Vibrational analysis of lead(II) phenylphosphonate Pb(O₃PC₆H₅)

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Abstract : The FT IR and FT Raman spectra of lead(II) phenylphosphonate, Pb(O₃PC₆H₅) are recorded and analysed based on the vibrations of O₃PC₆H₅. All the characteristic IR and Raman bands are identified The activation of the IR inactive phenyl ring out-of-plane deformation mode 20a indicates the lower site symmetry of the phenyl phosphonate, O₃PC₆H₅ group in the crystal lattice Strong hydrogen bonding is identified between the lone pairs of the CPO₃ tetrahedron and the hydrogen atom at a corner of the phenyl ring.

The authors are interested in the study of the vibrational spectra of phosphate compounds [1–6]. In the present investigation, the IR and Raman spectra of a new lead(II) phenylphosphonate, Pb(O₃PC₆H₅) are analysed to understand the symmetry of the vibrating groups and the various bondings in the crystal.

The polycrystalline sample of Pb(O₃PC₆H₅) was prepared by slow addition of a solution of phenylphosphonic acid (1 M) over a solution of lead(II) acetate (0.1 M) to a final P : Pb molar ratio of 1 : 3. The precipitate was refluxed for one week. The white powder was filtered, washed with water and air dried [7]. The IR and Raman spectra of the polycrystalline sample were recorded using a Bruker IFS 66V FT-IR/FT-Raman Spectrometer. The Raman spectrum over the range 50–3500 cm⁻¹ was recorded using a Nd:YAG laser at wavelength 1.064 μm and power 200 mW at a resolution of 4 cm⁻¹. The IR spectrum was also recorded at

a resolution of 4 cm⁻¹, over the range 400–4000 cm⁻¹ with the sample as KBr pellets using a globar source.

The X-ray powder diffraction data reveals that the compound crystallizes in the triclinic system with space group $P\bar{1}(C_i^1)$, having four formula units per unit cell [7]. Factor group analysis using the standard correlation method [8], with the phenylphosphonate group having C_{2v} symmetry in the general site C_1, predicts 189 modes (excluding acoustic modes). The irreducible representations are

$$\Gamma_{Pb(O_3PC_6H_5)} = 96A_g(R) + 93A_u(IR).$$

The IR and Raman spectra of the compound under investigation, are interpreted mainly on the basis of the characteristic vibrations of monosubstituted benzene ring and PO₃ group. The observed wavenumbers (cm⁻¹), their relative intensities and the assignments of the bands are given in Table 1.

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Table 1. Spectral data (cm⁻¹) and band assignments of Pb(O₃PC₆H₅).

Raman	IR	Assignments
3187 m		2(νCC 16a)
3144 m		2(νCC 16b)
3072 vs	3076 sh	νCH 12b(B₂)
3057 vvs	3051 w	νCH 1(A₁)
	3017 vvw	νCH 15b(B₂)
	2966 sh	νCC 13a+2(γCH 4)
	2924 w	2(νCC 13a)
2881 mbr		
2551 mbr	2854 vw	trio bands
2200 wbr		
2050 wbr		
	1971 vvw	δCC 6+γCH 7
	1743 vvw	δCH 14a+γCC 8
1594 s	1613 wbr	νCC 16a (A₁)
1572 m		νCC 16b(B₂)
	1544 vvw	ν_sPO₃ + δPO₃
1483 vvw		νCC 13a(A₁)
	1466 sh	γCH 4+γCC 8
1434 vvw	1436 w	νCC 13b(B₂)
1376 vvw		νCC 9(B₂)
	1333 vvwbr	γCH 4+δPO₃
	1250 vw	δCH 3(B₂)/νP=O
	1214 vw	
1183 w		δCH 17a(A₁)
1158 m		δCH 17b(B₂)
1137 s	1135 s	νCP 15a(A₁)
1076 vw	1085 vs	ν_{as}PO₃/δCH 10(B₂)
1048 sh	1061 vs	
1032 s	1024 vvs	δCH 14a(A₁)
1001 vs		δCC 6 (A₁)
976 vs	971 vs	ν_sPO₃/γCH 7(B₁)
857 vw		γCH 11a(A₂)
	750 m	γCH 4(B₁)
718 m	712 m	γCC 8(B₁)
	700 m	
619 w		δCC 18b(B₂)
	579 s	
559 vw	563 s	δPO₃
538 vw	543 s	
520 vw	517 sh	
457 vw		γCC 20b(B₁)
441 vw	448·ɣw	δCC 18a(A₁)
407 vvw	415 vw	γCC 20a(A₂)
359 vw		
328 vw		
314 vw		νPb—O
299 w		
240 vw		δCP 14b(B₂)
216 w		γCP 11b(B₁)
164 vs		
136 vs		External modes
111 vs		
84 vs		

Relative intensities : v–very; s–strong; m–medium; w–weak; sh–shoulder; br–broad.

