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THE VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF TETRACYCLOPROPYLLEAD

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Summary

All the fundamental frequencies observed in IR and Raman spectra have been assigned to the normal modes of the molecule $(C_3H_5)_4Pb$ (C_3H_5 = cyclopropyl). The calculated force field is compared to that of $(C_3H_5)_2Hg$ and the C—metal stretching force constants are discussed along with those of Me_4Pb and Me_2Hg; The similarity of the spectra of cyclopropyllead and cyclopropylmercury proves that the vibrations of cyclopropyl structural units are isolated in both molecules.

Introduction

The molecular spectra of the cyclopropyl derivatives of Al [1], Ga, In [2] and also Sn and Hg [2,3], have been studied previously. Tetracyclopropyllead (Cpr_4Pb), obtained by Juenge and Houser [4] in 1964, has not yet been investigated by vibrational spectroscopic methods, and so we have examined its IR and Raman spectra, assigned the normal modes, and derived the force field parameters. To aid in the assignments the results of vibrational analysis of dicyclopropylmercury (Cpr_2Hg) and of tetramethyllead (Me_4Pb) have been used.

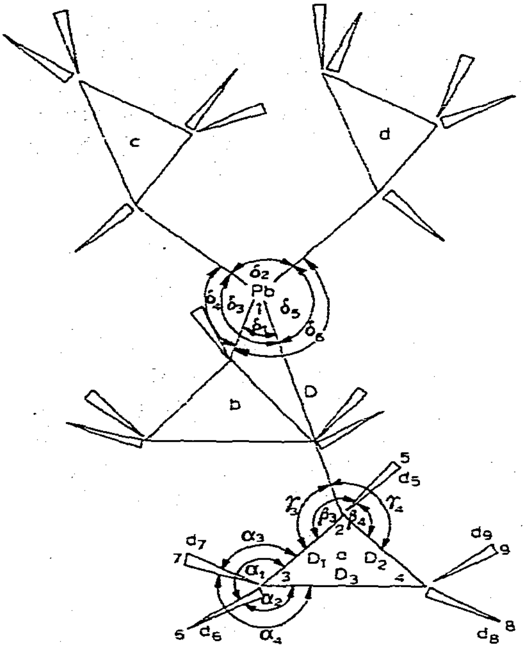
Experimental

Tetracyclopropyllead was made from cyclopropylmagnesium bromide and $PbCl_2$ in THF [4]. It was distilled from the reaction vessel during 50 h at 90°C, and redistilled at 50°C and 10^{-2} mmHg; n_D^{20} 1.5510. Its mass spectrum, measured on an LBK 9000 S spectrometer at 70 eV, showed fragmentation patterns showing the spacing of the groups of lines corresponding to the cyclopropyl molecular weight and the splitting of the four cyclopropyl units: viz. 372, 331, 290, 249, 208 and 41.

The IR spectra of the 0.017 mm films were obtained with a Zeiss UR-20 spectrophotometer in the range 4000—400 cm^{-1}, using LiF, NaCl and KBr prisms in the regions 4000—2800, 2800—750 and 740—400 cm^{-1}, respectively. The raman spectra, taken on samples sealed in a capillary tube, were measured on a Cary-82 laser (4860 Å, 60 mW) instrument within the range of 4000—0 cm^{-1}.

Theoretical treatment

The vibrational analysis was based on the standard GF matrix method of Wilson. The Cpr$_4$Pb molecule, containing 33 atoms, has 93 vibrational degrees of freedom, with a symmetry depending on the mutual steric position of the cyclopropyl units, the highest possible symmetry being D_{2d}, corresponding to the ring arrangement shown in Fig. 1. The 89 normal modes are distributed between irreducible representations of the D_{2d} group according to the formula $\Gamma = 13\,A_1 + 9\,A_2 + 13\,B_1 + 10\,B_2 + 22\,E$. The B_2 and E representations are IR-active and result in 32 IR-active modes; the A_1, B_1, B_2 and E representations ar Raman-active and are reflected in 58 active modes.



$$s_3 = \tfrac{1}{2}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)$$
$$t_3 = \tfrac{1}{2}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4)$$
$$w_3 = \tfrac{1}{2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)$$
$$r_3 = \tfrac{1}{2}(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4)$$

Fig. 1. The internal coordinates of the Cpr$_4$Pb molecule.

