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Comparative Analysis Of Structural And Dynamic Models Carbonic Acids With Six-Membered Basic Fragments

Michaeel D. Elkin , Vladimir V. Smirnov , Anatoley M. Likhter

Astrakhan State University,
414056, Astrakhan, Russia, Tatishchev St., 20a

Abstract

Within a method of functionality of density of DFT/b3LYP implemented model quantum calculations of the geometric structure and vibrational spectra of carboxy substituted benzene, benzoquinone, gamma-pyrone, tiopirona. At optimization of geometry of monomers of position tautomer for the called acids initial approach for a six-membered cyclic fragment and carboxyl group is borrowed from model calculations of geometry of benzole acid (bases 6-311G ** and 6-311+G **).

The paper proposes an interpretation of the spectrum of fundamental vibrations of the carboxyl fragment benzoic acid conformers benzoquinone, gamma-pyrene and tiopirenovoy acids. It is shown that the formation of dimers leads to a significant shift (~ 500-700 cm^{-1}) bands of stretching vibrations of OH (q_{OH}) in the long-wavelength range of the vibrational spectrum. For torsional vibrations of connections OH (χ_{OH}) observed the fact the band shift shortwave by ~ 300-350 cm^{-1}. Shift of the bands of stretching vibrations of the C = O (q_{OH}) in the long-wavelength range is estimated to be ~ 50-80 cm^{-1}. Frequencies of deformation fluctuations of a valent angle the COH (β_{OH}) can be displaced in short-wave range up to the size ~ 100 cm^{-1}. The fact of delocalization of the specified fluctuations with deformation fluctuations of connections of SN (β) remains. The mechanism of dimerization is strong hydrogen connection between atoms of oxygen of connection of C=O and atom of hydrogen of connection OH carboxyl groups of monomers.

The analysis of the presented results suggests that influence of monosubstituted with a force field of a benzene ring has local character. Such physical assumption will be agreed with a technique of classical approach to an assessment of harmonious parameters of adiabatic potential. Thus, the work showed signs of spectral identification of compounds and justified the

use of information technology «Gaussian» in predictive calculations of the structure and spectra of the investigated class of cyclic compounds.

Keywords: hydroxy substituted benzene, benzoquinone, gamma-pyrone, tiopirona, vibrational spectra, spectroscopic identification.

Introduction

Theoretical interpretation of the spectrum of the fundamental fluctuations of such known class of connections as monomers and dimers of carbonic acids, devoted a significant amount of publications in periodicals. They can be divided into two parts. One is based on a technique of the solution of the return oscillatory tasks (classical approach), using for this purpose experimental data on oscillatory spectra (IR and KP) of connections and the physical assumption of possibility of use of the available estimates of harmonious power constants for a number of molecular fragments. For details, refer to the well-known monograph [1], where, in particular, the proposed interpretation of the experimental data of such industrially significant connections, formic and acetic acid. Authors of the monograph in the extensive literary review pointed to the available divergences in reference of experimental strips for the specified simplest representatives of a class of carbonic acids, and, therefore, and in a theoretical assessment of harmonious parameters of adiabatic potential (harmonious force fields).

The analysis of the structural and dynamic models of carbonic acids offered in periodic literature which basic fragments were saturated and unsaturated hydrocarbons, is presented in the monograph [2]. The theoretical assessment of power constants was carried out n the framework of the above-mentioned methods for solving inverse tasks.

Use of quantum approach for an assessment of parameters of adiabatic potential became real with the advent of modern technologies of not empirical and hybrid quantum and chemical methods of calculation of a form of adiabatic potential [3]. It led to domination of quantum approaches in creation of structural and dynamic models of molecular objects, was reflected in the contents modern periodic publications on molecular modeling. There was an opportunity to perform predictive calculations of structure and spectra of difficult molecular connections, to interpret the having experimental data on spectra of IR and KP, to test results of estimates of the harmonious force fields received within a technique of the solution of the return tasks.

The purpose of this publication is justification of reliability of model quantum calculations of parameters of adiabatic potential for carbonic acids with six-membered basic fragments and creation of a number of structural and dynamic models of the specified class of connections.

