Single-crystal Vibrational Spectra of Tetragonal and Orthorhombic Lead Monoxide

By **David M. Adams** * and **David C. Stevens**, Department of Chemistry, University of Leicester, Leicester LE1 7RH

All the fundamental modes of vibration of tetragonal PbO have been observed and all but one assigned unequivocally by single-crystal techniques: B_{1u} 338.7, A_{1g} 146.5, E_g 321.5 and 81.0, A_{2u} 116, and E_u 243 cm^{-1}. From the i.r. longitudinal and transverse optic (LO and TO) frequencies, the principal components of the dielectric tensor are estimated to be ε_1 = 20.3 and ε_3 = 11.9. The first complete Raman spectrum, and single-crystal i.r. reflectance data, are reported for orthorhombic (yellow) PbO. The assignment has been partially established for the Raman spectrum with the aid of the group-theoretical prediction, based on a line-group approach, that i.r. and Raman modes should be in near coincidence. The high dielectric constant of the material has been accounted for, a principal contribution coming from the single B_{1u} mode (normal to the plane of the PbO chains) which is of unusual breadth.

LEAD MONOXIDE, PbO, exists in two polymorphic forms: litharge, which is red, tetragonal, and has a layer structure,[1] Figure 1; and massicot which is yellow, orthorhombic, and consists of zig-zag chains with a 2[PbO] repeat running parallel to the *b* axis of the cell.[2-4] These chains are stacked along the *c* axis to form layers which themselves stack along *a*, see Figure 2. The reasons for adoption of these structures, which exist in equilibrium at 491 ± 3 °C,[5] although the yellow form is also stable at ambient temperature, are associated with the need to accommodate a non-bonding pair of valence electrons, a situation that sometimes gives rise to unusual spectroscopic effects as, for example, in salts of $[MCl_6]^{2-}$ (M = Te or Se).[6-8]

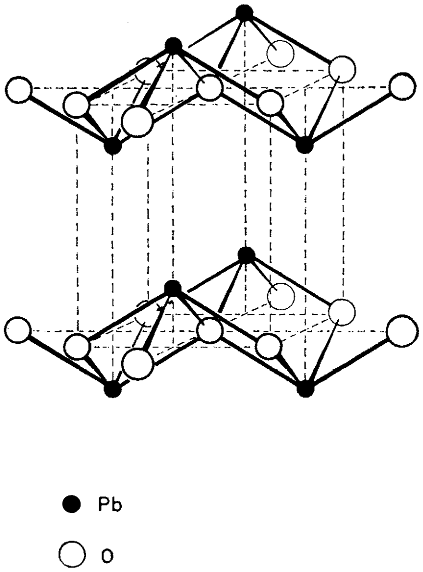

FIGURE 1 Structure of tetragonal PbO

There have been occasional mentions of i.r. absorption bands in tetragonal PbO[9,10] and a reflectance spectrum with $E \| a$ has been published,[11] but there has been only one significant attempt at a full assignment, in the course of which the only extant Raman data were reported.[12] In this paper we give the results of experiments with single crystals of tetragonal PbO aimed at more firmly establishing an experimental basis for the assignment.

Little is known of the vibrational spectrum of the orthorhombic material, which is of interest because of its unique structure, and the relation to the tetragonal form. It is said to have i.r. absorption bands at 505 cm^{-1},[9] and 500, 377, and 300 cm^{-1}.[13] Later workers reported bands at 380(sh), 353, and 300 cm^{-1} but not at *ca.* 500 cm^{-1}, and also that the Raman spectrum consisted of bands at 44, 86, 142, 288, 376, 388, and 420 cm^{-1}.[12] This solid has recently been shown to have a very high dielectric constant,[14] which cannot be accounted for on the basis of the known i.r. data. In view of these incomplete data we have also reinvestigated the i.r. and Raman spectra of yellow PbO.

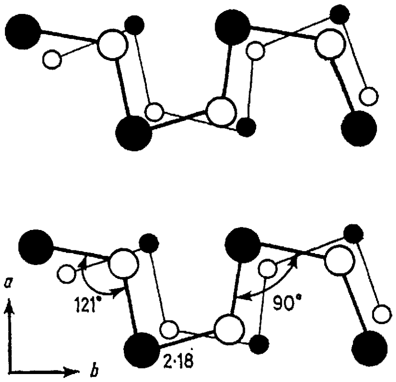

FIGURE 2 Crystal structure of orthorhombic PbO

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EXPERIMENTAL

Crystals of both litharge and massicot were a gift from Dr. C. J. M. Rooymans of Philips Research Laboratories, Eindhoven, to whom we are greatly indebted. The tetragonal phase had been grown under hydrothermal conditions.[15] The red crystals were in the form of thin square platelets of up to *ca.* 5 × 5 mm with the *c* axis normal to the platelets, which were up to 50 μm thick. Conoscopic examination showed the *a* and *b* (= *a*) axes to lay across the diagonals of the platelets and that the side faces were (110). In some of our experiments we used the orthogonal axis set x',y',z which is related to the normal tetragonal axis set by a $\frac{\pi}{4}$ rotation about z (which is coincident with c).

The orthorhombic crystals had been grown by vapour deposition and were in the form of very thin plates (*ca.* 20—40 μm) of rather irregular shape (*ca.* 10 mm^2). Conoscopic examination revealed two orthogonal extinction directions within the plane of each crystal, one of which was shown by *X*-ray scattering to be a (100) plane. The i.r. reflectance spectra (below) were obtained using crystals masked down to a diameter of 2 mm, and absorption spectra with similarly sized specimens. Supplementary work was done using powder samples of commercial litharge which was, in fact, massicot: its i.r. and Raman spectra were in complete accord with those obtained from the yellow crystals. Cooling the crystals to temperatures significantly below ambient resulted in their transformation to the more stable tetragonal (red) form. This prevented collection of single-crystal data except at ambient temperature, although the powder specimens could be cooled without change.