TABLE 1

STRUCTURAL PARAMETERS OF Cpr_4Pb

Bond	Length (Å)	Angle	Degrees
C—Pb	2.303	C—C—C	60
C—C	1.514	H—C—Pb	116.5
C—H	1.082	H—C—C	117.12
		H—C—H	116.5
		C—Pb—C	109.48

The structural data for Cpr_4Pb necessary for constructing the G matrix, listed in Tab. 1 (see also Fig. 1), were derived from the geometric parameters of Cpr_2Hg and Me_4Pb molecules, for the cyclopropyl unit and the C—Pb bond. The 36 stretching coordinates, i.e. the 4 stretching C—Pb, 12 stretching C—C and 20 stretching C—H, as well as the 54 angle deformation coordinates, form the internal coordinates set. The deformational coordinates include 6 deformational C—Pb—C, 8 deformational Pb—C—H and 40 deformational C—C—H coordinates. The total of 90 internal coordinates also comprises one redundant coordinate belonging to the set of six of the deformational C—Pb—C type. The choice of coordinates for the cyclopropyl unit was made as before [5] and in a manner very similar to that used by Duncan in his work on cyclopropane [6]. The numbering of internal coordinates and their relations with the symmetry coordinates are shown in Fig. 1 and in Tab. 2.

The choice of the force field was made as follows. For the initial force field of the cyclopropyl ring the values estimated for Cpr_2Hg [5] were used these are similar to those used by Duncan [6] for cyclopropane. The force field for the structural fragment containing the Pb centre was taken to be the same as that in Me_4Pb [7], the calculations were performed using the authors' VIBRAN program written for the ODRA-1204 computer.

The results of calculations of the initial force field are listed in Tab. 4. To achieve better agreement with the experimental data a convergence of the theoret-

TABLE 2

SYMMETRY COORDINATES OF Cpr_4Pb

The symbols of the internal coordinates relate to Fig. 1.

s_1	$Da \mp Db \mp Dc \mp Dd$
s_2	$D_{1a} \mp D_{1b} \mp D_{1c} \mp D_{1d} \mp D_{2a} \pm D_{2b} \mp D_{2c} \mp D_{2d}$
s_3	$D_{3a} \mp D_{3b} \mp D_{3c} \mp D_{3d}$
s_4	$d_{5a} \mp d_{5b} \mp d_{5c} \mp d_{5d}$
s_5	$d_{6a} \mp d_{6b} \mp d_{6c} \pm d_{6d} \mp d_{8a} \mp d_{8b} \mp d_{8c} \mp d_{8d}$
s_6	$d_{7a} \mp d_{7b} \mp d_{7c} \pm d_{7d} \mp d_{9a} \mp d_{9b} \mp d_{9c} \mp d_{9d}$
s_7	$\delta_1 \mp \delta_2$
s_8	$\delta_3 \mp \delta_4 \mp \delta_5 \mp \delta_6$
s_9	$\gamma_{3a} \pm \gamma_{3b} \mp \gamma_{3c} \mp \gamma_{3d} \pm \gamma_{4a} \mp \gamma_{4b} \mp \gamma_{4c} \mp \gamma_{4d}$
s_{10}	$\beta_{3a} \mp \beta_{3c} \mp \beta_{3b} \mp \beta_{3d} \mp \beta_{4a} \mp \beta_{4b} \mp \beta_{4c} \mp \beta_{4d}$
s_{11}	$s_{3a} \mp s_{3b} \mp s_{3c} \mp s_{3d} \pm s_{4a} \mp s_{4b} \mp s_{4c} \mp s_{4d}$
s_{12}	$t_{3a} \mp t_{3b} \mp t_{3c} \mp t_{3d} \pm t_{4a} \pm t_{4b} \mp t_{4c} \mp t_{4d}$
s_{13}	$w_{3a} \mp w_{3b} \mp w_{3c} \mp w_{3d} \mp w_{4a} \mp w_{4b} \pm w_{4c} \mp w_{4d}$
s_{14}	$r_{3a} \mp r_{3b} \mp r_{3c} \mp r_{3d} \mp r_{4a} \pm r_{4b} \mp r_{4c} \mp r_{4d}$