Results of model calculations and their discussion

At optimization of geometry of monomers of position tautomers for benzoquinone (BHA), gamma-pyrone (GPA) and tiopirenovoy (TPA) acids (Figure 1) initial

approach for a six-membered cyclic fragment and carboxyl group is borrowed from model calculations of geometry of the benzole acid (BA) within a method of functionality of density of DFT/b3LYP [3,4] (bases 6-311G ** and 6-311+G **).

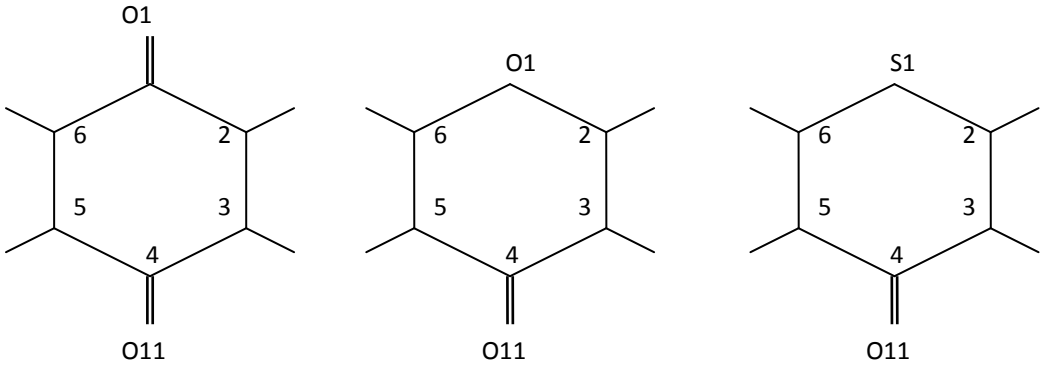

Fig.1. The numbering of the atoms in the Benzoquinone, 4-Gamma-pyrone 4-Tiospirone

Criterion of reliability of the received estimates for lengths of valent communications and values of valent angles was the fact of reproduction of frequencies of tortional fluctuations of carboxyl group concerning the plane of a six-membered cycle. This was achieved, if to proceed from belonging of a- and b-conformers BHA and b-conformers TPA to the symmetry group C1. By b-conformers includes those for which the initial approximation holds the shortest distance between the oxygen atoms of the C = O of the carboxyl and six-membered fragments. For a-conformers BHA received the following estimates (in degrees) of the dihedral angles: D (2,3,8,12) = 152, D (2,3,8,13) = - 26, D (4,3,8, 12) = - 27, D (4,3,8,13) = 155, b-conformers BHA: D (1,2,7,12) = - 35, D (1,2,7,13) = 148 , D (3,2,7,12) = 143, D (3,2,7,13) = - 34, for the b-conformers TPK: D (1,2,7,12) = 154, D (1 , 2,7,13) = - 29, D (3,2,7,12) = - 24, D (3,2,7,13) = 153. Manifested not coplanarity of the atoms carbon fragment COOH (~ 2º) is the result of errors of numerical methods for computer technology «Gaussian» [4], which we used to evaluate the geometry and parameters of the adiabatic potential of carboxylic acids.

The calculated values of lengths of valent communications and values of valent angles of the considered carbonic acids are compared to tab. 1. For BHA, GPA and TPA settlement estimates of geometrical parameters of basic connections also get to the specified ranges of their change for conformers of position tautomer: benzoquinone (BH), gamma-pyrone (GP) and tiopirona (TP). These tab. 1 suggest that influence of monoreplacement with change of geometry of a cyclic six-membered fragment of BH, GP, TP has local character.

Table 1 The calculated values of geometric parameters (GP) benzoic (BC), benzoquinone (BHA), gamma-pyrone (GPA) and thio-pyrone (TPA) acids