Raman spectra were obtained with a Coderg T800 spectrometer using 647.1 nm excitation from a krypton-ion laser. Infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer (400—800 cm^{-1}), or a Beckman–RIIC FS-720 Fourier spectrometer with wire-grid polarisers. Low-temperature data were obtained using a CTI model-20 closed-circuit liquid-helium cryostat or a Coderg Cryocirc cold cell.

A. TETRAGONAL (RED) PbO

Theory.—Red PbO crystallises in the tetragonal system with symmetry $P4/nmm$ (D_{4h}^7) and $Z = 2$.[1] Lead atoms are on sites $2c$ (C_{4v}) and oxygen on $2a$ (D_{2d}). The structure therefore consists of one layer per unit cell; the only translatory lattice modes are acoustic in type (A_{2u} + E_u) and there can be no rotatory modes. All the other modes are internal to the layer and are accounted for by the factor-group analysis (f.g.a.) of Table 1. From this it is clear that the i.r. spectrum should consist of only two bands ($A_{2u} + E_u$), and the Raman spectrum of four ($A_{1g} + B_{1g} + 2E_g$). The vectors of the f.g.a. table contributed by the lead and oxygen atoms show that the A_{1g} mode involves motion of the lead atoms alone (parallel to the *c* axis) whilst the B_{1g} mode similarly involves oxygen motion only (also parallel to *c*). In the A_{2u} mode both types of atom move in antiphase along the same axis. These considerations show that the frequency order of these three modes will be $B_{1g} > A_{1g}$ and that the A_{1g} and A_{2u} modes will not be very different in energy. The three *E* modes involve motion in the *ab* plane.

Results and Assignment.—Infrared spectrum. Previous reports [9,10] of the i.r. spectrum of this material indicated a single band at 465 cm^{-1}, except for Donaldson *et al.*[12] who found a single, very broad, absorption at 290 cm^{-1} which they attributed to both A_{2u} and E_u modes which were assumed to be accidentally degenerate. We found that the i.r. absorption spectra of powdered samples (Figure 3) showed three bands: cooling to liquid-nitrogen temperature revealed slight sharpening of the highest

TABLE 1

Factor-group analysis and mode activities for tetragonal PbO

D_{4h}	Pb	O	N_T *	T	Γ	I.r.	Raman	
A_{1g}	1		1		1		$x^2 + y^2, z^2$	$(x')^2 + (y')^2, z^2$
A_{2g}								
B_{1g}		1	1		1		$x^2 - y^2$	$x'y'$
B_{2g}							xy	$(x')^2 - (y')^2$
E_g	1	1	2		2		(xz,yz)	$(x'z \pm y'z)$
A_{1u}								
A_{2u}	1	1	2	1	1	z		
B_{1u}								
B_{2u}								
E_u	1	1	2	1	1	(x,y)		

* Total number of modes: T = acoustic modes; Γ = vibrational modes internal to the layer.

TABLE 2

Raman and i.r. wavenumbers (cm^{-1}) for tetragonal PbO and their assignment

(*a*) Raman

295 K	120 K	Assignment
338.7	344.0	B_{1g}
321.5 [a]	327.0 [b]	E_g
146.5	150.0	A_{1g}
81.0	83.4	E_g

(*b*) I.r.

Mulls		Crystal		
295 K	120 K	295 K	120 K	Assignment
470 ± 4	476 ± 2	470	n.i.[c]	A_{2u}
		432		LO E_u
278 ± 5 [d]	290 ± 5 [d]	243		TO
		150		LO E_u
ca. 120 [d]	*ca.* 120 [d]	116		TO

[a] ±2 cm^{-1}; all other modes ±0.5 cm^{-1}. [b] ±1 cm^{-1}; all other modes ±0.5 cm^{-1}. [c] Not investigated. [d] Due to a mixture of transmission and reflection effects and not corresponding to reflectance TO values.

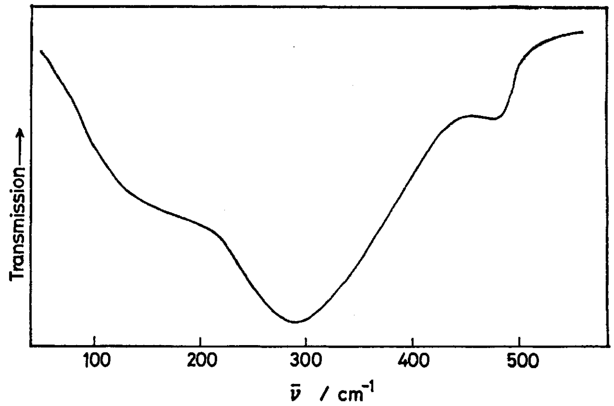

FIGURE 3 Infrared transmission spectrum of a mull of tetragonal PbO at liquid-nitrogen temperature

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[15] C. J. M. Rooymans and W. F. T. Langenhoff, *J. Crystal Growth*, 1968, **3**,**4**, 411.

component. The main absorption band, which is centred at *ca.* 278 cm^{-1}, is of exceptional breadth and is overlapped substantially by a further component at *ca.* 120 cm^{-1}.

Single-crystal absorption spectra were uninformative as the samples, although thin, totally absorbed all the radiation in the interval 60—550 cm^{-1}: cooling to low temperatures did not improve the situation. However, very high-quality i.r. reflectance spectra were obtained from the (001) face of a single crystal (Figure 4). It was unnecessary to polarise the incident radiation for these experiments (although the radiation is elliptically polarised by the beam splitter of the Fourier spectrometer before reaching the sample) as only the E_u mode can be excited by reflectance from this face at near-normal incidence. Nevertheless some work was performed using a polariser, but the results were identical with those obtained without one.

