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M D Elkin[1], V V Smirnov[1], O M Alykova[1], G P Stefanova[1], I N Zavestovskaya[2], A F Alykova[2], A V Rybakov[1]

[1]Astrakhan state university, Astrakhan, Russia
[2]National Research Nuclear University MEPhI Moscow Engineering Physics Institute), Moscow, Russia

E-mail: olga-alykova@mail.ru

Abstract. On the basis of modelling not empirical quantum calculations of geometrical and electronic structure of some isomers of substituted benzoic acids are investigated regularity in behaviour of parameters of the adiabatic potential a carboxyl fragment.
Keywords: benzoic acids, adiabatic potential, intermolecular interaction, oscillatory spectra.

1. Introduction

Substituted benzoic acids have wide enough application as reliable indicators of environmental contamination by waste of mineral oil, components by manufacture of the pesticides making of pharmacological preparations, dyes of textile manufactures. In detail about it, it is possible to learn from the literary review in work [1].

Research of structure and spectra of the specified representatives aromatic benzoic acids one of stages of studying of physical and chemical properties of the ligands (benzoic and salicylic acids) with metals within the limits of new in the physic of molecules of a scientific direction - molecular modelling. A theoretical basis of such researches are not empirical methods of quantum mechanics of molecular systems.

Benzoic an acid, as well as other representatives of class carboxylic acids, easily form dimers with strong hydrogen communications. Intermolecular interaction between monomers is evidently shown in oscillatory spectra of connections. Especially it concerns a high-frequency range (2500-3500 sm^{-1}). The spectrum of dimers in this area has complex structure, including valent fluctuations of communications CH benzoic a skeleton, OH bonds of carboxyl fragment and overtones of deformation fluctuations of the specified communications. The theoretical interpretation of strips offered in the periodic literature, is controversial, it is enough to refer to publications [2-6]. If to follow the presented results to them, property of characteristical strips of carboxyl fragment, taking place for monomers of carboxylic acids, is cardinally broken at formation dimers OH bonds.

For dimers of carboxylic acids and of some its substituted interpretation of an oscillatory spectrum in overwhelming majority of researches is based on use of scaling parities [7]. by updating results of modelling calculations in harmonious approach of the theory of molecular fluctuations [1].

As shown in the works [8-10], the results received on this way for a range of 2500-3500 sm-[1] essentially miss the data received at the decision of a problem in inharmonious approach. Technique of the account offered in publications [9,10] inharmonic shift of the strips uses as initial data the decision of a problem on molecular fluctuations monomers of carboxylic acids. Interpretation of oscillatory spectra of monomers allows to identify the strips concerning valent fluctuations of communications CH of a base fragment (for example, the benzene skeleton) to estimate influence of intermolecular interaction on shift and splitting of strips at formation dimer bonds. The technique is approved on such representatives of a class carboxylic acids, as benzoic and isonicotinic acid [9-11].

Preliminary stage of construction of structurally-dynamic models substituted benzoic acids is the analysis of influence of electronic structure of the assistant on parametersof the adiabatic potential of carboxyl fragment depending on mutual position (ortho-, metha-, pair [12]) assistants concerning an aromatic ring. Such analysis also is a subject of the given publication.

2. Mathematical model of inharmonic shift of oscillatory conditions

For the description inharmonic shift of oscillatory conditions we shall take advantage of a parity for the description of molecular fluctuations within the limits of the theory of indignation [13].

$$E^n = v_s\left(n_s + \frac{1}{2}\right) + \chi_{sr}\left(n_s + \frac{1}{2}\right)\left(n_r + \frac{1}{2}\right). \tag{1}$$

Corresponding modelling hamiltonian has, an appearance:

$$H^{(v)} = \frac{1}{2}v_s(P_s^2 + (Q^s)^2) + \mu^{1/4}P_\alpha\mu^{-1/4}P_\beta\mu^{1/4} + \frac{1}{3}F_{srt}Q^sQ^rQ^t + \frac{1}{12}F_{srtu}Q^sQ^rQ^tQ^u. \tag{2}$$