GP	BC	BHA	GPA	TPA	GP	BC	BHA	GPA	TPA
R(1,2)	1,39	1,50	1.34-1,36	1.72-1,75	A(4,5,9)	118	116	118-119	114-116
R(1,6)	1,40	1,49	1,35-1.37	1,74	A(6,5,9)	120	123	120	119
R(2,3)	1,39	1,34	1,34-1.35	1,35-1.36	A(1,6,5)	119	122-123	123-124	125-127
R(3,4)	1,40	1,49	1,47-1.49	1,47-1.49	A(1,6,10)	121	115	111	112-113
R(4,5)	1,40	1,48	1,47	1,46-1.48	A(5,6,10)	120	123	125	121-122
R(5,6)	1,39	1,34	1,34	1.34-1,35	A(2,1,15)	120	123	-	-
A(2,1,6)	120	117	118	100-101	A(6,1,15)	120	120-121	-	-
A(1,2,3)	120	120	123-125	125-127	R(C-C)	1.49	1.48-1.50	1.49-1.50	1.49-1.50
A(1,2,7)	118	119-123	111-115	112-117	R(C=O)		1.21-1,22	1,22	1.22-1,23
A(3,2,7)	122	117-121	122-126	119-123	R(CH)	1,08	1,08	1,08	1,08
A(2,3,4)	120	122-123	120-121	123-126	R(C=O)	1,21	1,20-1.21	1.20-121	1,20-1,21
A(2,3,8)	118	121-122	115-120	118-119	R(CO)	1,36	1.34-1,35	1.34-1.37	1,35-1.36
A(4,3,8)	122	116	119-126	115-124	R(OH)	0,97	0,97	0,97	0,97
A(3,4,5)	121	117	112-113	116-117	A(CC=O)	125	123-125	123-126	123-126
A(3,4,11)	120	121	123-126	121-124	A(CCO)	113	112-113	111-114	112-115
A(5,4,11)	120	122	122-124	119-122	A(O=CO)	122	124	122-124	122-124
A(4,5,6)	122	121	121-122	125-125	A(COH)	106	106-107	106-107	106-107

Note. Lengths of valent communications of R (i, i) in Å, values of valent angles in A (i, j, k) in degrees.

Results of theoretical interpretation of fluctuations of cyclic fragments of BC, BHA, GPA and TPA, their comparison with those data for the monodeuterated substituted of basic connections (BH, GP, TP) are presented in tab. 2-5. Such approach gives the chance to establish the general nature of correlation of fundamental fluctuations of a six-membered fragment at monosubstituted.

Table 2 Interpretation of fluctuations of a cyclic fragment of the benzoic acid (BA)

Fluctuation mode	C6H5F		C6H5Cl		C6H5COOH				311G**		311G+**	
	$\nu_{эксп}$	$\nu_{выч}$	$\nu_{эксп}$	$\nu_{выч}$	$\nu_{эксп}$	$\nu_{г}$	$\nu_{м}$	$\nu_{анг}$	ИК	КР	ИК	КР
Q,γ,β	1603	1602	1583	1586	1605	1646	1592	1605	17	62	19	76
Q,γ,β	1595	1598	1580	1582	1585	1625	1573	1582	5	4	6	5
β,Q	1496	1487	1479	1471	1500	1525	1477	1494	1	1	2	1
β,Q	1460	1450	1443	1440	1455	1483	1437	1458	17	1	15	2
β,Q	1326	1311	1322	1310	1325	1350	1310	1319	6	1	9	2
β,Q	-	1290	1263	1286	1291	1339	1299	1316	3	0	3	0
β	1156	1151	1174	1169	1187	1190	1156	1171	135	15	156	20
β	1156	1147	1157	1154	1130	1184	1150	1171	1	6	1	6
β	1065	1064	1083	1072	1026	1093	1063	1068	83	0	116	0
γ,β,Q	1021	1015	1024	1019	-	1046	1018	1030	15	9	20	11
γ	1009	995	1002	992	1000	1019	991	1004	0	31	0	42

γ	806	805	702	692	-	777	757	769	10	14	8	17
γ	613	615	615	615	615	633	618	627	0	6	0	6
γ	519	514	418	405	384	384	376	381	5	4	5	4
β_{CX}	407	396	279	292		217	212	215	1	0	1	0
ρ	997	968	987	980	-	1018	990	993	0	0	0	0
ρ	970	949	965	956	-	998	971	986	0	0	0	0
ρ	896	886	903	896	-	963	937	942	1	1	1	0
ρ	818	813	830	822	854	866	844	851	0	1	0	0
ρ	754	751	740	737	810	826	805	810	0	0	0	1
χ	687	682	682	688	664	707	690	692	8	0	7	0
χ,ρ_{CX}	519	501	470	470	425	435	426	426	10	1	12	0
χ	407	416	418	409	418	415	406	408	1	0	1	0
ρ_{CX},χ	242	235	196	184	191	158	155	154	1	3	1	2

Note. Frequencies of fluctuations (ν) in cm-1, intensity in IR ranges in km/mol, in KP ranges in Å/aem.