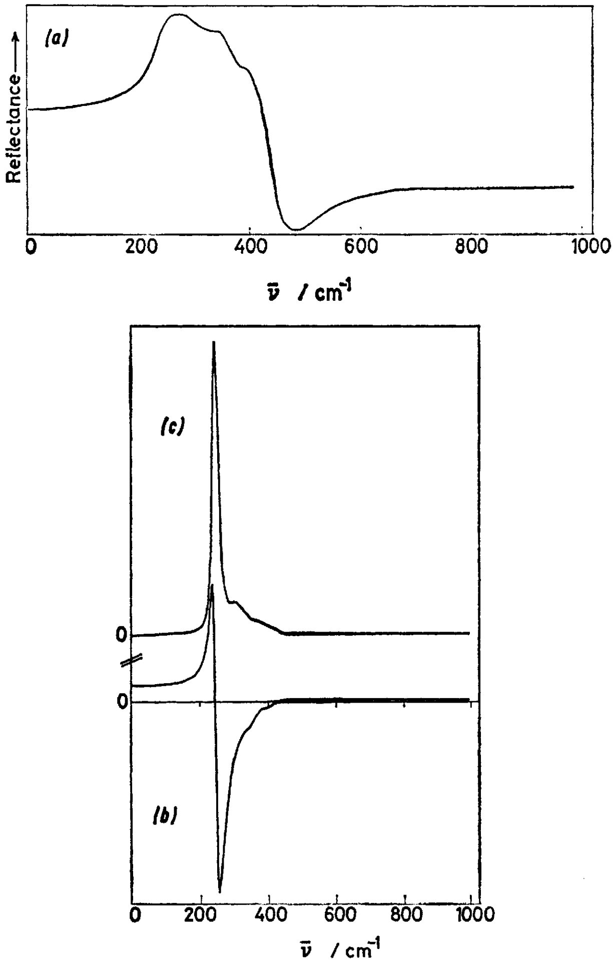

FIGURE 4 Infrared reflectance spectrum of tetragonal PbO at 295 K, with $E||a$ showing: (*a*) observed reflectance, R; (*b*) the real (ε') and, (*c*) the imaginary (ε''), parts of the complex dielectric constant

The high-frequency reflectance, R, of the crystals can be estimated using equation (1). At frequencies above the lattice vibrations the refractive index, n, is 2.665. Thus $R = 0.205$, or 20.5%, a value which corresponds well with observation. The real and imaginary parts of the complex dielectric constant, $\varepsilon^* = \varepsilon' - i\varepsilon'' = (n^*)^2$, were extracted from the observed reflectance data by the

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad (1)$$

Kramers–Kronig procedure, yielding the oscillator frequencies $\omega_{TO} = 243$ and $\omega_{LO} = 432$ cm^{-1}. These are in good agreement with the values obtained by van den Broek[11] using a harmonic-oscillator approach. The transverse optic (TO) mode is the one seen in absorption and is considerably displaced from the maximum of the mull absorption spectrum due to the large reflectance component also present in the latter.

The reflectance results confirm the exceptional breadth of the E_u band and show that red PbO acts as a mirror for a sufficiently large interval to make it attractive as a restrahlen filter. Several second-order features developed in the reflectance spectra as the crystal was cooled in stages to 40 K and will be the subject of a later report.

Although these results establish the E_u longitudinal optic (LO) and TO frequencies, we cannot yet disprove the suggestion[12] that the A_{2u} mode is accidentally coincident with it. The A_{2u} mode can be excited only with radiation polarised perpendicular to the plane of the sheets. Unfortunately the crystals available were very thin. A reflectance spectrum of moderate quality was eventually obtained by making a small stack of these crystals, clamping them together, and polishing their exposed (110) faces which had an area *ca.* 5 × 1 mm^2. The spectrum of Figure 5 was obtained and unequivocally shows that the A_{2u} mode has a TO frequency of 116 cm^{-1}. The LO frequency was estimated at 150 cm^{-1}.

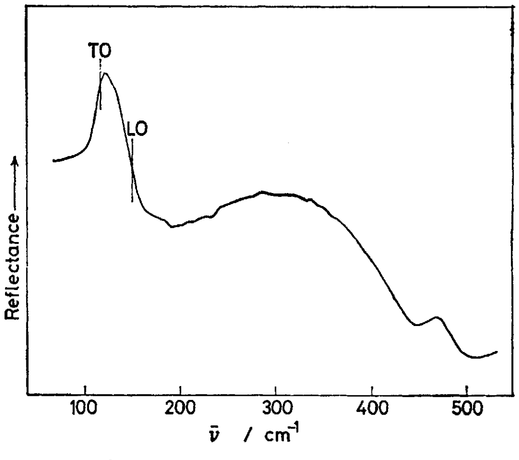

FIGURE 5 Infrared reflectance spectrum of tetragonal PbO at 295 K with $E||c$

Since the two fundamentals have been accounted for, the weak band at 470 cm^{-1} must be a second-order feature. Overtones cannot be i.r. active in D_{4h} but i.r.–Raman combinations are allowed. A consideration of all the possible i.r. and Raman (see below) zone-centre combinations revealed only one reasonable candidate, A_{2u} (116 cm^{-1}) + B_{1g} (338.7 cm^{-1}) = A_{2u} (454.7 cm^{-1}), although many other possibilities arise for $k \neq 0$. We determined the symmetry species of the band at 470 cm^{-1} directly by i.r. reflectance and find it to be A_{2u}.