TABLE 3

EXPERIMENTAL AND CALCULATED FREQUENCIES FOR THE Cpr_4Pb MOLECULE D_{2d} (cm^{-1}) AND THEIR POTENTIAL ENERGY DISTRIBUTION VALUES

Experimental		Calculated			PED values
Raman	IR	Initial	Final	Sym.	
3066	3067	3009	3025	B_2	$50s_5$, $49s_6$
3066	—	3009	3025	A_1	$50s_5$, $49s_6$
3066	3067	3009	3025	E	$50s_5$, $49s_6$
2998	3003	2992	3009	E	$52s_5$, $46s_6$
2998	—	2992	3009	B_1	$52s_5$, $45s_6$
—	—	2992	3009	A_2	$52s_5$, $45s_6$
2907	2900	2975	2932	A_1	$50s_6$, $49s_5$
	2900	2975	2832	B_2	$50s_6$, $49s_5$
		2975	2932	E	$50s_6$, $49s_5$
2907	2900	2941	2928	E	$54s_6$, $46s_5$
—	—	2927	2928	A_2	$52s_6$, $45s_5$
2907	—	2927	2928	B_1	$52s_6$, $45s_5$
2862	2863	2941	2875	B_2	$98s_4$
2862	—	2941	2875	A_1	$98s_4$
2862	2863	2927	2875	E	$99s_4$
1458	—	1430	1467	A_1	$45s_{11}$, $41s_{10}$
1458	1461	1428	1467	B_2	$45s_{11}$, $41s_{10}$
1458	1461	1429	1466	E	$46s_{11}$, $43s_{10}$
1437	1439	1378	1451	E	$45s_{11}$, $25s_{13}$
—	—	1378	1451	A_2	$60s_{11}$
1437	—	1378	1451	B_1	$61s_{11}$
		1310	1363	E	$25s_{10}$, $23s_{12}$, $8s_2$
		1310	1363	B_2	$30s_{11}$, $25s_{12}$, $20s_{10}$
	—	1310	1361	A_1	$30s_{11}$, $25s_{12}$, $20s_{10}$
1229	1232	1188	1244	E	$22s_{10}$, $19s_{13}$, $12s_2$
—	—	1140	1244	A_2	$32s_{10}$, $25s_{14}$
1229	—	1140	1244	B_1	$32s_{10}$, $25s_{14}$
1193	—	1191	1192	A_1	$63s_2$, $27s_3$
	1190	1185	1187	B_2	$62s_2$, $27s_3$
1193	1190	1140	1186	E	$63s_2$, $28s_3$
	1105	1006	1169	B_2	$28s_{10}$, $23s_{12}$, $17s_{11}$
	—	1006	1169	A_1	$28s_{10}$, $23s_{11}$, $19s_{21}$
	1105	1179	1169	E	$28s_{12}$, $25s_{13}$
1053	1057	1024	1097	E	$25s_{13}$, $13s_{10}$, $12s_{12}$
—	—	1079	1098	A_2	$29s_{12}$, $28s_{13}$, $21s_{10}$
1053	—	1080	1096	B_1	$29s_{12}$, $28s_{13}$, $21s_{10}$
1028	1031	1006	1037	E	$27s_{12}$, $27s_{13}$
—	—	1024	1037	A_2	$38s_{13}$, $25s_{12}$, $12s_{10}$
1028	—	1024	1037	B_1	$38s_{13}$, $25s_{12}$, $12s_{10}$
994	998	954	984	E	$30s_{14}$, $25s_{12}$, $22s_{13}$
994	998	954	984	B_2	$27s_{13}$, $25s_{12}$, $22s_{14}$
994	—	954	984	A_1	$27s_{13}$, $25s_{12}$, $22s_{14}$
862	—	900	885	A_1	$60s_{14}$
862	870	891	882	B_2	$60s_{14}$
862	870	896	882	E	$54s_3$, $27s_2$
862	—	756	874	A_1	$43s_3$, $22s_2$
862	870	756	870	B_2	$51s_3$, $26s_2$
862	870	890	869	E	$54s_3$, $27s_2$
—	—	890	814	A_2	$36s_2$, $32s_{10}$
812	—	893	814	B_1	$35s_{10}$, $33s_2$
812	813	778	814	E	$60s_{10}$, $35s_2$
—	—	782	791	A_2	$45s_2$, $29s_{14}$
784	790	756	790	E	$50s_2$, $29s_{14}$
784	—	778	778	B_1	$48s_2$, $29s_{14}$