In periodic literature interpretation of fundamental fluctuations of BQ monomer is considered settled. We will refer, for example, to links in work [5]. The divergence is observed in reference of strips in the range of 1400-1100 cm^{-1} where deformation fluctuations of valent angles of A(CCH) of a benzene fragment (β) and carboxyl group A(COH) are shown. Reason for that delocalization of a form of normal fluctuations. It is possible to eliminate the arisen divergence with comparison to a range of fundamental fluctuations the haloid of substituted of benzene for which results of model quantum calculations of oscillatory states will well be coordinated as with the theoretical interpretation executed within classical approach and with the available experiment [1]. Such approach is also shown in tab. 1. We will note that the choice of basis of quantum calculation (311G **, 311+G **) has no basic value. Shift of strips is size ~ 10 cm^{-1} therefore average data on frequencies of fluctuations are provided in tab. 1. Nature of manifestation of intensities of strips remains.

In the range above 1000 cm^{-1} appears exhibit specific frequency strips. For strips in the range below 800 cm-1 shift of strips in low-frequency area is caused by kinematic parameters of the deputy (weight and connection long C-X). We will note low intensity of strips non-flat (χ,ρ [1]) fluctuations. Especially it concerns strips in the KP spectrum.

The analysis of the presented results suggests that influence of monosubstituted with a force field of a benzene ring has local character. Such physical assumption will be agreed by a technique of classical approach to an assessment of harmonious parameters of adiabatic potential [1].

Interpretation of fluctuations of a cyclic fragment in the conformer of BHA is offered in tab. 3.

Table 3 Interpretation of fluctuations of a cyclic fragment in the conformers monokarboksi benzoquinone (BHA)

Fluctuation mode	ν_{norm} []	BH-d1		Cl-BH		a-conformer			b-conformer		
		ν_{norm}	ν_{calc}	ν_{norm}	ν_{calc}	ν_{calc}	IR	KP	ν_{calc}	IR	KP
$Q_{C=O}$	1686	1679	1702	1683	1711	1698	209	6	1702	261	45
$Q_{C=O}$	1686	1664	1685	1661	1690	1693	65	208	1693	104	208
Q,β	1635	-	1624	1620	1636	1638	5	27	1639	12	27
Q,β	1614	1588	1589	1589	1591	1604	7	10	1607	3	10
β,Q	1394	1363	1356	1368	1347	1363	41	21	1361	41	18
β,Q	1354	1323	1307	1311	1286	1342	63	2	1347	35	4
β,Q	1299	1284	1250	1276	1251	1256	65	5	1255	97	5
β,Q	1211	1201	1171	1202	1171	1187	32	22	1185	80	14
β,Q	1147	1100	1088	1096	1080	1088	21	14	1086	44	11
β_{CX}	1051	875	859	239	227	174	1	2	185	1	2
γ,Q	942	962	956	843	828	845	5	3	842	5	5
γ,Q	770	765	746	780	763	798	5	2	797	9	2
$\gamma,\beta_{C=O}$	728	-	700	637	626	626	13	2	615	27	1
$\gamma,\beta_{C=O}$	599	595	581	560	547	517	16	3	553	20	4
$\gamma,\beta_{C=O}$	447	-	447	461	457	458	4	8	460	4	8
$\gamma,\beta_{C=O}$	447	445	435	432	422	419	23	2	412	6	1
γ	409	407	404	345	335	305	1	1	314	2	2
ρ,χ	996	988	1002	1004	999	1004	2	0	1004	0	1
ρ,χ	969	933	949	-	907	941	34	2	950	27	2
ρ,χ,ρ_{CC}	882	850	856	-	831	854	39	3	857	46	4
ρ,χ,ρ_{CO}	793	792	783	780	772	778	1	5	780	0	5
$\rho_{C=O}$	747	670	678	-	591	546	28	2	525	9	3
χ	505	474	478	-	386	326	2	0	328	2	1
χ	310	300	325	-	259	239	1	2	242	1	2
χ	244	238	224	-	149	130	2	0	135	2	0
χ	89	108	92	-	83	75	8	1	72	8	1