Raman spectrum. A randomly orientated crystal gave the spectrum shown in Figure 6(*a*) in which three prominent bands are present, the highest being much broader than the others. Cooling to 100 K caused this band to sharpen dramatically, revealing a second one close to it, Figure 6(*b*). The band found[12] at 36 cm^{-1} did not appear in any of our spectra either of powders or crystals and we conclude that it was due to a grating ghost or a laser plasma line. Our spectra have revealed the four bands required by theory: they were assigned by the following single-crystal experiments.

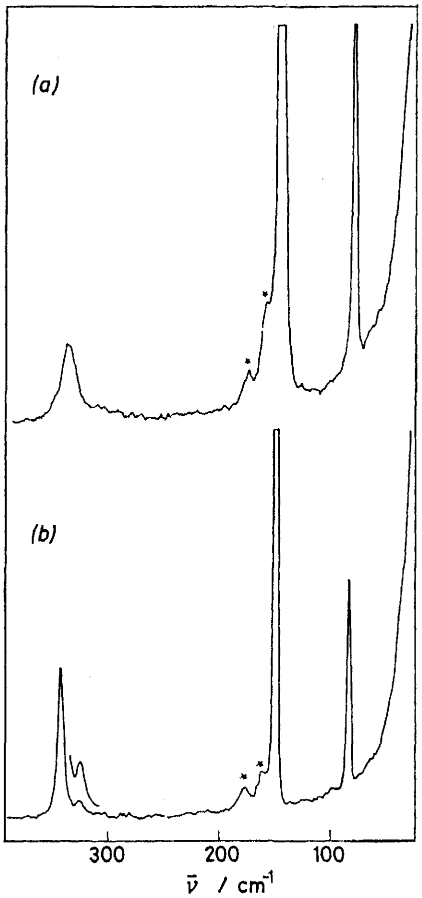

FIGURE 6 Raman spectra of crystalline tetragonal PbO randomly orientated. 647.1-nm Excitation, *ca.* 300 mW at the sample, spectra slit width 1 cm^{-1}. (*a*) 295 K, (*b*) 100 K. Laser lines are indicated by asterisks

Because the crystals were thin we initially attempted to obtain spectra using back (180°) scatter from the large (001) face. The spectra so obtained were very weak due to the small amount of crystal traversed by the laser beam. 180° Scatter from the (110) face gave stronger spectra (Figure 7) in which bands could be seen at 146.5 and 81.0 cm^{-1}: reasonable extinctions were obtained between the $x'(zz)\bar{x}'$, $x'(y'y')\bar{x}'$, $x'(y'z)\bar{x}'$, and $x'(zy')\bar{x}'$ spectra which established the assignment as 146.5 cm^{-1} (A_{1g}) and 81.0 cm^{-1} (E_g). 180° Scatter from the (110) faces cannot yield the B_{1g} mode which, in the $x'y'z$ axis set, transforms as $x'y'$, explaining its absence from the above set of results. The second E_g mode (321.5 cm^{-1}, see below) is much weaker than the one at 81.0 cm^{-1} and could not be detected in 180° scatter.

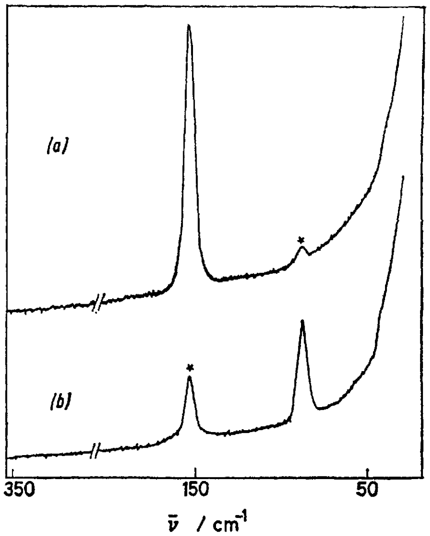

FIGURE 7 Single-crystal Raman spectrum of tetragonal PbO at 295 K, 674.1-nm excitation, 300 mW at the sample, spectral slit width 1cm^{-1}, 180° geometry. Peaks which should have zero intensity are indicated by asterisks. (*a*) $x'(zz)\bar{x}'$ (A_{1g}), (*b*) $x'(y'z)\bar{x}'$ (E_g)

Further experiments were conducted in 90° scattering geometry and clearly established the band at 338.7 cm^{-1} as being of B_{1g} symmetry (Figure 8). Extinctions were not as good as in 180° scatter but nevertheless fully confirmed the assignments mentioned. In particular, the experiment $x(yy)z$, in which the laser beam was input at a small (100) face cut on one corner of a crystal, yielded A_{1g} (146.5 cm^{-1}) and B_{1g} (338.7 cm^{-1}) modes, whereas the

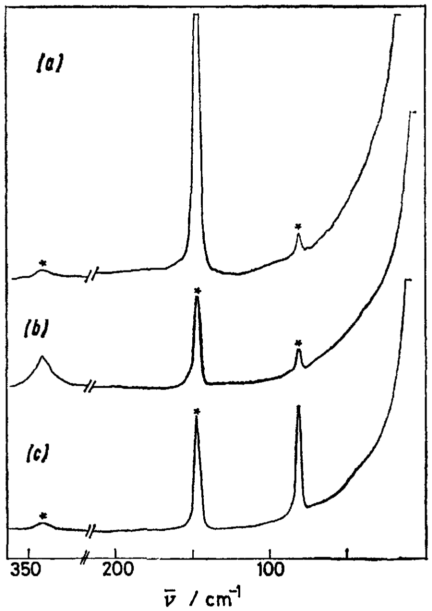

FIGURE 8 Single-crystal Raman spectrum of tetragonal PbO at 295 K in 90° scattering geometry. Conditions as for Figure 7. (*a*) $x'(yy')z$ (A_{1g}), (*b*) $x'(y'x')z$ (B_{1g}), (*c*) $x'(zy')z$ (E_g)

experiment. $x'(y'y')z$ yielded only the A_{1g} mode as required by theory (Table 1).