Here $P_\alpha = L(\alpha, sr)Q^sP_r$; $L(\alpha, sr)$ - Constants Coriolis, v_s - frequencies of harmonious fluctuations (in sm^{-1}); Q^s - the dimensionless normal oscillatory coordinates linearly connected with the Cartesian displacement of atoms; F_{srt} and F_{srtu} - cubic and quartic force constants (parameters adiabatic potential of a molecule), n_s - quantum numbers of a considered oscillatory condition. The size of the inharmonic shift of a separate strip of fundamental fluctuation is defined by size inharmonic amendments $X_{ss} = 2\chi_{ss}$ and $X_s = \chi_{sr}/2$. Expressions for inharmonic constants χ_{sr} are offered in publications [9,10].

$$\chi_{ss} = \frac{1}{16}F_{ssss} - \frac{5}{48}(F_{sss})^2\frac{1}{\nu_s} + \frac{1}{32}(F_{ssr})^2\left(\frac{1}{2\nu_s - \nu_r} - \frac{1}{2\nu_s + \nu_r} - \frac{4}{\nu_r}\right)(1 - \delta_{sr}), \tag{3}$$

$$\begin{aligned}\chi_{sr} = {} & \frac{1}{16}F_{ssrr} - \frac{1}{8}(F_{ssr})^2\left(\frac{1}{2\nu_s - \nu_r} + \frac{1}{2\nu_s + \nu_r}\right)(1 - \delta_{sr}) + \\ & + \frac{3}{8}(F_{srt})^2\left(\frac{1}{\nu_t + \nu_r + \nu_s} + \frac{1}{\nu_t - \nu_r - \nu_s} + \frac{1}{\nu_t - \nu_r + \nu_s} + \frac{1}{\nu_t + \nu_r - \nu_s}\right)\times \\ & \times(1 - \delta_{sr})(1 - \delta_{st})(1 - \delta_{rt}) + \frac{1}{2}L(\alpha, sr)^2\left(\frac{1}{\nu_s - \nu_r} + \frac{1}{\nu_s + \nu_r}\right).\end{aligned} \tag{4}$$

All set of fundamental fluctuations of substituted benzoic acid can be divided acids on two parts. The first part concerns to fluctuations of the benzene skeleton (C_6H_4).The received results concerning properties characteristical oscillation para-, meta-and ortho substituted benzenes will completely be coordinated with conclusions of the monography [12]. For chloro-and carboxy-benzoic acid such information is presented to publications [14] which basic purpose was research of influence of nuclear basis on results of modelling calculations of parameters adiabatic potential. It is found out, that the choice of basis influences predictive values of the frequencies calculated in harmonious approach valent and torsional vibrations of the OH carboxyl fragment. The preference should be given bases 6-311G **, 6-311+G **, 311+G ** [15]. Accounting for the diffusion parameters of the basis (+,++) shifts the frequency of torsional vibrations of OH in the low-frequency spectrum by ~ 30 cm^{-1}. Qualitative assessment of band intensities in IR and Raman preserved.

3. Results and discussion

The results of model calculations of the vibrational states of the carboxyl fragment of chlorine, cyano, hydroxy-and carboxy-benzoic acid (method of the functional density DFT/B3LYP with basis 6-311 + G **) are presented in Tables 1-6.

Characteristic frequency, form and intensity in the IR and Raman is the stretching vibrations of OH (Q_{OH}), for which there is practically no doublet splitting in dicarboxy benzenes.

Characteristic frequency and intensity should recognize and respect, and oscillation of the C=O($Q_{C=O}$).

For the other vibrations of the bands and their intensity depends, in varying degrees, the relative position of substitute and the carboxyl fragment.

In the para substituents of benzoic acid components of the influence of substitute impact on the strips interpreted as deformation fluctuation of valent corner COC (γ_{OCO}) of a carboxyl fragment (a range of values of 600-720 sm^{-1}). Significantly different estimates of the intensities of bands in the infrared spectrum. The remaining variations should be attributed to the characteristic frequency, if we neglect the divergence of the torsional vibrations of a doublet ρ_{OH} (Δ ~20 sm^{-1}). Such behavior of the fundamental frequency as compared with benzoic acid (X = H) is associated with spatial distance from the substitute-carboxyl fragment (> 7 Å). The intensity of the stripes is defined by the electronic structure of substitute.

