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VIBRATIONAL SPECTRA OF PHENYLMERCURY COMPOUNDS

J. MINK AND G. VÊGH
Institute of Isotopes of the Hungarian Academy of Sciences, Budapest (Hungary)
YU. A. PENTIN
Department of Chemistry, Moscow State University, Moscow (U.S.S.R.)

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SUMMARY

A study of the vibrational spectra of PhHgX (X = Cl, Br and I), Ph_2Hg and $(C_6D_5)_2Hg$ is reported. A normal coordinate analysis has been performed for in-plane vibrations of PhHgX. The characteristic frequency ranges for the aromatic ring are given for the phenyl derivatives of mercury.

The phenyl derivatives of mercury are among the most extensively investigated organomercuric compounds. Nevertheless, in most experiments investigations have been confined either to a few bands[1-4] or to one of the intervals[5-7] of the IR spectrum. The only reported detailed analyses of the IR spectrum are those of Green[8] and Rodionov *et al.*[9,10].

TABLE 1

EXPERIMENTAL AND CALCULATED FUNDAMENTAL FREQUENCIES OF PHENYLMERCURY DERIVATIVES FOR IN-PLANE VIBRATIONS

Frequency (cm^{-1})										Assignments[a]	
C_6H_5HgCl		C_6H_5HgBr		C_6H_5HgI		$(C_6H_5)_2Hg$		$(C_6D_5)_2Hg$			
Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.[b]	Exp.	Calcd.		
Symmetry species A_1											
3079	3082	3075	3082	3067	3082	3063	3067	2283		ν(CH)	2
3049	3067	3048	3067	3046	3067	3043	3062	2274		ν(CH)	13
3019	3063	3017	3063	3011	3063	3006	3058	2230		ν(CH)	7a
1577	1670	1579	1669	1575	1668	1577	1543	1563		ν(CC)	8a
1481	1516	1481	1516	1478	1515	1478	1521	1353		ν(CC)	19a
1193	1202	1192	1201	1191	1199	1197	1162	865		β(CH)	9a
1093	1142	1096	1141	1095	1137	1081	1056	959		ν(CX)	20a
1019	1025	1017	1025	1014	1025	1023	1019	840		β(CH)	18a
997	985	996	985	995	985	996	980	973		α(CCC)	12
674	666	674	664	671	661	678	654	638		ν(CCX)	1
333	344	257	263	167[c]	174					ν(HgX) (Cl, Br, I)	
220	241	216	204	242	247	255	245	252		α(CCCX)	6a

(*Table continued*)

TABLE 1 (*continued*)

Frequency (cm^{-1})										Assignments[a]	
C_6H_5HgCl		C_6H_5HgBr		C_6H_5HgI		$(C_6H_5)_2Hg$		$(C_6D_5)_2Hg$			
Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.[b]	Exp.	Calcd.		
Symmetry species B_1											
3049	3070	3048	3070	3046	3070	3043	3063	2283		ν(CH)	20b
3019	3061	3017	3061	3011	3061	3006	3057	2256		ν(CH)	7b
1542	1592	1544	1592	1545	1592	1555	1600	1500		ν(CC)	8b
1435	1445	1435	1445	1431	1444	1433	1427	1300		ν(CC)	19b
1331	1326	1331	1326	1328	1326	1316	1389	1267		ν(CC)	14
1304	1292	1304	1292	1300	1291	1297	1263	986		β(CH)	3
1162	1157	1163	1157	1161	1156	1158	1125	949		β(CH)	9b
1064	1073	1064	1073	1063	1073	1066	1038	828		β(CH)	15
614	604	613	604	613	604	617	615	600		α(CCC)	6b
184	223	198	228	213	223	208	230	200		β(CX)	18b
78	45	59	32	51	24		85			δ(CHgX) δ(CHgC)	(X=Cl, Br, I)

[a] The fundamentals of the phenyl groups have been designated using Wilson's notation[20]. [b] Calculated frequencies for a simplified C_6H_5Hg model were taken from ref. 9. [c] Frequency from the Raman spectrum of the crystalline sample.

TABLE 2

EXPERIMENTAL AND CALCULATED FREQUENCIES OF PHENYLMERCURY DERIVATIVES FOR OUT-OF-PLANE VIBRATIONS

Experimental frequencies (cm^{-1})					Calcd.[a] freq. (cm^{-1})	Assignments[b]	
C_6H_5HgCl	C_6H_5HgBr	C_6H_5HgI	$(C_6H_5)_2Hg$	$(C_6D_5)_2Hg$			
Symmetry species A_2							
(970)	(969)	(970)	(963)	875	977	γ(CH)	17a
851	840	845	842	629	817	γ(CH)	10a
393	398	397	397	327	406	γ(CC)	16a
Symmetry species B_2							
987	986	984	982	923	1005	γ(CH)	5
908	908	906	907	743	890	γ(CH)	10b
726	726	724	732, 736	590	738	γ(CH)	11
692	692	692	695	538	685	δ(CC)	4
453	454	451	462	417	468	γ(CH)	17b
180	175	160		(160)	163	δ(CCX)	16b
100	95	87	100			δ'(CHgX) (X=Cl, Br, I) δ'(CHgC)	

[a] Calculated frequencies from ref. 9. [b] The fundamentals of phenyl groups have been designated using Wilson's notation[20].

X-ray data for the phenylmercury halides[11] and diphenylmercury[12,13] indicate the existence of linear CHgX and CHgC skeletons and of a centre of symmetry in diphenylmercury[14]. From an analysis of the vibrational spectra, both the phenylmercury halides and diphenylmercury can be considered as molecules with C_{2v} symmetry.