Table continued

TABLE 3 (continued)

Experimental		Calculated			PED values
Raman	IR	Initial	Final	Sym.	
460	458	385	458	B_2	$61s_1$, $30s_9$
460	440	380	455	E	$57s_1$, $35s_9$
441	—	368	431	A_1	$61s_1$, $31s_9$
270	—	211	244	A_1	$75s_9$
256		219	226	B_2	$56s_9$
225		211	224	E	$62s_9$, $33s_1$
—	—	135	131	A_2	$47s_9$, $44s_{10}$
196		147	116	E	$58s_9$, $24s_8$
	—	157	99	B_1	$82s_9$
	—	67	58	B_1	$52s_{10}$, $36s_8$
		51	56	B_2	$55s_7$, $41s_8$
		57	53	E	$54s_8$, $29s_9$
	—	55	50	A_1	$87s_7$

ical and experimental frequencies was carried out. A modification of some force constants was allowed, particularly of those most susceptible to perturbation (see the procedure described in ref. 5). The iteration was ended when the rate of convergence appeared to be negligible at an acceptable level of change in the force constants. The frequency values for the final force field parameters are listed in Tab. 3. The L matrix elements and the PED values were used to interpret the respective frequencies, the latter being given for the most characteristic symmetry coordinates.

Results and discussion

In spite of the large number of degrees of freedom, because of the high symmetry of the Cpr_4Pb molecule, the Raman and IR spectra are very clear; they show only a limited number of bands, about 20 in both types of the spectrum. This corresponds approximately to the number of modes in one cyclopropyl unit, and proves that the corresponding frequencies in the various cyclopropyl rings have the same value. A similar feature was observed in the spectra of Cpr_2Hg [5]. Both the IR and Raman spectra of Cpr_4Pb and Cpr_2Hg show strong similarity, which can be explained by assuming: (i) a very limited influence of the metal atom on the vibrations of the cyclopropyl group and/or (ii) a lack of interaction between the cyclopropyl rings. The latter case would result in the remarkable similarity between the spectra of the molecules containing two and four cyclopropyl rings. One would then expect that for Cp_4Pb every observed band corresponds to four normal modes.

C—H stretching vibrations. In the region of ca. 3000 cm^{-1}, the four well shaped bands having almost the same frequencies in Raman and in IR: appear at 3066, 2998, 2907, 2862 cm^{-1} (3067, 3003, 2900, 2863 cm^{-1}, the IR frequencies are always given in parentheses, unless otherwise stated). The 3066 cm^{-1} band contains a shoulder on its longwave side, while the (2863 cm^{-1}) band, in more precise measurements was found to be a doublet. The twenty C—H normal modes are expected in this region, as they are arranged in five groups corresponding to