Intensity of strips is defined by an electronic structure of the substitute. Identification of isomers of hydroxy (OH) and carboxy (COOH) para substituents of benzoic acid is complicated (Table 1).

In metasubstituted benzoic acids are possible two isomers for substitutes X=Cl, CN (Table 2), four isomers, if X=OH (Table 3), three isomers for X=COOH (Table 4).

According to data of table 2, for such substitutes as Cl and CN spectral identification of the isomers in the para-and ortho-positions is difficult, which is also related to the long distance between the atoms of the X substituent and carboxyl fragment (> 5 Å for metasubstitution and 3.9 Å for parasubstitution).

Spectral identification of isomers of meta hydroxy substituted benzoic acid (Table 3) is complicated. Frequency shift, according to modelling calculations is 20 sm^{-1}, qualitative assessment of the intensity remains. The distance between the hydrogen atom of the hydroxyl moiety and the oxygen atoms of the carboxyl fragment exceeds the value of 4.7 Å.

Table 1. Interpretation of fluctuations of carboxyl a fragment vapor substituted benzoic acids (C_6H_4COOH)

X=	The form	$\nu_{эксп}$	$\nu_г$	$\nu_{анг}$	IR	Raman	The form	$\nu_{эксп}$	$\nu_г$	$\nu_{анг}$	IR	Raman
H		3570	3772	3577	99	137		1325	1363	1327	116	12
Cl		3581	3771	3571	111	146		1358	1365	1345	136	24
CN		-	3769	3580	107	174		1334	1378	1336	129	20
OH_1	Q_{OH}	3570	3774	3584	91	152	β_{OH}, Q_{CO}	1325	1370	1328	127	11
OH_2		3570	3774	3584	92	152		-	1380	1338	147	18
COOH_1		-	3768	3579	224	322		-	1365	1324	243	35
COOH_2		-	3770	3580	224	323		-	1364	1324	240	32
H		1690	1785	1753	395	92		1073	1114	1088	42	1.2
Cl		1698	1786	1753	418	147		1095	1102	1075	222	12
CN		1710	1808	1747	331	93		-	1110	1079	133	2.8
OH_1	$Q_{C=O}$	1775	1797	1737	357	88	Q_{CO}, β_{OH}	-	1100	1070	132	1.1
OH_2			1796	1735	355	83		-	1106	1075	192	2.1
COOH_1			1789	1727	800	260		-	1104	1073	359	12
COOH_2			1790	1730	774	264		-	1103	1072	336	7.2
H			640	634	49	0,4		571	578	577	71	2.5
Cl			677	668	14	0.7		549	577	571	59	3.1
CN		691	705	687	41	1.3		588	605	591	28	3.2
OH_1		630	603	589	58	0.5		560	591	577	49	6.9
OH_2	γ_{OCO}	-	602	588	62	0.4	ρ_{OH}	-	572	578	48	7.1
COOH_1		-	720	701	102	0		-	591	577	134	00
		-	646	630	0	7.5		-	570	557	0	5.5
COOH_2		-	719	701	92	1.6		-	589	575	134	0.2
		-	646	630	0.7	8.6		-	570	557	0	5.4

The note. Frequencies of fluctuations in sm^{-1}, intensity in spectra IR in Km/mol, in Raman spectra in $Å^4$/amu.

