Infrared and Raman spectra of matrix isolated lead oxide species. Structure of Pb_2O_2 and Pb_4O_4

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Abstract—Lead oxide vapor mixed with N₂ gas was quenched on a cold substrate (~ 15 K) in a closed cycle cryo-cooler The i r and Raman spectra of the condensed material revealed several sharp features which were analysed in terms of the vibrational modes of PbO, Pb₂O₂ and Pb₄O₄ species Normal coordinate analyses of the data confirm the ring structure for the dimer (point group D_{2k}) and a distorted cube structure for the tetramer (point group T_d)

INTRODUCTION

Disproportionation is commonly observed when materials are vaporized and the vapors condensed [1-3] This implies the presence of monomers, dimers, etc in the vapor phase which may react to produce heavier clusters and ultimately result in condensation when a critical size is approached Such species have been detected in the mass spectra of several metals and their oxides [2, 4, 5] A knowledge of the structures of these species can provide valuable information on the mechanisms which lead to nucleation and condensation In this regard silicon oxide, a high temperature ceramic, has been investigated in great detail. The 1r spectra of matrix isolated silicon oxide were interpreted in terms of the vibrational modes of monomers, dimers, trimers and possibly pentamers Ring structures for the dimer (point group D_{2k}) and trimer (point group D_{3h}) were proposed on the basis of 1 r data alone [6-8] Raman spectral studies of matrix isolated silicon oxides, attempted in our laboratory [9], were of limited utility because of extremely weak scattering by silicate structures, nevertheless, the spectral data were suggestive of an open structure for S12O2 This is inconsistent with the results of quantum mechanical calculations [10, 11] which predict a ring with Si-O bonds to be the most stable structure for the dimer An earlier quantum mechanical result employing a minimal basis set [12] predicted a centrosymmetric structure with an Si-Si bond for the dimer The ir spectra of matrix isolated species of other divalent oxides (PbO, SnO and GeO) [13-15] have been interpreted in a similar manner

It is clear that a comparison of the 1r and Raman spectra of a species along with a normal coordinate analysis can, in principle, provide a more complete elucidation of the structure of the species under investigation. In view of the expected larger Raman scattering cross section for heavier molecules it was felt desirable to investigate the Raman spectra of matrix isolated species of lead oxide Earlier results of the 1r investigations of this material [14] were analysed in terms of monomer PbO and cyclic dimer and tetramer structures. Our investigations of the 1r and Raman spectra of matrix (N_2) isolated lead oxide and the normal coordinate analyses confirm the ring structures. The results of these investigations are presented in this report

EXPERIMENTAL

Lead oxide (reagent grade) was heated in an oven which was coupled to the cryo-cooler assembly (Air Products CS-202) Through a controlled leak valve a stream of N₂ gas was injected and directed towards the substrate window (CsI for 1r and gold plated brass for Raman) which was cooled to ~ 15 K The temperature of the oven was controlled by adjusting the voltage on the heater assembly wound over the oven After some experimentation it was possible to generate an adequate vapor pressure of lead oxide to obtain matrix isolated species of the monomer and the *n*-mers

The 1r spectra were recorded on a Perkin-Elmer 225 spectrometer from 1000 to $200 \,\mathrm{cm^{-1}}$ under $\sim 1 \,\mathrm{cm^{-1}}$ resolution The Raman spectra were recorded on a Spex 1401 dual monochromator under $\sim 4 \,\mathrm{cm^{-1}}$ resolution An argon laser and a photon counting system were employed for exciting and detecting the spectra, respectively The temperature of the sample was controlled by an external controller unit to within $\pm 1 \,\mathrm{K}$ from 15 to 30 K to carry out diffusion controlled reactions among the species (PbO)_n The tracings of the spectra are reproduced in Figs 1 and 2

DISCUSSION

The 1r peaks in our study and the effect of heat treatment of the sample on the spectra are in general agreement with those reported earlier, thus enabling the classification of three species There are a number of extremely weak and broad features possibly due to higher species and bulk amorphous lead oxide Clearly, the 1r and Raman peaks at 714 cm^{-1} are to be associated with the PbO monomer The force constant for the Pb–O bond which is essentially a double bond is evaluated to be 455 md/A

The 1r spectrum of the sample shows two strong peaks at 558 and 467 cm⁻¹ (Fig 1) which initially decrease in intensity on heat treatment (32 K, ~ 20 min) Similarly, the Raman peaks at 524 and 463 cm⁻¹ behave in a similar fashion on heat treatment (Fig 2) We check the possibility of assigning