TABLE 4

VALENCE FORCE FIELD CONSTANTS FOR THE Cpr_4Pb MOLECULE

Diagonal			Interaction			Interaction		
Stretching (mdyn/Å)			Stretching—bending (mdyn)			Bending—bending (erg X 10^{-11})		
Type of force const.	Initial	Final	Type of force const.	Initial	Final	Type of force const.	Initial	Final
C—Pb	1,9000	1,9531	C—Pb/CPbC	0,2000	0,1332	C(2a)PbC(2b)/C(2a)PbC(2a)	0,0500	0,0511
C(2)—C(3)	4,2900	4,0959	C—Pb/CPbC	0,0500	0,0511	C(2a)PbC(2b)/C(2c)PbC(2b)	0,0500	0,0536
C(2)—H(5)	5,1700	4,8575	C—Pb/PbCC	0,2500	0,1358	C(2a)PbC(2b)/PbC(2)C(3)	0,0500	0,0599
C(3)—C(4)	4,2907	4,1165	C(2)—H(5)/H(5)C(2)C(3)	0,3200	0,3582	C(2c)PbC(2d)/H(5)C(2)C(3)	0,0000	−0,0044
C(3)—H(6)	5,1675	5,2166	C(2)—C(3)/H(6)C(3)C(2)	0,3200	0,4198	PbC(2)C(3)/H(5)C(2)C(3)	0,1000	0,2644
			C(3)—C(4)/H(6)C(3)C(4)	0,3166	0,3166	PbC(2a)C(3a)/PbC(2b)C(3b)	0,0000	0,0005
Bending (erg X 10^{-11})			C(2)—C(3)/H(5)C(2)C(4)	−0,0600	0,0502	PbC(2)C(3)/H(5)C(2)C(3)	0,0500	0,1350
			C(2)—C(3)/H(6)C(3)C(4)	−0,0584	−0,0584	PbC(2)C(3)/H(6)C(3)C(2)	0,0500	−0,0194
H(5)C(2)C(3)	0,8400	0,7950	C(3)—C(4)/H(6)C(3)C(2)	−0,0584	−0,0584	PbC(2)C(3)/H(5)C(2)C(4)	0,0000	0,0100
H(6)C(3)C(2)	0,8400	0,8986	C(2)—C(3)/H(8)C(4)C(2)	−0,0700	−0,1089	PbC(2)C(3)/H(8)C(4)C(2)	0,0000	0,0100
CPbC	0,3000	0,2925	C(2)—C(3)/H(8)C(4)C(3)	−0,0679	−0,0679	PbC(2)C(3)/H(7)C(2)C(4)	0,0000	−0,0060
PbCC	0,4000	0,4560	C(3)—C(4)/H(5)C(2)C(3)	−0,0679	−0,0679	PbC(2)C(3)/H(9)C(4)C(3)	0,0000	0,0080
H(6)C(3)C(4)	0,8388	0,9901	C(2)—H(5)/H(5)C(2)C(3)	−0,0400	0,0197	H(5)C(2)C(3)/H(5)C(2)C(4)	−0,1700	0,0497
			C(3)—H(6)/H(6)C(3)C(2)	−0,0363	−0,0363	H(6)C(3)C(2)/H(7)C(3)C(2)	−0,0661	−0,0661
Interaction			C(3)—H(6)/H(7)C(3)C(2)	−0,0363	−0,0363	H(6)C(3)C(4)/H(7)C(3)C(4)	0,1558	0,1558
			C(2)—H(5)/H(6)C(3)C(2)	0,0521	0,0521	H(6)C(3)C(4)/H(8)C(4)C(3)	−0,0661	−0,0661
Stretching—stretching (mdyn/Å)			C(3)—H(6)/H(5)C(2)C(3)	0,0521	0,0521	H(6)C(3)C(2)/H(6)C(3)C(4)	−0,1700	−0,1700
C—Pb/C—Pb	0,1500	0,1396	C(3)—H(6)/H(5)C(2)C(4)	−0,0521	−0,0521	H(5)C(2)C(3)/H(6)C(3)C(4)	0,0356	0,0356
Pb—C/C(2)—C(3)	0,1000	0,1742	C(2)—C(3)/PbC(2)C(3)	0,2000	0,2267	H(5)C(2)C(3)/H(8)C(4)C(3)	0,0114	0,0114
C(2)—C(3)/C(2)—C(4)	−0,1500	−0,0275	C(2)—C(3)/H(5)C(2)C(3)	0,0000	−0,0100	H(5)C(2)C(3)/H(8)C(4)C(2)	0,0356	0,0356
C(2)—C(3)/C(3)—C(4)	−0,1483	−0,1166	C(3)—C(4)/PbC(2)C(3)	0,0000	−0,0069	H(6)C(3)C(2)/H(7)C(3)C(4)	0,1650	0,1650
C—Pb/C(2)—H(5)	0,0300	0,0348	C(2)—H(5)/PbC(2)C(3)	0,0000	−0,0100	H(6)C(3)C(2)/H(8)C(4)C(2)	0,0114	0,0114
C(2)—C(3)/C(2)—H(5)	0,0900	0,1906	C(2)—H(6)/PbC(2)C(3)	0,0000	−0,0100	H(6)C(3)C(2)/H(8)C(4)C(3)	0,0356	0,0356
C(2)—C(3)/C(3)—H(6)	0,0948	0,3728	C(3)—H(6)/H(5)C(2)C(3)	0,0000	−0,0100			
C(3)—C(4)/C(3)—H(6)	0,0948	0,2636	Pb—C/H(5)C(2)C(3)	0,0000	−0,0100			
C(2)—H(5)/C(3)—H(6)	0,0370	0,0370	Pb—C/H(6)C(3)C(2)	0,0000	0,0063			
C(2)—H(5)/C(3)—H(7)	−0,0033	−0,0033	Pb—C/H(6)C(3)C(4)	0,0000	0,0076			
C(3)—H(6)/C(4)—H(8)	0,0370	0,0370						
C(3)—H(6)/C(3)—H(7)	0,0370	0,0982						
C(3)—H(6)/C(4)—H(9)	−0,0033	−0,0033						
C(2)—C(3)/C(4)—H(8)	0,0000	0,0000						