Table 2. Interpretation of fluctuations carboxil fragment the metha-and ortho- substituted benzoic acids ($C_6H_4COOH\_X$. X=Cl, CN)

Form	X=	methasubstitution						Orthosubstitution					
				Isomer_1		Isomer _2				Isomer _1		Isomer _2	
		$\nu_г$	$\nu_{анг}$	IR	Raman	IR	Raman	$\nu_г$	$\nu_{анг}$	IR	Raman	IR	Raman
Q_{OH}	Cl	3742	3556	64	166	65	175	3725	3539	55	164	65	152
	CN	3770	3581	103	157	104	167	3766	3577	104	144	104	147
$Q_{C=O}$	Cl	1808	1747	333	57	310	55	1788	1728	344	41	298	52
	CN	1810	1749	333	54	296	54	1799	1768	316	51	254	45
β_{OH},	Cl	1383	1341	105	8.8	89	7.6	1396	1353	87	10	57	6.5
Q_{CO}	CN	1381	1339	128	16	95	14	1381	1340	124	13	95	9.9
$Q_{CO,}$	Cl	1096	1066	98	1.7	19	7.2	1126	1095	96	0.5	68	2.9
β_{OH}	CN	1098	1088	99	1.2	52	2.8	1137	1105	119	1.3	85	0.9
γ_{OCO}	Cl	647	631	41	0.1	46	2.4	642	627	41	3.4	45	0.2
	CN	652	636	42	0.2	52	2.4	642	627	39	2.7	40	0.2
ρ_{OH}	Cl	627	612	104	6.1	108	5.5	631	616	57	6.7	76	7.4
	CN	623	608	91	6.4	89	7.8	595	581	72	5.1	57	4.2

Table 3. Interpretation of oscillations of carboxi fragment meta hydroxy substituted benzoic acids

Form	Isomer _1			Isomer _2			Isomer _3			Isomer _4		
	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman
q_{OHg}	3638	63	123	3636	59	101	3635	61	99	3637	63	122
Q_{OH}	3583	88	154	3582	88	151	3581	90	153	3581	88	155
$Q_{C=O}$	1742	308	57	1743	318	59	1738	316	59	1743	314	56
β_{COH},Q_{CO}	1337	131	16	1336	123	19	1340	109	14	1335	172	13
Q,β,β_{OH}	1321	21	0.6	1324	28	2.1	1325	38	1.8	1321	14	0.5
q_{CO},β_{OH}	1251	51	17	1253	69	17	1249	83	14	1250	36	15
Q_{CO},β	1058	87	1.1	1054	84	1.2	1084	99	0.7	1075	44	0.9
β_{OCO},γ	633	44	0.1	634	42	0.2	629	45	2.6	628	48	2.2
χ_{OH}	597	96	5.4	596	89	5.5	601	87	5.2	601	96	5.2
x_{OHg}	326	108	3.1	349	109	2.5	356	112	2.5	326	107	3.1

For isomers of metacarboxybenzen holds the doublet splitting of the band, interpreted as a deformation vibration of the bond angle β_{COH} carboxyl fragment (~ 20 cm^{-1}).

Significantly different intensities of the bands in the infrared spectrum for the isomers.

Possible to identify the isomer of the intensity of the band, interpreted as stretching vibrations of C = O.

Table 4. Interpreting oscillations of the carboxyl fragment of metadicarboxibenzene

Form	Symbol type	Isomer 1			Symbol type	Isomer _2			Isomer _3		
		$\nu_{анг}$	IR	Raman		$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman
q_{OH}	A'	3580	88	171	A1	3581	22	282	3582	83	190
q_{OH}	A'	3580	128	127	B2	3581	193	22	3582	132	99
$Q_{C=O}$	A'	1730	343	98	A1	1739	697	124	1732	119	174
$Q_{C=O}$	A'	1727	434	83	B2	1728	16	49	1725	712	12
β_{COH},Q_{CO}	A'	1334	67	24	A1	1327	3.4	24	1339	199	24
β_{COH},Q_{CO}	A'	1315	78	5.1	B2	1318	86	1.5	1317	61	0.1
Q_{CO},β_{COH},	A'	1092	112	0.4	A1	1089	0.1	1.6	1107	125	0.5
Q_{CO},β_{COH}	A'	1063	131	1.2	A1	1077	46	1.5	1059	232	1.1
γ_{OCO}	A'	629	51	0.6	A1	626	1.5	4.6	630	42	1.1
γ_{OCO}	A'	626	71	2.7	B2	627	132	0.6	629	57	0.1
ρ_{OH}	A"	577	0.7	3.3	A2	579	0	4.1	576	0	2.6
ρ_{OH}	A"	555	164	1.1	B1	552	170	0.5	555	160	1.8

Orthohidroxisbstituted isomers of benzoic acid can be identified as on the bands (Δ ~ 50 cm^{-1}), interpreted as a deformation vibration of the valence angle β_{COH} and stretching vibrations of the CO carboxyl fragment, and on the intensities in the IR and Raman. Izomers_2 and 3 can be easily identified by their band, interpreted as stretching vibrations of OH hydroxyl fragment (q_{OHg}).