The IR spectra recorded and discussed in the present report were measured in the crystalline state for PhHgCl, PhHgBr and PhHgI and in solution for Ph_2Hg and $(C_6D_5)_2Hg$ (in CS_2, CCl_4 and C_6H_6) over the range 200–3200 cm^{-1}. Frequencies below 200 cm^{-1} have been taken from other reports[7,8]. The values of the measured fundamental frequencies and their interpretation are given in the Tables 1 and 2.

a. IN-PLANE VIBRATIONS

For the normal coordinate analysis of the in-plane vibrations (symmetry species A_1 and B_1) for the phenylmercury halides the following interatomic distances have been used: $r(C{=}C) = 1.4$ Å $r(C{-}H) = 1.08$ Å, $r(C{-}Hg) = 2.06$, 2.05 and 2.04 Å while for PhHgCl, PhHgBr and PhHgI $r(Hg{-}X) = 2.28$, 2.41 and 2.55 Å respectively, have been employed[11].

The force constants of the benzene ring were taken as those reported in ref. 15 and for the force field around the Hg atom the values obtained for the vinylmercury halides[16] were used. The computed values are in good agreement with the data previously reported[9]. Other than the CH stretching, the CC ring stretching and the 20a type of vibrations, the computed frequencies are in good agreement with the measured frequencies. No refining least-square fit of the force field has been made. The eigen-vectors of the computed frequencies indicate that in addition to the 18b, 6a, 1 and 20a modes (the so-called "X-sensitive" vibrations) the 9a mode is also slightly X-sensitive indicating considerable displacement of the mercury atom. Thus these fundamental frequencies of the benzene ring are weakly affected by the halogen atom.

b. OUT-OF-PLANE VIBRATIONS

The measured out-of-plane vibration frequencies are listed in Table 2. The inactive 10a and 16a type vibrations were observed as weak bands while the 17a type vibration produced a well-defined frequency band suggesting a 5 + 17a combination. In Table 2 the computed frequencies for a simplified C_6H_5Hg model[9] are given. The measured frequencies in the IR spectrum of $(C_6D_5)_2Hg$ (Tables 1 and 2) were assigned by making use of the computed and experimental data on $(C_6D_5)_2Zn$[9] and considering the assignments made for the vibrational spectra of $(C_6D_5)_4Ge$[17].

Spectroscopic data on the vibrations of the phenyl derivatives of mercury reported by different workers[8–10,18,19] have been used for the tabulation of the characteristic fundamental frequencies of the aromatic ring. Table 3 contains all the frequency intervals observed for the 30 fundamental vibrations of the benzene ring in about 15 phenyl derivatives of mercury. The Table can be used for the interpretation of the vibrational spectra of phenyl derivatives of other heavy metals.

It is almost impossible to make any inference from the IR spectra alone regarding the structure of diphenylmercury in solutions. Unfortunately, considerable technical difficulties were encountered in the measurement of the Raman spectra because of the strong fluorescence of Ph_2Hg and $(C_6D_5)_2Hg$, and for this reason the spectra obtained were rather poor.

TABLE 3

CHARACTERISTIC AROMATIC RING VIBRATIONAL FREQUENCIES OF PHENYLMERCURY DERIVATIVES

Number of fundamental[a]	Symmetry for C_{2v}	Vibrational mode	Range of frequencies (cm^{-1})	Intensity[b]
2 (Z_1)	A_1	ν(CH)	3080–3063	w, m
20b (Z_4)	B_1	ν(CH)	3060–3043	w, m
13 (Z_2)	A_1	ν(CH)	3057–3035	m, w
7a (Z_3)	A_1	ν(CH)	3035–3006	w
7b (Z_5)	B_1	ν(CH)	3035–3006	w
8a (*k*)	A_1	ν(CC)	1590–1575	m
8b (*l*)	B_1	ν(CC)	1575–1542	w, m
19a (*m*)	A_1	ν(CC)	1484–1476	s
19b (*n*)	B_1	ν(CC)	1436–1420	s
14 (*o*)	B_1	ν(CC)	1340–1316	m
3 (*e*)	B_1	β(CH)	1310–1297	w
9a (*a*)	A_1	β(CH)	1198–1182	w
9b (*c*)	B_1	β(CH)	1170–1158	w
20a (*q*)	A_1	ν(CX)	1096–1076	w, m
15 (*d*)	B_1	β(CH)	1074–1058	m
18a (*b*)	A_1	β(CH)	1021–1014	m, s
12 (*p*)	A_1	α(CCC)	1009–995	s, m
5 (*j*)	B_2	γ(CH)	989–982	w
17a (*h*)	A_2	γ(CH)	970–963	w, vw
10b (*i*)	B_2	γ(CH)	915–906	m, w
10a (*g*)	A_2	γ(CH)	860–840	w
11 (*f*)	B_2	γ(CH)	736–722	vs
4 (*v*)	B_2	δ(CC)	700–692	vs, s
1 (*r*)	A_1	ν(CCX)	678–660	m
6b (*s*)	B_1	α(CCC)	618–611	w
17b (*y*)	B_2	γ(CX)	462–450	s, vs
16a (*w*)	A_2	δ(CC)	398–396	vw
6a (*t*)	A_1	α(CCCX)	255–220	s, m, w
18b (*u*)	B_1	β(CX)	213–184	m
16b (x)	B_2	δ(CCX)	180–160	s, m

[a] The fundamentals have been designated using Wilson's notation[20] and using Randle and Whiffen's notation[21] (in parentheses). [b] Intensities: s, strong; m, medium; w, weak; v, very.

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