the C—H modes of the cyclopropyl unit. The shift of some bands towards lower frequencies, by ca. 150 cm^{-1} with respect to cyclopropane, is almost the same as with Cpr$_2$Hg. The vibrational analysis of the species in question alone is of no help in assigning a shifted band to a mode of the proper C—H bonds. It seems, however, that the bond most susceptible to perturbation is α-CH, with its vibrations ascribed to the lowest band, i.e. to 2862 (2863) cm^{-1}. The mode in question is isolated, so it does not mix with the modes of other C—H bonds remaining within the cyclopropyl unit. Some authors [2,8] consider this as an overtone of the 1430 cm^{-1} band, but its intensity seems much too high for this.

C—H deformational and C—C skeletal vibrations. The highest frequency in this region corresponds to the scissoring motion of CH$_2$ in cyclopropane. All Cpr$_4$Pb frequencies above 1400 cm^{-1} have therefore been identified as scissoring. The frequency at 1458 (1461) cm^{-1} originates in their symmetric combination; when one takes into account the two CH$_2$ groups in the cyclopropyl unit, scissoring contributes ca. 40%, with the lower frequency, at 1437 (1439) cm^{-1}, corresponding to their asymmetric combination. In the former band the α-CH deformation mode also participates with a significance value of 40%. The next band, at 1229 (1232) cm^{-1}, is assigned to the mode composed of both the deformational symmetrical α-CH bond mode and the deformational vibrations of the β-CH$_2$ groups, the former being predominant. It is noteworthy that every experimental maximum corresponds to the four normal modes which represent the same frequency, two of them degenerate as a result of symmetry. The next band observed at 1193 (1190) cm^{-1} presents a purely skeletal stretching vibration,