Without having experimental data on ranges of IR and KP, the presented results should be considered predictive. For justification of their reliability comparison to interpretation of a range of fundamental fluctuations of a hlorbenzokhinon (Cl-BH) for which the available data of experimental reference of strips [6] well will be agreed with quantum calculations of oscillatory states is carried out to tab. 3. A further justification of reliability provided by the results of theoretical interpretation of the experiment [7] for the deuterated benzoquinone (BH-d1). On the experiment of interpretation of an oscillatory range of basic connection (BH) presented in tab. 3 (the second column) it is possible to judge correlation of strips at monosubstituted.

The fact of a specificity of strips on frequency in the range over 1000 cm^{-1}

gives the grounds to draw a conclusion on local influence of the deputy on a force field of six-membered cycle BH. Dependence of shift of strips of deformation fluctuations (γ) in the long-wave range (range is lower than 1000 cm^{-1}) a range is defined by kinematics of the deputy. Intensity of the specified strips is insignificant. Spectroscopic identification conformers BHA is possible only if given the differences in intensity of the strips.

Table 4 Interpretation of fluctuations of a cyclic fragment in position conformers monokarboksi gamma pyrone (GPA)

Fluctuation mode	GP		ν_{calc}		ν_{calc}	GPA-2a		GPA-2b		ν_{calc}	GPA-3a		GPA-3b	
	ν_{norm}	ν_{calc}	d2	d3		IR	KP	IR	KP		IR	KP	IR	KP
Qc=o	1700	1696	1695	1691	1696	433	78	408	91	1706	257	46	138	19
Q,β,γ	1637	1628	1617	1624	1627	23	47	11	70	1636	40	50	40	42
Q,β	1593	1580	1561	1573	1579	12	26	27	26	1556	79	11	35	4
β,Q	1417	1392	1386	1385	1385	28	4	61	4	1381	79	6	111	4
β,Q,γ	1398	1386	1355	1369	1376	4	8	47	4	1362	6	2	57	4
β_{CX}	1319	1305	880	851	181	5	0	0	0	206	5	0	1	0
β,Q	1216	1198	1236	1304	1240	65	2	18	6	1297	164	1	125	0
β,Q	1197	1180	1198	1185	1197	1	1	6	1	1200	54	4	14	10
β,Q,γ	1029	1017	1067	1099	1028	4	10	7	14	1090	17	2	25	1
γ,Q	1004	997	987	1002	930	82	3	101	3	945	55	5	42	4
Q,γ	922	917	951	917	870	10	1	4	2	847	32	11	20	10
γ,Q	790	799	841	760	732	17	17	23	16	714	39	12	18	14
$\beta_{C=O}$	474	491	491	488	515	0	0	1	0	548	17	2	28	3
γ	638	631	623	627	501	2	4	2	3	529	4	4	12	4
γ	453	447	444	436	355	2	4	4	4	**372**	0	2	2	2
ρ,χ	969	954	947	947	958	0	0	0	0	957	5	2	0	0
ρ,χ	922	947	900	911	909	22	2	22	2	953	1	1	5	2
$\rho,\chi,\rho_{C=O}$	857	855	775	846	832	42	1	39	2	844	63	2	65	1
$\chi,\rho_{C=O}$	790	819	734	765	716	0	3	0	3	721	27	3	15	1
χ,ρ_{CC}	724	719	709	628	478	5	2	5	2	460	7	3	13	2
χ	430	436	423	429	405	12	1	8	0	397	2	0	5	0
χ	-	395	364	388	156	7	0	7	0	220	0	0	0	0
χ	-	155	155	152	136	1	1	1	1	95	2	1	3	1

The proposed interpretation of the spectrum of the fundamental fluctuations the cyclic fragment conformers for positional tautomers GPA is presented in Table 4. It should be considered as predictive. For justification of reliability of results of model quantum calculations experimental data [8] for basic connection (GP) and theoretical interpretation the monodeuterated substituted of tautomers of GP are given in tab. 3 (d1(2) and d1(3)). Thus it was supposed that when deuterating parameters of adiabatic

potential are borrowed from model calculations of GP. Their reliability is confirmed by the good agreement between the frequencies of the fundamental fluctuations given in [8] experiment with their theoretical interpretation in the framework of the density functional theory DFT / b3LIP [4].

