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Absorption and Resonance Raman Spectra of Pb_2 , Pb_3 , and Pb_4 in Xenon Matrices

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Abstract

Lead metal was vaporized and trapped in solid xenon at 12K. Electronic absorption and resonance Raman spectra were recorded of the resulting matrix, which was shown to contain Pb_2 , Pb_3 , and possibly Pb_4 molecular species. The vibrational frequency for Pb_2 is determined to be 108 cm^{-1} for the ground state, with a dissociation energy of $\sim 8200\text{ cm}^{-1}$. A D_{3h} symmetry is indicated for the Pb_3 species, with $\nu_1=117\text{ cm}^{-1}$ and $\nu_2=96\text{ cm}^{-1}$. The existence of Pb_4 is suggested by a fundamental and overtone of 111 cm^{-1} spacing.

Introduction

The development of matrix isolation techniques has promoted an interest in recent years in the spectroscopy of the vapors above high temperature solids, and in particular the study of simple species which may be trapped or grown through diffusion in low temperature inert solids. Recently, the powerful matrix isolation method has been applied to some of the heavier Group IV diatomic species. Teichman, et. al. [1] and Epting, et. al. [2] have reported detailed results of absorption, fluorescence, and resonance Raman spectra of Sn_2 in argon matrices.



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Brewer and Chang [3] reported the first electronic absorption spectra of Pb and Pb₂ in various matrices, which yielded values for the vibrational frequency of the excited A0_u⁺ state of the dimer close to the 159.2 cm⁻¹ value first determined by Shawhan [4] in gas phase studies using a tube furnace. Teichman and Nixon observed absorption and emission of Pb₂ in rare gas matrices [5]. From analysis of the laser-excited emission of the A-X transition, they proposed that the ground state is actually two near-degenerate low-lying states separated by about 110 cm⁻¹, each with a vibrational frequency of approximately 220 cm⁻¹. The vibrational frequency is in agreement with that reported by Weniger [6] in the analysis of the E-X transition in gaseous Pb₂. Finally, in the most recent work, Bondybey and English [7] have reinvestigated the emission and excitation spectra of Pb₂ in argon matrices. They note at least five new electronic states lower in energy than the previous A state, and have proposed a re-labeling of the states. The A state is now designated F0_u⁺, a notation adopted in this paper. Analysis of the emission spectra, and reconsideration of the Deslandres table presented by Shawhan [4] shows a single ground state for Pb₂ with a vibrational frequency of 112 cm⁻¹ in solid argon. To date, there have been no reported Raman spectra of molecular lead species, (as recently noted [2]), and no spectra of any type for Pb aggregates higher than the diatomic molecule.

In our laboratory, we have initiated an experimental program utilizing matrix isolation techniques for the study of free radical and high temperature molecules. As a first effort to explore the problems of obtaining Raman spectra of matrix isolated species, it was decided to investigate the spectra of lead molecules. In particular, since the F-X transition of Pb₂ in xenon [3] is resonant with several of the Ar ion laser emissions, we were interested in the possibilities of obtaining resonance Raman spectra of this species. We report the successful results of our efforts to record this spectrum, as well as data which suggests the isolation of higher order Pb aggregates.

Experimental Technique

The low temperature apparatus used in this work consisted of a CTi Model 21 cryocooler operated at 12K, with a spectroscopic sample chamber equipped with quartz windows. Samples were deposited on a sapphire (Al_2O_3) window substrate mounted to the cryocooler cold station. Temperature of the substrate was monitored by a 0.07 at. % Fe-doped gold vs. chromel thermocouple sandwiched between the sapphire plate and the sample mount. Lead (Baker Reagent grade, granular) was vaporized from a small resistively heated stainless steel oven with a 1 mm orifice approximately 15 cm from the cold substrate. A stream of xenon gas (Airco) was directed against the plate at a 45° angle to the lead beam. In order to prevent fogging of the matrix, it was necessary to maintain the temperature of the substrate at about 30K during the deposition process, which took place over a 4-6 hour period. Spectra were recorded at the base temperature of 12-15K, except where noted. Absorption spectra were recorded using a Cary Model 14 spectrophotometer. A custom Raman system, consisting of a Spex 1401 double monochromator with photon counting electronics was used for the Raman work. A Coherent Model 52 Ar ion laser, with a power estimated at 100-200 mW at the sample on the 488 nm line was used to excite the spectra. Resolution was typically 4 cm^{-1} .