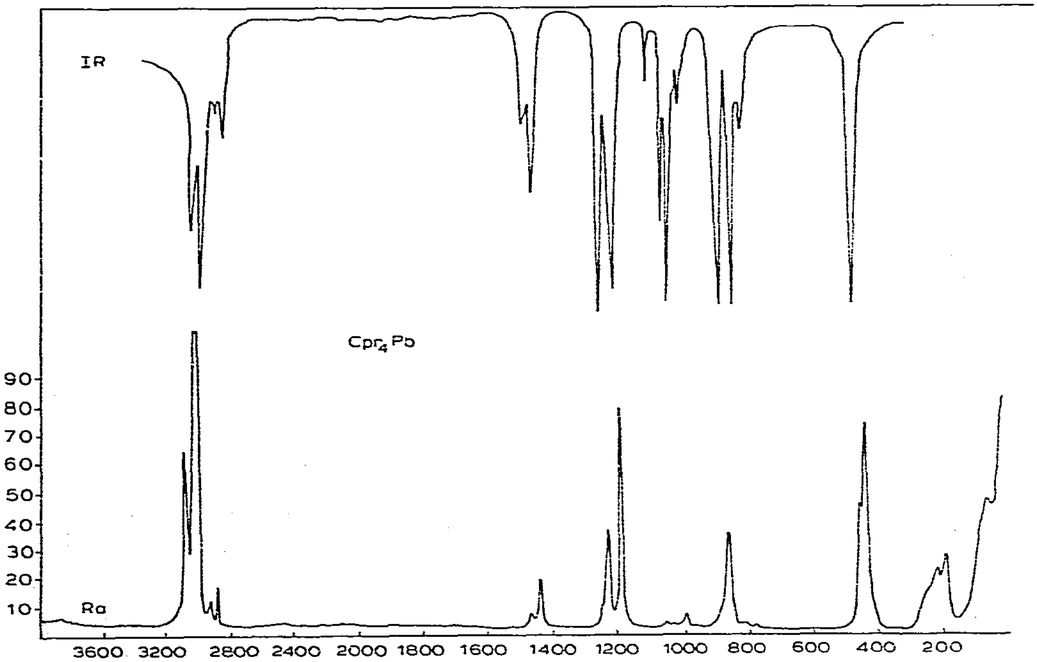


Fig. 2. The IR and Raman spectra of Cpr$_4$Pb.

contribution being as much as 91%. The characteristic feature of the cyclopropyl unit vibrations is the absence of well separated twisting modes. Usually these twisting modes participate in the other deformation modes of the CH_2 group, i.e., in those of the wagging and rocking type; they also mix with those of the deformational type involving the α-CH bond. Such a feature is also typical of the (1105 cm^{-1}) band, as its vibrations show a significant contribution not only of twisting modes but also of α-CH deformations. The latter do not exhibit any characteristic frequency either, but usually mix with other deformational modes. The next bands appearing both in Raman and in IR, at 1053 (1057) cm^{-1} and at 1028 (1031) cm^{-1}, are interpreted mainly as the wagging modes. The neighbouring 994 (998) cm^{-1} band is highly delocalized over the entire cyclopropyl ring and corresponds to the wagging, twisting and rocking modes, participating in 22, 25 and 30%, respectively. The 862 (870) cm^{-1} band exhibits the character of the deformational skeletal mode of the cyclopropyl ring; a similar mode in Cpr_2Hg appears at a slightly lower frequency, i.e. at 835 cm^{-1}. The range near 800 cm^{-1}, which contains the two bands at 812 (813) cm^{-1} and 784 (790) cm^{-1}, is typical of the rocking modes, although these of the skeletal deformational type also participate in it to some extent.

The bands in the 1450—750 cm^{-1} region, show no frequencies representing a higher degree of character distinction. The calculations show that the higher frequency modes refer to scissoring, while those of the lowest frequency relate to the rocking modes, very much as in the cyclopropane molecule.