FREQUENCY (cm) Fig 1 Infrared spectra of matrix isolated lead oxide species (a) Freshly prepared sample at ~ 15 K, (b) heat treated at ~ 32 K for 20 min, (c) heat treated at ~ 40 K for 30 min *Absorption due to N₂ matrix

these peaks to the dimer species by a detailed vibrational analysis below

First, there is no coincidence between the Raman and 1 r data, thereby suggesting that the species under question is, possibly, centrosymmetric A centrosymmetric structure with a Pb-Pb or O-O bond is ruled out because each of these structure would be expected to give rise to one 1 r absorption due to Pb-O stretch Therefore, we examine the data in the light of a cyclic dimer structure with Pb-O bonds For this structure the six normal modes are classified among the symmetry species of D_{2h} as

$$\Gamma = 2A_g(\mathbf{R}) + B_{1g}(\mathbf{R}) + B_{1u}(\mathbf{1r}) + B_{2u}(\mathbf{1r}) + B_{3u}(\mathbf{1r})$$

where the selection rules (R Raman active, 1r infrared active) are given in parentheses One of the A_a modes and the B_{1u} mode correspond to in-plane and out-ofplane bending vibrations, respectively, and have frequencies in the region below 200 cm⁻¹ which was not covered by our investigations Even in the Raman spectra the scattering by the N₂ matrix gives a strong Rayleigh wing which extends to ~ 200 cm⁻¹ The other modes are essentially Pb–O stretches Clearly, the 558 and 467 cm⁻¹ 1r peaks are assigned to the B_{2u} and B_{3u} species whereas the 524 cm⁻¹ (relatively stronger) and the 463 cm⁻¹ Raman peaks are assigned to A_g and B_{1g} species, respectively A further check on these assignments is provided by a normal coordinate analysis

The formation of a dimer from two monomers would result in a Pb–O bond which is closer to a single bond Since some of the potential energy resides in the angles, the Pb–O bond strength (and, hence, the force constant) in the dimer is expected to be somewhat less than half of the corresponding value for the monomer Assuming negligible interaction between the stretching and bending modes of the dimer unit, the four stretching frequences of Pb₂O₂ are given by [7]

$$\lambda_{1} (A_{g}) = 2(f_{r} + 2f_{rr}) (\mu_{Pb} \cos^{2} \theta + \mu_{0} \sin^{2} \theta)$$

$$\lambda_{2} (A_{g}) = \frac{4 \mu_{Pb} \ \mu_{0} \ (f_{\alpha} + f_{\beta})}{(\mu_{Pb} \cos^{2} \theta + \mu_{0} \sin^{2} \theta)}$$

$$\lambda_{3} (B_{1g}) = 2(f_{r} - 2f_{rr}) (\mu_{Pb} \sin^{2} \theta + \mu_{0} \cos^{2} \theta)$$

$$\lambda_{4} (B_{2u}) = 2(f_{r} + 2\tan^{2} \theta r_{0}^{2} f_{\alpha}) (\mu_{Pb} + \mu_{0}) \cos^{2} \theta$$

$$\lambda_{5} (B_{3u}) = 2(f_{r} + 2\cos^{2} \theta r_{0}^{2} f_{\beta}) (\mu_{Pb} + \mu_{0}) \sin^{2} \theta$$

where $\lambda_i = u\pi^2 \tilde{v}_i^2 c^2$, $\theta = \alpha/2$, α being the angle OPbO, r_0 = equilibrium bond length, f_r , f_{rr} have the usual significance as stretching force constant and stretch-stretch interaction constant, respectively, f_{α} and f_{β} are the bending constants and μ s refer to reciprocal masses of the atoms Assuming negligible contribution of f_{α} and f_{β} to the B_{2u} and B_{3u} frequencies the bond angle at Pb is given by

$$\operatorname{an} \alpha/2 = (\tilde{v}_5/\tilde{v}_4)$$

which gives $\alpha \sim 80^{\circ}$ Assuming $f_r \sim 2.2 \text{ md/A}$ [slightly less than 1/2 f_R (monomer)] and f_r to be approximately 0.1 f_r the calculated frequencies $v_1 \sim 507 \text{ cm}^{-1}$, $v_3 \sim 481 \text{ cm}^{-1}$, $v_4 \sim 543 \text{ cm}^{-1}$ and $v_5 \sim 455 \text{ cm}^{-1}$ agree well with the 1r and Raman data Using the experimental frequencies we calculate back the force constants f_r , f_{π} , $nd f_{\beta}$ as well as the frequency of the A_g bending mode v_2 , which are given in Table 1 These data give convincing evidence for a cyclic structure of the Pb₂O₂ unit and suggest very little strain in the ring

The 1 r peaks at 474 and 374 cm⁻¹ were assigned by OGDEN and RICKS [14] to the Pb₄O₄ species The association of these peaks with the trimer unit was rejected by these authors on the basis of a comparison with the 1 r data for matrix isolated (SiO)_n species The selection rules for both the trimer (D_{3h}) as well as the tetramer (T_d) predict two 1 r active Pb–O stretching modes

$$\Gamma_{\text{trumer}} (\text{Pb-O st}) = A'_1 (\text{R}) + 2E'(\text{R}, 1\text{ r})$$

$$\Gamma_{\text{terramer}} (\text{Pb-O st}) = A_1 (\text{R}) + E(\text{R}) + 2F_2 (1\text{ r})$$