Results

A number of experiments were conducted to determine conditions for obtaining optimum isolation and quality of spectra. Of these, five experiments provided excellent results, and are presented here in the figures and discussion. Tracings of the visible/near-ultraviolet absorption spectra are shown in Figure 1, with data derived from these given in Table 1. Spectra were recorded at approximately 5K intervals from 45K to 15K to determine frequency shifts of the absorptions with

temperature, in the hope that the maxima could be "tuned" by temperature variation in or out of exact resonance with the laser emissions. However, no significant shifts were noted over this range, the major change being a strong increase in the opacity (or scattering) of the matrix as the temperature was lowered. This limited the short wavelength accessibility to above 350 nm. The strongest absorptions were those attributed to Pb_2 by earlier investigators, and two weaker absorptions in the blue were also seen. No structured absorptions which could be assigned to species other than the dimer were recorded.

Raman spectra were recorded using the available Ar ion laser excitation wavelengths 514.5 nm, 501.7 nm, 496.5 nm, 488.0 nm, and 476.5 nm. Of these, the most powerful is the blue-green 488.0 nm line. The positions of these emissions relative to the Pb_2 F-X absorption are shown in Figure 1. Strong signals were observed using all excitation frequencies. The Raman spectra for 496.5 nm, 488.0 nm and 476.5 nm excitations, shown in Figure 2, are strongly modulated by self-absorption of the scattered light. All of the excitation lines result in spectra exhibiting one or more progressions, the longest and most pronounced arising from excitation using the 496.5 nm laser wavelength, which from Figure 1, can be seen to be exactly resonant with an absorption maximum in the structured band near 500 nm. The raw Raman data for all laser excitations are presented in Table 2.

Discussion

A. Pb_2

The absorption spectra presented in Figure 1 are very similar to the spectra of lead vapor trapped in solid xenon published by Brewer and Chang [3]. The structured band near 500 nm, in the notation proposed by Bondybey and English [7], has been assigned to the F-X transition in diatomic lead. Our calculated vibrational parameters for the FO_u^+ state, from the data in Table 1, yield $\omega_e' = 172 \text{ cm}^{-1}$ and $\omega_e'x_e' = 1.8 \text{ cm}^{-1}$, in good agreement with the

values reported by previous investigators for both gas and matrix studies [3-7]. The unstructured band in the red, extending from 15600-16300 cm^{-1} , has been assigned by Bondybey and English to the CO_U^+-X transition in Pb_2 . Spectra published by Teichman and Nixon [5] show this band with a well-defined vibrational structure. These researchers also reported two weak bands in the blue to ultraviolet near 23000 cm^{-1} and 34000 cm^{-1} , respectively, which they tentatively attributed to Pb_2 . Although we were unable to obtain spectra below 350 nm, our spectra show two weak and unstructured bands near 22000 cm^{-1} and 24000 cm^{-1} . The Raman data presented below suggest that the 22000 cm^{-1} band in particular may be due to Pb_3 instead of the dimer. As mentioned above, no appreciable frequency shifts were noted when the matrix temperature was varied.