The skeletal modes of the $Pb(C)_4$ structural fragment. In this region no accidental degeneration of frequency, so common in the region containing characteristic cyclopropyl unit frequencies, was observed. The interactions among the internal coordinates of the $Pb(C)_4$ fragment, both kinetic and dynamic, are strong enough to cause the splitting of the band. Particular attention should be paid to the intense band at 441 (458) cm^{-1}. It shows an absorption shoulder both in the Raman and in IR which allow observation of the two C—Pb stretchin modes which helps in drawing conclusions regarding the symmetry of the Cpr_4Pb molecule. The region under consideration also includes the deformational modes of the C—C—Pb angle, with the 8 coordinates corresponding to the 8 normal modes of the frequencies calculated between 244 and 100 cm^{-1}. The four maxim were observed in this region experimentally, three of them belonging to the same broad band; the possibility could not be excluded, therefore, that this region might contain some additional maxima as well. Unfortunately we have no experimental IR data for this region. The assignment of Raman bands to the proper normal modes is difficult. Assuming D_{2d} symmetry, the modes allowed in this region were as follows: 244, 226, 224 and 116 cm^{-1}. Torsional modes should appear there as well, arising from both the rotation of the cyclopropyl rings around the C—Pb bonds and the C—Pb—C angle deformation. The frequencies of the latter are similar to those in Cpr_2Hg [5] below 100 cm^{-1}. Although it was easy to interpret the observed maxima in the range above 300 cm^{-1} for the mercury compound, it was much more difficult in the case of the Cpr_4Pb molecule. The corresponding assignments, presented above, are this to some extent hypothetical.

The force field. Of the 78 force constants introduced, 48 were kept constant and equal to the corresponding values for the cyclopropane molecule. After modification the force constants have values rather close to those in the initial stages, confirming the correct choice of the stretching force field.

Most conspicuous is the change in the α-CH stretching force constant. In cyclopropane it is equal to 5.217 mdyn/Å, the same value characteristic in Cpr_4Pb with the β-CH bond. However, in the case of α-CH it decreases to 4.858 mdyn/Å. Modification in the stretching force constant of the C—C bond adjacent to C—Pb also appeared necessary, since it was 4.096 mdyn/Å, compared with 4.291 mdyn/Å for cyclopropane. The decrease in the stretching force constant of the C—C bond opposite to the α-C atom was not as marked, $f = 4.117$ mdyn/Å. Changes also appear in the diagonal force constants for the angle coordinates $C—C_\alpha—H$ when compared with those corresponding to $C—C_\beta—H$ and to cyclopropane. The respective values are: 0.795, 0.898 and 0.840 mdyn/Å.

The C—Pb bond interacts with only one adjacent C—H bond and with the three C—C bonds. The respective values are: 0.035 (with CH), 0.179 (with adjacent CC), and —0.007 mdyn/Å (with opposite CC). The initial stretching C—Pb force constant, 1.900 mdyn/Å, had to be modified to 1.953 mdyn/Å. It then became higher than the corresponding force constant in the Me_4Pb molecule by 0.053. The values for Cpr_2Hg and Me_2Hg [7] are equal to 2.091 and 1.920 mdyn/Å. Assuming that the value of the force constant is related to the bond strength, the latter would increase for the compounds under consideration in the following order: $Me_4Pb < Me_2Hg < Cpr_4Pb < Cpr_2Hg$.

The force constants referring to the interaction between the stretching C—metal—C—metal coordinates, and to the interaction of the latter with the bending C—metal—C coordinates, should also be mentioned. Their values for the cyclopropyl derivatives of lead are, respectively, 0.137 mdyn/Å, 0.133 mdyn (for that of mercury: 0.075 mdyn/Å and 0.00 mdyn [5]). The C—Pb bond appears to be less covalent in the Cpr_4Pb molecule than is the C—Hg bond in Cpr_2Hg, taking into account the corresponding stretching force constants. The more limited stability of the former compound supports this opinion. A quantum chemical analysis of this problem would be useful and, although the necessity of considering the participation of the *d*- and *f*-type orbitals of the metal creates difficulties the calculations are now in progress in this laboratory.

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