The bending frequencies expected to be below 200 cm^{-1} are ignored in our discussion. The absence of any coincidence in the 1r and Raman data, though not the ultimate test, prefers the tetramer structure to be associated with the 1r peaks described above. The results of a normal coordinate analysis similar to the one carried out for the dimer give stronger support to





Fig 2 Raman spectra of matrix isolated lead oxide species (a) Freshly prepared sample at ~ 15 K, (b) heat treated at ~ 30 K for 20 min, (c) heat treated at ~ 35 K for 20 min *Peak due to bulk PbO possibly caused by local heating by the laser beam **Peak due to N₂ matrix

Observed	Calculated	-
(cm ⁻¹)	(cm ⁻¹)	Force constants (md/Å)
	Monomer	
v ₁ 714 (1 r , R)	714	£ = 4 55
	Dimer (D_{2h})	
$\tilde{v}_1(A_q)$ 524 (R)	524	$f_{\rm r} = 2.25$
$\tilde{v}_2(A_g)$ —	74	$f_{rr} = 0.30$
$\tilde{v}_3 B_{1g}$ 463 (R)	463	$r_0^2 f_a = 0.05$
$\tilde{v}_4 (B_{2u})$ 558 (1 r)	558	$r_0^2 f_0 = 0.01$
$\tilde{v}_5(B_{3u})$ 463 (1 r)	467	α (OPbO) = 80°
	Tetran	ner (only stretching
		frequencies)
\tilde{v}_1 (A ₁) 442 (R)	460	$f_{\rm r} = 1.38$
\tilde{v}_2 (E) 323 (R)	331	$f_{rr} = 0.26$
\tilde{v}_3 (F ₂) 464 (1 r)	474	$OP6O = 86^{\circ}$
\tilde{v}_4 (F ₂) 372 (1r)	374	$Pb\hat{O}Pb = 94^{\circ}$

Table 1 Vibrational frequencies and force constants of PbO, Pb_2O_2 and Pb_4O_4 matrix isolated units

the tetramer structure as being responsible for the additional peaks

The formation of a tetramer unit from four monomers introduces 24 bond angles into which part of the potential energy resides, consequently, the Pb-O bond strength in the tetramer is expected to be less than that in the dimer Using $\tilde{v}_3(F_2)$ and $\tilde{v}_4(F_2)$ from the ir data we calculate f_r and f_{rr} to be 1.38 and 0.17 md/Å, respectively The symmetrized F and G matrices for the tetramer species are taken from MARONI and SPIRO [16] and OGDEN and RICKS [14] With these force constants we calculate the frequencies of A and Estretches to be 460 and 312 cm^{-1} , respectively (Table 1) The Raman spectra reveal a strong (relatively) peak at 442 cm^{-1} and a peak at ~ 323 cm^{-1} (Fig 2) against a broad background which agree with the calculated values The association of these peaks with the trimer do not give internally consistent results For example, assuming $f_r \sim 1.8 \text{ md/A}$ (expected to be somewhat less than that for dimer but more than that of tetramer) and $f_{rr} \sim 0.2 \text{ md/A}$ the stretching frequencies for trimer are estimated to be

$$v_1(A'_1 - R) 275 \text{ cm}^{-1}$$

 $v_2(E') 550 \text{ cm}^{-1}$
 $v_3(E') 360 \text{ cm}^{-1}$

which do not agree with the experimental data at all Thus, the assignment of major sharp peaks in the 1 r and Raman spectra of matrix isolated lead oxide to monomer, dimer and tetramer appears reasonable A smaller stretching force constant for the tetramer compared to that of the dimer is also consistent with the presence of more bond angles The interaction constant, whose significance cannot be put to the test, is approximately the same in both the dimer as well as the tetramer

It is interesting to note that the 1r and Raman spectra of $Pb_4(OH)_4Cl_4$ [17] which is an ionic solid have been well interpreted in terms of a distorted cubic structure (point group T_d) [16] of the ion $Pb_4(OH)_4^{4+}$ The Pb-O stretching constant in the ionic unit (~168 md/Å) is somewhat larger than that in the Pb_4O_4 unit but still smaller than the corresponding value for the dimer unit

The spectroscopic data on matrix isolated lead oxides provide fairly conclusive evidence for the ring structures of the dimer and tetramer species In contrast, the structures of $(SiO)_n$ (n = 2, 3,) are still uncertain and can possibly be most logically elucidated by obtaining good quality Raman spectra of matrix isolated silicon oxides

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