The raw Raman data presented in Table 2 indicate the presence of at least two distinct molecular species in the matrix. It can be seen that, as the excitation wavelength is changed from the green to the blue, one strong progression is replaced by another of different spacing. The low fundamental frequencies of these progressions suggest that they are due to molecular lead species. The data of Table 2 are reorganized and presented in Table 3 to show the progressions observed. The progression of approximately 107 cm^{-1} spacing is undoubtedly due to diatomic lead, since the resonance of the 496.5 nm excitation line with a maximum in the F-X absorption spectrum induces a progression in this spacing with some 10 overtones. In addition, excitation at 476.5 nm, above the absorption band, produces no scattering at these frequencies. A least squares fit of the vibrational spacings gives ground state molecular parameters $\omega_e'' = 108 \text{ cm}^{-1}$, and $\omega_e''x_e'' = 0.4 \text{ cm}^{-1}$. The estimated error in frequencies of 2 cm^{-1} for the Raman data makes the anharmonicity value unreliable, however. This confirms the calculated ground state vibrational frequency for Pb_2 in solid argon of 112 cm^{-1} deduced by Bondybey and English from their emission spectra. From a rough calculation, the dissociation energy is estimated at 8200 cm^{-1} , consistent with a value of 8000 cm^{-1} estimated from mass spectral data [8].

B. Pb_3

Excitation at shorter wavelengths brings another progression into prominence with spacing of approximately 117 cm^{-1} . A single feature at 117 cm^{-1} first appears using 496.5 nm excitation, and becomes a progression with five overtones with the 488.0 nm line. The much weaker 476.5 nm laser emission still produces the same progression with two overtones; however, no scattering at these frequencies is observed with either of the two green laser frequencies. This implies a second species in the matrix, which most probably is the triatomic Pb_3 . If a D_{3h} geometry is assumed for the trimer, two vibrational modes of A'_1 and E' symmetry, both Raman active, are allowed. When the dimer stretching force constant, $f_r = 0.71 \text{ mdyne/\AA}$, is assumed for the trimer, with an interaction constant $f_{rr} = -0.1 f_r$, the frequencies of these two modes are calculated as 118 cm^{-1} and 98 cm^{-1} , respectively. Therefore, it is reasonable to assign the 117 cm^{-1} progression to the totally symmetric stretching of the D_{3h} trimer. A least squares fit of these frequencies to a line gives $\omega'_e = 117 \text{ cm}^{-1}$ and $\omega'_e x'_e = 0.2 \text{ cm}^{-1}$. Closer inspection of the Raman spectra reveals a feature at 191 cm^{-1} with 488.0 nm and 476.5 nm excitation of an intensity proportional to the 117 cm^{-1} feature in both. This may be assigned to the first overtone of the degenerate stretch, giving the fundamental frequency for this mode as approximately 96 cm^{-1} . Recalculation of the vibrational parameters using these frequencies gives $f_r = 0.68$ and $f_{rr} = -0.06$, in units of mdyne/\AA .

An argument may be advanced for the choice of D_{3h} symmetry over the two other choices, C_{2v} and linear. For the bent model, three frequencies are expected, corresponding to a symmetric and asymmetric stretch and a symmetric bend. Only the symmetric modes are expected to show resonance effects, and the bending mode should be much lower in frequency than the stretches. The observation on two resonance enhanced modes is inconsistent with this interpretation. A similar argument holds for the linear model. In it, only the symmetric stretch is Raman active. For the D_{3h} model, both modes are close in frequency as the calculation indicates, and the overtone of the degenerate mode contains totally symmetric character, which permits resonance enhancement.

The increase in intensity and number of overtones of the Pb_3 progression with increasing excitation frequency implies that the weak absorption band near 22000 cm^{-1} is attributable to this species rather than the dimer. An attempt was made to promote diffusion and reaction in the matrix by raising the temperature; however, no changes were observed, the same result noted by earlier researchers [3]. This indicates that the heavy lead species is insufficiently mobile in the nearly as heavy Xe matrix to diffuse and give detectable products in a reasonable time. Therefore, the 22000 cm^{-1} feature can only be tentatively assigned to Pb_3 .