The shift of this stripe to the low-frequency region by ~ 120 cm^{-1} for izomer_2 and ~ 300 cm^{-1} for izomer_3 associated with the presence of an intramolecular interaction between the oxygen atom of C = O and CO, respectively, the carboxyl group and a hydrogen atom of the hydroxyl fragment (R_{OH} ~ 1.75 Å).

There is reason to believe that the mechanism of this interaction is the intramolecular hydrogen bond.

Results of the simulation of the adiabatic potentials of orthodicarboxsibenzol are represented interesting (Table 6).

Torsional low-frequency vibrations of carboxyl fragments are reproduced only for the original non-planar configuration of the compound (the angle between the carboxyl fragments of ~ 53 º, the angle between the carboxyl fragment and the plane of the benzene ring ~ 38 º). Geometry optimization indicates the presence of one isomer of C2 symmetry. Doublet splitting is only important for the band, interpreted as the stretching vibration of CO bond. For the range below 1700 cm^{-1} in the IR spectrum the most intense antisymmetric vibrations in the Raman spectrum – symmetric.

Table 5. Interpretation of fluctuations of the carboxyl fragment ortho-hydroxi-substituted benzoic acids

Form	Isomer _1			Isomer _2			Isomer _3			Isomer _4		
	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman	$\nu_{анг}$	IR	Raman
q_{OHg}	3627	61	114	3507	286	91	3188	306	65	3623	58	123
Q_{OH}	3569	76	158	3581	76	142	3570	106	144	3588	85	148
$Q_{C=O}$	1721	356	44	1750	391	61	1683	392	57	1749	362	61
β_{COH}	1341	85	7.5	1371	44	5.4	1393	169	16	1331	89	4.1
β, β_{COH}	1324	49	2.1	1315	41	8.9	1358	76	6.7	1319	35	4.9
q_{CO},Q	1246	47	9.9	1240	125	3.2	1267	61	2.1	1260	22	6.6
Q_{CO}	1102	182	1.4	1054	97	8.6	1064	59	1.3	1114	97	0.1
β_{OCO},γ	627	45	2.7	622	41	2.3	639	52	0.4	631	44	0.1
x_{CO},χ	586	64	6.5	547	152	5.7	573	81	6.4	572	82	7.0

Table 6. Interpretation of oscillatory conditions orthodicarboxsibenzol

Form	$\nu_{эксп}$ [16]	$\nu_г$	$\nu_{анг}$	IR	Raman	$\nu_{эксп}$ [16]	$\nu_г$	$\nu_{анг}$	IR	Raman
	Symmetry type A					Symmetry type B				
q_{OH}	3570	3761	3573	98	198	-	3761	3572	88	110
$Q_{C=O}$	1760	1814	1753	358	68	-	1794	1734	310	28
β_{COH}	1325	1363	1322	69	11	1306	1359	1318	126	3.1
Q_{CO},β_{COH}	1070	1114	1082	23	2.8	1051	1065	1036	202	0.4
γ_{OCO}	630	641	625	25	2.9	-	639	624	65	0.5
ρ_{OH}	570	598	584	24	2.1	-	602	588	116	2.3

4. Conclusion

Comparison of the results of model calculations of the geometric structure and vibrational states of substituted benzoic acid monomer with various electron-donating properties with available experimental data gives basis to assert that the density functional method DFT/B3LYP allows carries out accurate predictive calculations of geometric and electronic structure of the investigated class of compounds and use them to build a structurally dynamic models.

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