not create difficulties in the interpretation of low frequency range

The determined conformity related to the spectrum bands of the benzol fragment of   1,2,4- trisubstituted benzol allows to interpret the fundamental vibrations of the fragment of CH_2-CH_2NH_2.Their agreement with the experimental data on the characteristic frequency vibrations for the normal paraffins and methylamine[5] confirms the relevance of the harmonic strain constanta from the close molecular fragments system system transfer scheme used in the work of [5] to solve the reverse problems in classical theory of molecular vibrations.

The interpretation of spectrum fundamental vibrations of adrenaline suggested in the table 2 confirms the arguments given above which are related to dopamine spectrum identification. All fundamental vibrations of the compounds could be divided into two groups. The first one is connected with benzol skeleton of $C_6H_3X_3$.The adrenaline symmetry decrease to the group of C_1 does not influence on the bands' position and evaluation of their intensity. The second group is interpreted as the vibrations of the fragment $CHOH$-CH_2NHCH_3. The hydrogen atom substitution into the methyl group in the fragment NH2 leads to the same patterns in the frequency vibrations behavior that happen while transferring from methylamine to dimethylamine [5]. The bands interpreted as valent (q_{OH}) and nonplane deformational vibration of the bond OH (χ_{OH}) of the fragment $CHOH$-CH_2NHCH_3 is difficult to use for the conformers compounds spectral identification.

Tablr 2. Interpretation of fundamental adrenaline vibrations

Form of vibration	Model A			Model B			Model _C		
	$\nu_{\text{анг}}$	IR	CR	$\nu_{\text{анг}}$	IR	CR	$\nu_{\text{анг}}$	IR	CR
Q,γ,β	1616	16	80	1619	4.4	68	1615	11	62
Q,γ,β	1604	29	7.7	1602	43	7.4	1601	32	29
β	1517	118	9.2	1506	160	3.0	1520	118	6.4
Q,β,β_{OH}	1439	98	3.7	1454	11	15.0	1436	8.7	5.5
β,β_{OH}	1373	28	16	1372	15	8.5	1364	20	27
Q,β	1279	210	21	1286	59	19	1287	142	19
Q,β	1274	23	1.7	1273	132	6.9	1280	3.9	2.5
Q_{CO},γ,β	1252	84	4.2	1253	39	5.5	1261	30	6.1
β,β_{OH}	1188	77	21	1183	31	3.6	1173	278	2.5
β_{OH}	1146	59	12	1147	100	8.5	1156	57	3.3
β,β_{OH}	1139	42	4.9	1139	26	8.2	1148	4.9	11
γ	1092	53	2.6	1090	65	10	1089	44	5.4
γ	933	23	7.5	938	34	5.8	940	27	6.3
ρ	931	6.7	1.1	910	0.9	1.0	909	0.6	1.6
ρ	824	32	7.1	853	6.1	7.7	822	22	4.6
ρ	816	0.3	1.1	790	29	5.0	793	18	3.9
γ	785	11	11	782	7.1	3.6	784	14	5.4
γ	771	40	18	773	42	23	769	20	23
χ,ρ_{CO}	698	1.8	0.9	697	1.7	1.0	698	1.3	0.8
χ,ρ_{CO}	621	9.6	3.1	627	6.1	3.2	627	9.3	3.2
γ,β_{CO}	617	8.7	1.3	616	25	1.5	616	15	1.5
γ	582	13	3.9	581	7.0	6.8	575	8.0	4.4
$\rho_{CO},\beta_{OH},\chi$	456	4.5	0.4	456	0.1	0.3	457	6.6	0.1
ρ_{CO},β_{OH}	441	17	1.0	441	5.8	0.9	444	4.7	0.7
χ	390	5.8	1.4	390	1.7	1.4	352	101	5.8
β_{CO},β_{OH}	309	14	1.2	308	43	1.1	310	23	1.7
β_{CO}	295	19	1.4	296	11	1.3	307	35	3.1
χ	246	0.7	2.6	247	9.2	1.6	279	12	0.4

β_{CC},β_{OH}	201	24	1.1	199	33	1.6	201	0.7	0.8
χ	170	6.7	1.3	171	7.5	1.1	167	0.3	0.7
Vibrations of fragment CHOH-CH$_2$NHCH$_3$									
q_{OH}	3714	69	97	3715	86	131	3698	30	173
q_{OH}	3690	25	89	3691	25	89	3697	90	56
q_{OH}	3658	105	78	3655	105	77	3690	25	88
q_{NH}	3408	3.7	71	3407	3.4	72	3408	3.6	71
$\alpha_{HNC},\alpha_{HCH}$	1488	25	10	1488	26	10	1488	24	10
Q_{CN},β_{NCH}	1158	28	1.4	1159	10	2.0	1163	80	10
Q_{NC}	1107	23	7.6	1107	39	8.5	1107	32	7.9
β_{CNH}	740	128	2.7	742	133	2.7	741	131	2.8
Q_{CO}	1037	69	3.2	1035	38	4.1	1037	62	3.3
α_{OCC}	519	15	1.6	518	13	1.5	517	13	1.6
χ_{OH}	419	72	1.3	418	65	0.9	393	20	1.5
χ_{OH}	352	107	6.6	350	89	6.1	325	138	1.4
χ_{OH}	205	110	1.5	207	101	2.2	242	5.8	2.2

4. Conclusions

The carried modeling calculations of the vibrational state of rank 1,2,4 replaced benzol particulary dopamine and adrenaline allow us to confirm that the method of the density functional DFT/B3LYP can be used to construct structural and dynamical models of the complex molecule compounds of the given type. The given fundamental vibrations could be relatively divided into two groups. The first group is related to the vibrations of the benzol fragment $C_6H_3X_3$. If to carry out the mass compare (X=F, CH$_3$, OH) the vibrations could be considered as characteristic according to the frequency and form. Another group is related to the fundamental vibrations of a molecular fragment which is obtained by 4 varied molecular fragments .substitution of a hydrogen atom of a methyl group in a position.

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