And for GPK influence of monosubstituted with a force field of a six-membered cyclic fragment can be considered as local that is shown in property of a specific of strips in the range over 1000 cm^{-1}. The divergence in the provision of strips in the range below 1000 cm^{-1} is explained by kinematic property of the deputy. For spectroscopic identification of conformers for a particular position tautomer it is necessary to use distinction in intensity of strips. The difference in the position of the fringes for conformers a- and b- values of less than 20 cm^{-1}, so that they are presented in Table 4, averaged values. Note the weak intensity of the majority of the strips assigned to the non-flat fluctuations of a cyclic fragment. This is especially true of the KP spectrum.

We don't have, experimental data on the spectra tiopirona and monodeytroanalogov (d1 (d2) and d1 (3)), therefore, proposed in Table 5. interpretation of the spectrum of the fundamental fluctuations is predictive. Justification reliability can serve in the nature of the correlation pattern of frequencies of the fundamental fluctuations, which took place for the GP. Shift of frequencies in long-wave range should be considered result of replacement of atom of oxygen in a six-membered cycle on atom of fluorine (kinematic effect).

Table 5 Interpretation of cyclic fluctuations fragment conformers positional tautomers monocarboxy substituted 4-tiopirona (TPK)

Fluctuation mode	ν_{calc} (GP)			ν_{calc}	GPA_2a		GPA_2b		ν_{calc}	GPA_3a		GPA_3b	
	do	d1(2)	d1(3)		IR	KP	IR	KP		IR	KP	IR	KP
Qc=o	1687	1687	1683	1663	383	95	382	97	1676	303	53	184	35
Q,β,γ	1597	1590	1592	1584	16	51	15	70	1586	23	45	22	39
Q,β	1558	1548	1548	1552	9	7	17	6	1525	83	44	31	20
β,Q	1361	1350	1349	1360	2	7	23	2	1340	7	0	5	3
β,Q,γ	1350	1295	1333	1282	11	1	50	3	1316	19	4	22	2
β,Q	1235	1233	1215	1236	2	3	2	4	1201	57	9	16	10
β_{CX}	1123	848	858	173	7	0	0	0	203	4	1	2	1
β,Q,γ	1173	1148	1127	1143	141	2	163	14	1120	18	3	51	6
β,Q,γ	899	949	973	870	9	1	5	2	861	39	2	27	1
γ,Q	746	738	742	774	4	1	6	2	769	4	16	4	14
Q,γ	733	674	705	710	31	2	42	2	732	5	1	9	2
γ,Q	684	665	670	600	27	2	32	4	582	10	3	18	4
$\beta_{C=O}$	557	552	553	458	2	3	4	2	527	17	3	35	1
γ	427	425	420	432	4	8	3	8	426	5	9	4	2
γ	408	406	407	315	4	3	6	3	320	0	3	2	3
ρ,χ	973	965	965	961	0	0	0	0	962	0	0	0	0

ρ,χ	964	920	892	918	16	2	16	1	899	18	1	19	1
ρ,χ,$\rho_{C=O}$	843	812	828	808	58	1	55	2	832	54	2	44	2
χ,$\rho_{C=O}$	734	719	697	634	21	3	30	2	752	13	1	9	3
χ,ρ_{CC}	613	592	546	408	11	1	13	1	374	3	0	0	1
χ	365	365	363	362	1	0	0	0	360	0	1	3	1
χ	361	332	353	146	1	1	1	1	180	0	0	0	1
χ	113	112	111	108	3	2	4	2	65	1	1	4	2

For tautomers TPA observed pattern of characteristic frequencies in the range above 1000 cm-1 can be interpreted as a manifestation of the fact the local influence of the substituents on the force field six-membered cycle TP.

The divergence in the provision of strips of conformers of a specific tautomer doesn't exceed size ~ 20 cm-1 therefore for their spectroscopic identification it is necessary to be guided by intensity of strips. The tendency of low intensity of strips of non-flat fluctuations of six-membered cycle TP remains.