Extinctions were not improved on cooling to liquid-nitrogen temperature. Although the band at 327.0 cm^{-1} was then clearly resolved, we did not succeed in establishing its symmetry species directly to our satisfaction and it is assigned as E_g by elimination. Comparison of our assignment with that of ref. 12 shows that the previous workers misassigned all the Raman and one of the two i.r. bands. We note that the order $B_{1g} > A_{1g} \approx A_{2u}$ predicted above was in accord with the results.

Discussion.—The LO and TO frequencies, ω_{LO} and ω_{TO}, may be used to estimate the principal values of the radiofrequency dielectric constant of the solid according to the Lyddane–Sachs–Teller formula (2) which must be

$$\varepsilon^{\frac{1}{2}} = n\left(\frac{\omega_{LO}}{\omega_{TO}}\right) \tag{2}$$

applied separately for each symmetry species. For the A_{2u} mode, taking n_E (the extraordinary-ray refractive index) as 2.665, $\varepsilon_3 = 11.9$. The two equal values of ε_1 are 20.3, taking n_O (the ordinary-ray refractive index) as 2.535,[16] and the known E_u frequencies. The highly anisotropic nature of this tensor is hardly surprising in view of the layer structure involved. Taking ε_1, and $\omega_{TO} = 243$ cm^{-1}, the restrahlen frequency, ν_r, of tetragonal PbO was found, using Havelock's formula (3),[17]

$$\nu_r = \omega_{TO}\left(1 + \frac{\varepsilon_1 - \varepsilon_\infty}{6\varepsilon_\infty - 4}\right) \tag{3}$$

to be 340 cm^{-1}. Our values of ε_1 and ε_3 (Nye's notation) [18] may be compared with that of 25.9 at 15 °C and 10^8 Hz quoted in ref. 19. As this is a little higher than ours, it is likely that other oscillators, probably represented by the secondary features of the i.r. reflectance spectra, also contribute.

B. ORTHORHOMBIC (YELLOW) PbO

Theory.—The orthorhombic crystals have the symmetry $Pbcm \equiv D_{2h}^{11}$ with $Z = 4$.[3] In this (standard) axis set the chains are parallel to b and the layers of chains stack along a. The crystals are in the form of (100) plates. Kay [4] uses a non-standard setting, $Pbma$.

There are two chains per cell, in planes ab at heights $\frac{1}{4}$, $\frac{3}{4}$ along c, separated by distances that indicate van der Waals bonding. We therefore consider first a line-group approximation. The symmetry elements of an isolated chain are: E; a two-fold screw axis along the chain axis (z); a mirror plane, taken as (zx); and a glide plane in (yz). Together these define the chain line group as being isomorphous with C_{2v}, from which it follows that the $3n - 4$ vibrational modes of each chain span the representation $3A_1 + A_2 + 3B_1 + B_2$. All these modes are Raman active and only the A_2 mode is i.r. inactive. Hence, on this approximation, coincident i.r. and Raman spectra are expected, with one A_2 mode in the Raman spectrum only.

A full description of the vibrations of the crystal is given by the factor-group analysis (f.g.a.) of Table 3 which was completed by the method of Adams and Newton.[20,21] We note that all the symmetry elements of each chain are also operations of D_{2h}^{11}; *i.e.* the 'site' of each polymer chain centre of gravity, which is a line $(0,y,0)$, is of C_{2v} symmetry. No such Wyckoff sites occur in D_{2h}^{11}, but the sites $2m$ in D_{2h}^{1} are of this type and may be used for our purpose as the factor group is the same.

TABLE 3

Factor-group analysis and correlation for orthorhombic PbO

(*a*) F.g.a.

D_{2h}	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}	
N(total) [a]	4	4	2	2	2	2	4	4	2 × row 4D of no. 57 [b]
$T + T_A$	1	1	0	1	0	(1)	(1)	(1)	row 2M of no. 47
$R(y)$	0	0	1	0	1	0	0	0	$R(xyz) - R(x) - R(z)$ in row 2M of no. 47
Γ_{vib}	3	3	1	1	1	1	3	3	
I.r.						z	y	x	
Raman	x^2 y^2 z^2	xy	xz	yz					

(*b*) Correlation

Line group	Site group		Crystal	
$C_{2v}(z)$	$C_{2v}(y)$	$\xrightarrow{\times 2}$	D_{2h}^{11}	
$3A_1$	$3A_1$		$3(A_g + B_{2u})$	$\equiv$ row Γ_{vib} of A
$1A_2$	$1A_2$		$1(B_{2g} + A_u)$	
$3B_1$	$1B_1$		$1(B_{3g} + B_{1u})$	
$1B_2$	$3B_2$		$3(B_{1g} + B_{3u})$	

[a] Total no. of modes $= 3N$; T = optic branch translatory modes; T_A = acoustic modes, in parentheses; $R(y)$ = chain rotatory modes; Γ_{vib} = internal modes of chains. [b] The numbers refer to space-group representations of ref. 21.

The correlation in Table 3(*b*) shows the relation between the line-group and factor-group approaches. From this it is seen that, if the coupling between the chains is small, there will be near-coincident i.r. and Raman spectra: the i.r.–Raman frequency differences are the only means of telling which approach more correctly describes the crystal since both predict the same numbers of i.r. and Raman bands. Finally, we note that the i.r. spectrum consists solely of modes internal to the chains.