The phenylphosphonate group contains fifteen atoms giving rise to thirty nine normal modes of vibrations. The distribution of the normal modes of vibrations of the group belonging to the C_{2v} symmetry [9] is $12A_1 + 7A_2 + 9B_1 +$ $11B_2$. The normal modes associated with the phenyl ring are numbered using Herzberg's notation [10,11].

In the present investigation, the high wavenumber side of the Raman spectrum shows a very broad medium intense band extending from ~2310 cm⁻¹ to ~3400 cm⁻¹ with very prominent peaks at 3057 and 3072 cm⁻¹. These are assigned to the νCH 1(A₁) and νCH 12b(B₂) modes of CH stretching vibrations. In the IR spectrum the band at 3076 cm⁻¹ appears as a shoulder to the weak absorption band at 3051 cm⁻¹. The very weak absorption band at 3017 cm⁻¹ is due to the νCH 15b(B₂) mode of vibration. The Raman bands at 3187 and 3144 cm⁻¹, on the broad medium intense band, may be due to the overtones of the ring stretching vibrations νCC 16a and νCC 16b [12].

The ring stretching mode νCC 16 that appears around 1600 cm⁻¹ has two components in substituted benzenes. In the Raman spectrum, the strong band at 1594 cm⁻¹ and the medium intense band at 1572 cm⁻¹ are due to the 16a(A₁) and 16b(B₂) vibrations, respectively [13,14]. The ring stretching vibrations νCC 13a and νCC 13b are also good group vibrations like 16a and 16b. The doublet observed in the range 1434–1483 cm⁻¹ in the Raman spectrum is assigned to these modes. The fifth ring stretching mode νCC 9 appears as very weak band around 1376 cm⁻¹.

In the absorption spectrum, the CH in-plane deformation mode δCH 3(B₂) appears to be broadened and have two components at 1250 and 1214 cm⁻¹. The very intense absorption band at 1024 cm⁻¹ is assigned to the CH in-plane deformation mode δCH 14a. In monosubstituted benzenes, the 6(A₁) mode due to the phenyl ring in-plane trigonal deformation δCC is very intense in Raman and is an excellent group frequency. As expected, this mode is observed as a highly intense band at 1001 cm⁻¹ in the Raman spectrum and is absent in the IR spectrum. As expected, the two characteristic Raman bands of a monosubstituted benzene ring, viz., the δCC 18b(B₂) and γCC 20a(A₂) modes are observed at 619 and 407 cm⁻¹, respectively. In the IR spectrum, the 20a mode is observed as a weak band at 415 cm⁻¹. The activation of this IR inactive mode indicates the lower site symmetry of the benzene ring in the lattice [15].

The out-of-plane CH deformation mode γCH 4(B₁) near 770 cm⁻¹ and the out-of-plane ring deformation γCC 8(B₁) absorbing near 690 cm⁻¹ usually form a pair of strong absorption bands, characteristic of mono-substituted benzenes. In the present study, medium intense bands are observed in this region. The absorption band at 750 cm⁻¹ is assigned to

mode $4(B_1)$ and the bands at 712 and 700 cm⁻¹ are assigned to the vibration $8(B_1)$.

The asymmetric stretching of PO_3 is a doublet in both IR and Raman spectra. The symmetric stretching vibration causes very strong bands in both the IR (971 cm⁻¹) and the Raman (976 cm⁻¹) spectra. The CH out-of-plane deformation mode γCH $7(B_1)$ also occur in this region. The bending vibrations are observed in the region 579–517 cm⁻¹. In this range, the IR spectrum shows four components and the Raman spectrum shows three components. This multiplicity of bands observed for the deformation mode δPO_3 may be due to the different O–P–O bond angles [7].

The Pb–O stretching vibrations are assigned in the region 359–299 cm⁻¹ [16]. The four bands observed for νPb–O vibrations may be attributed to the irregular lead coordination environment due to the inert pair of Pb^{2+} cations resulting in Pb–O bond distances between 2.30 and 3.00 Å [7].

As expected [12,17], in the 2000–1700 cm⁻¹ IR region, the so called benzene fingers are observed (Table 1). Most of the bands in the range 3000–2000 cm⁻¹ in the IR, may also be due to the combinations and overtones. However, the very broad medium intense Raman bands at 2881 and 2551 cm⁻¹ are quite unusual. Similar result was reported earlier [18]. The weak broad bands centered at 2200 and 2050 cm⁻¹ together with the above bands, suggest a strong hydrogen bonding in the sample. On considering the three-dimensional structure of the compound, it can be suspected that the oxygen of the P=O in the CPO_3 tetrahedra may come closer to any of the corners of the benzene ring, thus forming a strong C–H----O hydrogen bond [19]. The splitting observed in the CH in-plane deformation mode $3(B_2)$, out-of-plane ring deformation $8(B_1)$, stretching and bending vibrations of PO_3 all support such a hydrogen bonding in the compound. Therefore, the weak broad bands observed in the region 2881–2050 cm⁻¹, can be attributed to the trio (ABC) bands of strong hydrogen bonding.

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