The offered interpretation of a range of fundamental fluctuations of a carboxyl fragment in BC, the conformers of BHA, GPA and TPA, is presented in tab. 6. Thus the fact of delocalization of flat valent fluctuations of communications of CH (β) of a six-membered fragment and a valent angle the COH (β_{OH}) of hydroxyl group was considered. The interpretation of fundamental fluctuations of a six-membered fragment offered in tab. 2-4 allows to resolve the arising question. Here, as described above, a preliminary step was reference of fluctuations the monohaloid of substituted of benzene, benohinona, and gamma-pyrone- tiopirona.

Table 6 Interpretation of fluctuations of a carboxyl fragment in monokarboks of the substituted benzene, benzopyrone, gamma-pyrone, tiopirona.

molecule	q_{OH}(3550-3583)			$q_{C=O}$(1752-1788)			β_{OH}(1280-1334)			β_{OH}(1145-1187)			χ_{OH}(570-638)		
	ν_{calc}	IR	KP	ν_{calc}	IR	KP	ν_{calc}	IR	KP	ν_{calc}	IR	KP	ν_{calc}	IR	KP
BC	3573	88	152	1769	327	56	1344	108	10	1189	120	20	564	64	7
BHA_A	3625	86	160	1785	331	70	1304	8	5	1148	270	1	618	87	2
BHA_B	3620	87	170	1757	271	13	1308	20	5	1158	220	9	624	79	2
GPA_2A	3639	111	131	1785	306	71	1326	162	0	1149	259	29	591	107	4
GPA_2B	3630	102	153	1772	243	28	1326	177	2	1164	314	13	625	106	6
GPA_3A	3619	78	154	1740	442	7	1353	36	5	1170	132	9	632	40	3
GPA_3B	3640	85	149	1791	455	58	1328	89	2	1147	184	7	636	29	1
GPA_2A	3637	115	156	1755	284	48	1346	98	2	1158	209	33	583	93	6
GPA_2B	3635	115	172	1773	249	24	1326	82	3	1148	250	7	591	83	7
GPA_3A	3616	78	191	1731	344	15	1367	80	4	1166	264	13	599	26	6
GPA_3B	3635	84	169	1786	409	64	1359	118	3	1150	265	9	572	47	4

In tab. 6 were limited to consideration of strips which spectroscopic characteristics significantly change for the condensed conditions of carbonic acids. Formation of dimer leads to essential shift (~ 500-700 cm-1) strips of valent fluctuations of communications OH (q_{OH}) in the long-wave range of an oscillatory range. For tortional fluctuations of communications OH (χ_{OH}) is observed the fact of shift of a strip in short-wave range at a size ~ 300-350 cm^{-1}. Shift of strips of valent fluctuations of communications of C=O (q_{OH}) is estimated at long-wave range by size ~ 50-80 cm^{-1}. Frequencies of deformation fluctuations of a valent corner the COH (β_{OH}) can be displaced in short-wave range up to the size ~ 100 cm^{-1}. The fact of delocalization of the specified fluctuations with deformation fluctuations of communications of CH (β) remains. The mechanism of dimerization is strong hydrogen communication between atoms of oxygen of communication of C=O and atom of hydrogen of communication OH carboxyl groups of monomers.

The specified shift of strips is predicted also by model quantum calculations of dimer of carbonic acids within a method of functionality of density [9-11] which results, for example, are subjected, for example, to the comparative analysis in publications [12-14]. The proposed method will allow to establish the fact of redistribution of the intensities in the presence of anharmonic resonances, evaluate the reliability assessments of the quantum anharmonic parameters of the adiabatic potential.

Conclusion

The analysis of results of model quantum calculations of structure and fundamental oscillatory conditions of carbonic acids with six-membered basic fragments allows to draw the following conclusions.

The method of functionality of density of DFT/b3LYP allows to carry out reliable quantum estimates of parameters of adiabatic potential for position tautomer and their possible conformer in the monosubstituted six-membered cyclic connections. Influence of monosubstituted with a force field of a six-membered cycle has local character that is shown in properties of a specific of a number of fluctuations on the frequency and intensity.

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