Results.—(*a*) *Raman spectrum*. As the crystal plates were extremely thin we were unable to obtain orientational data, by the methods of single-crystal Raman spectroscopy, of sufficiently high quality to allow an assignment to be made. The Raman spectra of these crystals, and of powder samples at 295 and 90 K, are shown in Figure 9. Three of the bands (87, 144, and 385 cm^{-1}) are close to bands in the red PbO spectrum [12]

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[20] D. M. Adams and D.C. Newton, *J. Chem. Soc.* (*A*), 1970, 2822.

[21] D. M. Adams and D. C. Newton, 'Tables for Factor Group and Point Group Analysis,' Beckman, Croydon, 1970.

and it is important to show that they are not of this origin. Apart from the frequency differences, spectra of mixtures of the red and yellow forms clearly showed the presence of bands from both forms, indicating that all the features in Figure 9 are indeed due to the yellow form.

The spectrum at 100 K shows 11 bands including three rather broad features centred at *ca.* 171 and 250 cm^{-1} which may or may not be due to first-order scattering processes. Both line-group and factor-group theories require eight chain internal modes plus four lattice modes. It is clear that nearly all have been located.

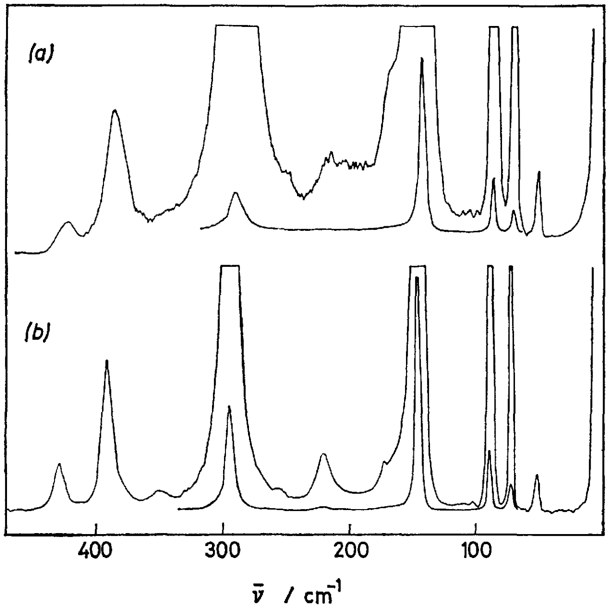

FIGURE 9 Raman spectrum of orthorhombic PbO at (*a*) 295 K, (*b*) 100 K. Spectral slit width 2 cm^{-1}, 647.1-nm excitation

The only literature report [12] of the Raman spectrum of yellow PbO is in partial agreement with ours. We found a single band at 385 cm^{-1}, even at 100 K, and not a doublet; we did not find a band at 44 cm^{-1}, and we found five bands not previously reported. The previous workers also considered that the intense band at 144 cm^{-1} was not a fundamental.

(*b*) *Infrared spectrum.* The i.r. spectrum of a mull of yellow PbO shows three clearly defined bands which sharpen considerably on cooling and are at 300, 362, and 515 cm^{-1} at *ca.* 100 K [Figure 10(*a*)] together with an unresolved component at *ca.* 392 cm^{-1}. Below this there exists an intense and exceptionally broad absorption envelope which is not significantly affected by cooling. Transmission experiments using single crystals yielded no further information as they were totally absorbing over almost the entire i.r. range studied even though they were thin.

The (100) platy crystals of yellow PbO are made up of layers, each of which consists of a stack of zig-zag chains which are in the *ab* plane. Hence, an electric vector along *b* will stimulate the B_{2u} modes (which are in the plane of the chain), whereas a vector along *c* will stimulate the B_{1u} modes, which are normal to the planes of the chains. We examined crystals in i.r. reflection as described above, having first identified the axes by Weissenberg *X*-ray photographs and found them to be in agreement with Leciejewicz.[3] The spectra were analysed by the Kramers–Kronig procedure yielding the TO(ε'' maxima) and LO(ε' zeros) values of Table 4.

With $E||b$ the spectrum of Figure 10(*b*) resulted. It is a classic reflectance spectrum showing three principal oscillators and some weak secondary features. The highest band shows a large LO–TO splitting of 139 cm^{-1}. The bands with TO frequencies at 146, 279, and 347 cm^{-1} are attributed to the three predicted B_{2u} modes. Reflectance with $E||c$ should yield a single B_{1u} mode (Table 4). In practice the spectrum of Figure 10(*c*) is obtained. The cut-off at the high-frequency end is of an unusual type. There are apparently two secondary oscillators and it is not clear whether the LO mode of the B_{1u} fundamental should be taken as *ca.* 330 or *ca.* 480 cm^{-1}. However, both Kramers–Kronig and simple-harmonic-oscillator analyses concurred in giving the LO mode the higher value and this was supported by calculations of dielectric parameters (see below). The existence of this broad reflectance band largely accounts for the curious i.r. spectrum of the mull in this region, since intense reflectance implies strong absorption.