C. Pb_4

The Raman spectrum excited by the 488 nm laser line gives two weak features at 111 cm^{-1} and 222 cm^{-1} , whose intensities relative to the dimer and trimer peaks as well as to each other suggest their assignment to the fundamental and first overtone of the totally symmetric stretch of a Pb_4 molecule. Two symmetric structures for a tetramer are possible. For a square planar (D_{4h}) model, the distribution of vibrational modes is:

$$A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_u \quad (D_{4h});$$

whereas for a tetrahedral structure, the distribution takes the form:

$$A_1 + E + F_2 \quad (T_d).$$

In either case, only one totally symmetric mode is expected with significant intensity in the Raman spectrum even though three modes are Raman active. A clear distinction between the two structures is, therefore, not possible. However, the cubic close-packed structure of bulk lead [9] suggests that a tetrahedral model is preferable. This choice is consistent with a mechanism for the growth of the tetramer from a D_{3h} trimer by simple atom addition and new bond formation, a process which, for a resulting tetrahedral Pb_4 , requires no bond breaking. Such bond breaking is required for the square planar structure.

The 111 cm^{-1} feature is therefore attributed to the $A_1 (T_d)$ fundamental. For the totally symmetric species, the G and F matrix elements are evaluated to be $4\mu_{\text{Pb}}$ and $(f_r + 4f_{rr})$, respectively. A value for $f_r = 0.62\text{ mdyne/\AA}$ is estimated if the value of the interaction term f_{rr} is carried over from the trimer. The lower force constant value for the tetramer is possibly due to delocalization of the valence electrons in forming more bonds (compared to dimer and trimer) with neighboring atoms.

Conclusions

Analysis of the visible electronic absorption and resonance Raman spectra of lead vapors isolated in solid xenon matrices has provided strong evidence for the existence of several molecular species, some of which have not previously been reported. The presence of Pb_2 is confirmed by the visible absorption, and Raman spectra yield a vibrational frequency for the ground state of 108 cm^{-1} , and a dissociation energy of 8200 cm^{-1} . A second resonance Raman progression indicates a Pb_3 species of D_{3h} symmetry. Finally, two additional Raman features at approximately 111 cm^{-1} spacing are evidence for the existence of a third species, tentatively identified as Pb_4 . The assumption of tetrahedral symmetry for this species is supported by estimated stretching force constant decrease consistent with the trend shown from dimer to trimer.

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Table 1: Electronic absorption maxima of $\text{Pb}_2 (\text{FO}_U^+ \leftrightarrow \text{XO}_U^+)$ in xenon

<u>λ, nm</u>	<u>ν, cm^{-1}</u>	<u>$\Delta\nu$, cm^{-1}</u>	<u>Assignment</u>
521.30	19183		0 -- 0
		169	
516.75	19352		1 -- 0
		164	
512.40	19516		2 -- 0
		163	
508.15	19679		3 -- 0
		156	
504.15	19835		4 -- 0
		153	
\sim 500.3	19988		5 -- 0
		152	
\sim 496.5	20140		6 -- 0

Note: Estimated frequency accuracy is 2 cm^{-1} .

Table 2: Observed Raman frequencies of molecular Pb species in xenon matrices

Excitation wavelength (in nm):

<u>514.5</u>	<u>501.7</u>	<u>496.5</u>	<u>488.0</u>	<u>476.5</u>	<u>Assignment</u>
107	107	107	107		Pb ₂ (ν_1)
			111		Pb ₄ (ν_1)
		117	117	116	Pb ₃ (ν_1)
			191	191	Pb ₃ ($2\nu_2$)
212	213	213	213		Pb ₂ ($2\nu_1$)
			222		Pb ₄ ($2\nu_1$)
			233	233	Pb ₃ ($2\nu_1$)
319	319	319	319		Pb ₂ ($3\nu_1$)
			350	349	Pb ₃ ($3\nu_1$)
425		424	425		Pb ₂ ($4\nu_1$)
			466		Pb ₃ ($4\nu_1$)
530		528			Pb ₂ ($5\nu_1$)
			581		Pb ₃ ($5\nu_1$)
		632			Pb ₂ ($6\nu_1$)
			696		Pb ₃ ($6\nu_1$)
		735			Pb ₂ ($7\nu_1$)
		835			Pb ₂ ($8\nu_1$)
		937			Pb ₂ ($9\nu_1$)
		1038			Pb ₂ ($10\nu_1$)
		1138			Pb ₂ ($11\nu_1$)

Note: All frequencies are in cm^{-1} units. Frequency accuracy is estimated at 2 cm^{-1} .