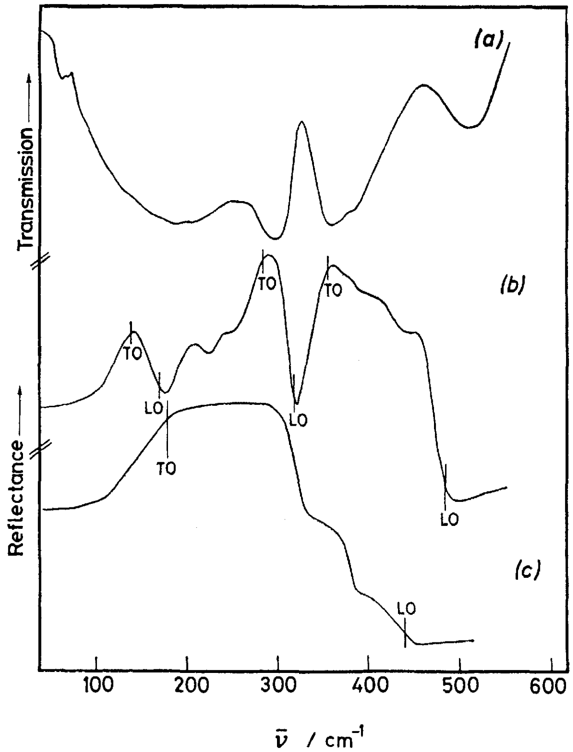

FIGURE 10 Infrared spectra of orthorhombic PbO: (*a*) mull at 100 K, (*b*) reflectance with $E||b$ and, (*c*) with $E||c$, both at ambient temperature

Two of the four high-frequency features in the mull were located in the $E||b$ reflectance spectrum. By elimination, the bands at 392 and 515 cm^{-1} are attributed to B_{3u}, the species that we cannot locate by reflectance because that would require use of the very fine edges of the crystals. They could only be shown with the aid of a crystal having well developed *ab* or *ac* faces.

Discussion.—The three B_{2u} modes should be either near or coincident with three A_g Raman modes, depending on the strength of the coupling between chains. The corresponding pairs are 146(144), 279(289), and 347(349) cm^{-1}, where the first of each pair is the i.r. band. The Raman bands at 144 and 289 cm^{-1} are the most intense in the spectra, supporting their supposed A_g origin. The Raman band at 349 cm^{-1} was only seen clearly at low temperature but there seems no reason to doubt its correlation with the i.r. band at 347 cm^{-1}.

TABLE 4

Raman and i.r. wavenumbers (cm^{-1}) for orthorhombic PbO

Raman		I.r.				
		Single-crystal reflectance 295 K		Mulls		
295 K [a]	100 K [b]	TO	LO	295 K	100 K	Assignment
				500	515	B_{3u} combination
424w	427.5					B_{1g} (combination?)
385m	389.5			sh	392 ± 5 (sh)	B_{1g}, B_{3u}
	349 ± 3	347	486	356	362	A_g, B_{2u}
289vvs	293.2	279	320	290	300	A_g, B_{2u}
250vvw	255.0					B_{1g}
217vw	219.2					B_{1g}
171 (sh)	172.0	177	486			B_{3g}, B_{1u}
144vvs	145.5	146	170	*c*	*c*	A_g, B_{2u}
87s	89.0					lattice modes
72s	72.5					
52w	52.5					

[a] All bands ± 1 cm^{-1} except 171, 217, and 250 cm^{-1} for which the error is ± 2 cm^{-1}. [b] All bands ± 0.5 cm^{-1} unless otherwise shown. [c] Region of intense absorption [see text and Figure 10(*a*)].

The B_{1u} mode at 177 cm^{-1} appears to have its Raman counterpart at 171 cm^{-1}. The A_u (inactive), B_{2g} pair, like B_{1u}, B_{3g}, corresponds to motion out of the plane of the chains and is therefore also expected at a fairly low frequency. The only Raman bands not yet accommodated are of B_{1g} symmetry and three are required in near coincidence with the B_{3u} i.r. modes (which cannot be located in reflectance). It is safe to regard the Raman bands at 424 and 385 cm^{-1} as B_{1g}, although the higher one might not be a fundamental as it has no i.r. equivalent.

The i.r. band at 500 cm^{-1} does not appear in our reflectance spectra with $E \| b$ or c and is presumed to have B_{3u} symmetry. It has no Raman counterpart and may not be a fundamental. In tetragonal (red) PbO the highest TO frequency [11] is 240 cm^{-1} and the shortest Pb–O distance is 2.33 Å,[1] compared with 2.21 Å for the orthorhombic form.[3,4] Although the difference of 0.12 Å implies that the latter form will have somewhat higher frequencies than the tetragonal form, we think it improbable that they will be more than twice as high and hence regard the band at 500 cm^{-1} as a combination (overtones are not permitted in D_{2h}). This could arise from any of the products $A_g \times B_{3u}$, $A_u \times B_{3g}$, $B_{1g} \times B_{2u}$, or $B_{1u} \times B_{2g}$, of which the second is improbable as it involves an inactive species. Several pairs of i.r.–Raman bands are reasonable candidates, and many more possibilities arise if modes with $k \neq 0$ contribute. Having identified one B_{1g}, B_{3u} combination at *ca.* 390 cm^{-1} it remains to locate two more and there is a strong probability that the B_{1g} components are to be identified with the two Raman bands at 217 and 250 cm^{-1}.

Finally, we relate the main features of the i.r. spectra to the dielectric behaviour of this solid. The difference between the radiofrequency dielectric constant, ε, and the optical-frequency constant $\varepsilon_\infty = n^2$, where n is the refractive index is as in (4), where

$$\varepsilon - \varepsilon_\infty = \sum_i s_i \qquad (4)$$

s_i is the strength of the ith i.r. absorption band. A convenient way of estimating ε from observed i.r. reflectance data is by use of the extended Lyddane–Sachs–Teller relation (5) [22] where $\omega_{\mathrm{LO}}{}^i$ and $\omega_{\mathrm{TO}}{}^i$ are the

$$\varepsilon = n \prod_i \left(\frac{\omega_{\mathrm{LO}}{}^i}{\omega_{\mathrm{TO}}{}^i}\right) \qquad (5)$$

longitudinal and transverse optic mode frequencies which bound the ith reflection band. The equation is applied separately for modes of each i.r.-active symmetry species and then yields the principal values of the dielectric tensor.