Table 3: Observed Raman frequencies of molecular Pb species in xenon

Species:

<u>Pb₂</u>	<u>Pb₃ (A₁['])</u>	<u>Pb₃ (E['])</u>	<u>Pb₄ (A₁)</u>
107	117	---	111
213	233	191	222
319	349		
424	466		
528	581		
632	696		
735			
835			
937			
1038			
1138			

Note: All frequencies in cm⁻¹, with estimated accuracy of 2 cm⁻¹.

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Figure 1: UV-visible absorption spectrum of Pb species in a solid xenon matrix at 12K. Arrows indicate the positions of the argon ion laser wavelengths used to excite the Raman spectra.

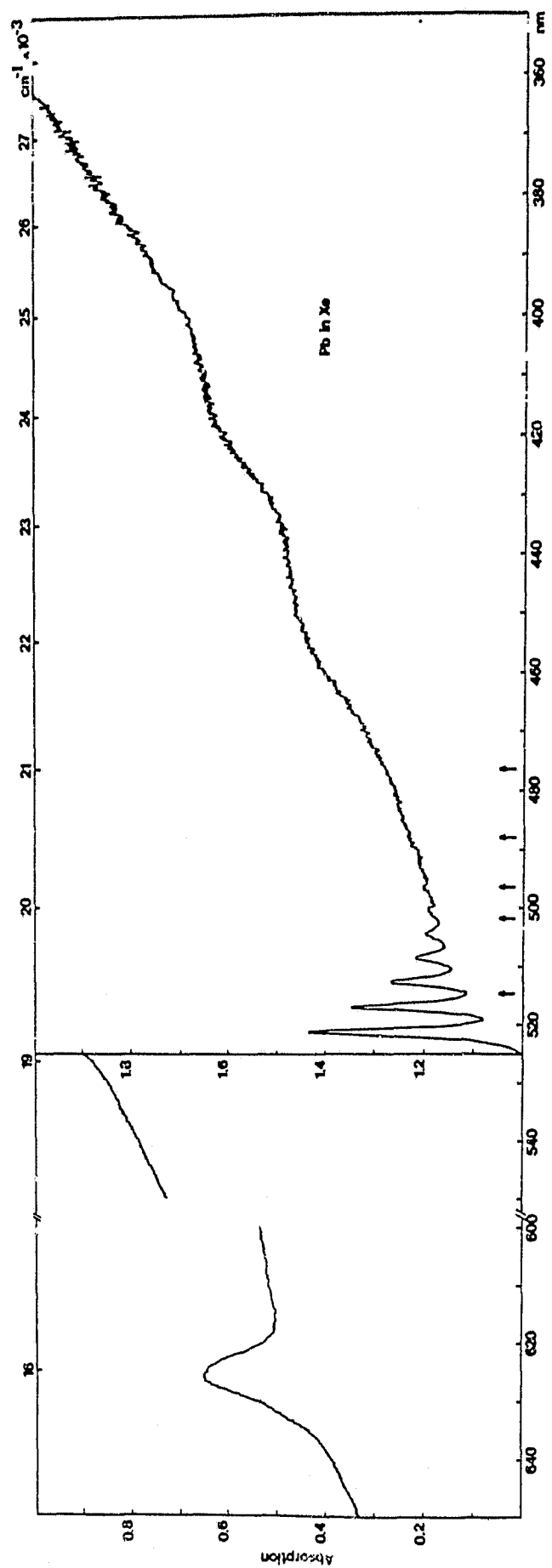


Figure 2: Resonance Raman spectra of molecular Pb species in a solid xenon matrix, recorded at 12 K. Vertical bars denote the count rates, not normalized to laser power or instrumental response. (a) Excitation using the 476.5 nm laser wavelength. (b) Excitation at 488.0 nm. (c) Excitation at 496.5 nm.