For the B_{2u} species, taking $n(y)$ as 2.61, we obtain $\varepsilon(y) = 23.8$. For the single B_{1u} mode, the value of $\varepsilon(z)$ is highly sensitive to the choice of ω_{LO} for which two alternative values initially seemed possible. Again taking $n(z)$ as 2.61, $\varepsilon(z) = 50.4$ for $\omega_{\mathrm{LO}} = 486$ cm^{-1} but is 23.7 for $\omega_{\mathrm{LO}} = 330$ cm^{-1}. As we have no LO data for the B_{3u} species $\varepsilon(x)$ cannot be estimated, but it seems likely that it is comparable to $\varepsilon(y)$. The average of these tensor components is close to the value of 36.4 at 296 K quoted recently for a solidified melt [14] if we take the higher LO frequency in B_{1u}. It would be interesting to have our values checked by independent measurements of the dielectric parameters.

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[22] W. Cochran, 'The Dynamics of Atoms in Crystals,' Arnold, London, 1973, p. 92.

The extreme breadth of the B_{1u} mode may be associated with the presence on Pb of an inert pair of electrons. In salts of the type $[MCl_6]^{2-}$ ($M = Se^{IV}$ or Te^{IV}) the dynamic rehybridisation of the inert pair also generates ν_3 bands of unusual breadth.[6,7] In orthorhombic PbO the inert pair is said to be in a 6*s* orbital.[23] We propose that, in the course of the B_{1u} (out-of-plane of the chains) mode, this pair achieves directional character, thereby making the mode very highly polar.

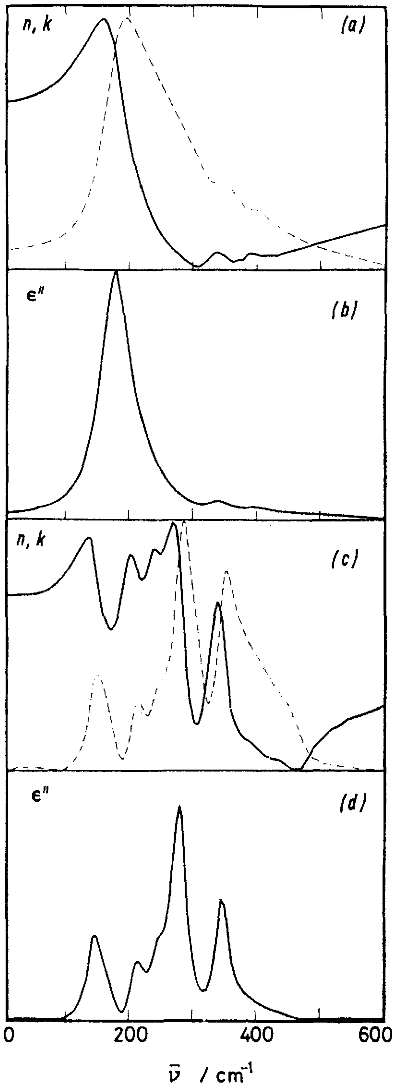

FIGURE 11 The real (*n*, full line) and imaginary (*k*, dashed line) parts of the complex refractive index n^*, and the imaginary part (ε'') of the complex dielectric constant, as calculated from the reflectance spectra of Figure 10. (*a*) and (*b*), B_{1u}; (*c*) and (*d*), B_{2u} spectrum. LO and TO mode frequencies are given by the *n*–*k* crossover points (reading from high to low frequencies). ε'' maxima correspond to TO mode frequencies and are preferred to *n*–*k* crossover values in multioscillator situations

The tetragonal ↔ orthorhombic phase transition. This is a first-order phase transition and, in contrast to second-order transitions, will not be driven by a specific vibrational mode. Indeed Söderquist and Dickens[5] showed that a probable mechanism for the transition involves displacements of the oxygen atoms (relative to the lead atoms) in directions both parallel and normal to the layers of the tetragonal phase. The lead atoms also move, but not nearly so much. Such movements could be accomplished by involving several normal modes, although from optical observations Söderquist and Dickens concluded that the transformation 'does not seem to take place through a distinct concerted movement of atoms.' Rather, the atoms 'probably diffuse more at random to their new positions.'

From a spectroscopic viewpoint we are impressed with the observation that the E_u mode in the red, and the B_{1u} mode in the yellow, form are both associated with extremely wide reflectance bands implying that the modes are both highly polar. Moreover, the atom displacements associated with these modes are, respectively, in the plane of the layers (for the tetragonal phase) and out of the plane of the chains (for the orthorhombic phase). These are precisely the modes which could play a major role in the transition because the two structures are related as follows:

tetragonal	*a*	*a*	*c*
orthorhombic	*b*	*c*	*a*

Here the standard setting has been used for the orthorhombic phase; *i.e.* the atom displacements in the B_{1u} and E_u modes are in the same direction.

The transition is accompanied by a change in disposition of the inert pair from a 6*s* orbital[23] (orthorhombic) to a directional hybrid[24] $(s,p_z\,d_{z^2})$ in the red form. It is curious that the high-temperature form, since it has a directionally inactive inert pair, does not adopt the CsCl structure to which the tetragonal form is closely related, or the NaCl structure (used by PbS) to which a feasible transition could be imagined. It appears that, in terms of energetics, a combination of strong covalent Pb–O bonds and van der Waals interchain attraction principally *via* Pb · · · Pb interactions stabilises the observed orthorhombic form relative to these other possibilities.

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[23] B. Dickens, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1495.

[24] B. Dickens, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1503.