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OPTICAL SPECTROSCOPIC STUDIES OF METAL ATOMS AND
MOLECULES IN THE LOW TEMPERATURE MATRICES

Chin-An Chang
(Ph.D. Thesis)

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OPTICAL SPECTROSCOPIC STUDIES OF METAL ATOMS AND
MOLECULES IN THE LOW TEMPERATURE MATRICES

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ABSTRACT

Lead has been trapped in various matrices to study the matrix effects on both the atomic and molecular lead absorption spectra. Pb is also codeposited with Ag to study the possible surface diffusion on the target. The observed spectra of Pb at various temperatures are correlated with some model calculations to get information about the origin of the matrix effects. The earlier theories on the matrix effects are discussed. A model is proposed to try to account for the observed matrix effects on most of the trapped metal spectra in a generalized way.

I. INTRODUCTION

It is well known that when metal atoms are trapped in inert gas matrices at very low temperatures, new features appear in the spectra of the trapped species. The absorption frequencies usually shift, either to the red or to the blue of the gas phase transitions; multiplet structures appear when transitions involving degenerate upper or lower state are observed; and the lines are broadened in the matrices. Let those matrix effects be denoted as static ones. In addition, there is a dynamic matrix effect that the components of the multiplet show different directions of shift on warming up the matrix. For most atoms involving $p \leftarrow s$ transitions, it is observed that the component highest in frequency of the triplet shifts reversibly to the blue, while the two lower frequency components reversibly shift to the red on warming up the matrix. Examples are Li^1 , Na^2 , Ag^3 , Ca^4 , Cd^4 , and Mg^4 .

Various groups of workers have tried to interpret these matrix effects in the past years. McCarty and Robinson⁵ suggested that the observed frequency shift is due to the interaction of the trapped species with the matrix environment. The observed triplet for Hg and Na in the matrices is attributed to the removal of the three-fold degeneracy of the P state involved in the transition by a Jahn-Teller distortion of the matrix. Using Lennard-Jones 6-12 and 6-8-12 potentials they successfully related the observed frequency shifts of Hg and NH in Xe, Kr and Ar matrices.

Brith and Schnepf⁶ studied the multiplet structure of Mn spectrum in Ar by calculating the splitting energy quantum mechanically. Two possible trapping site geometries of Mn in a fcc Ar matrix were tested. First, an octahedral field is approximated and two Ar atoms on one of the

axes are distorted. Second, one nearest neighbor Ar atom is missing. In both cases, the authors obtained the right order of magnitude of the splitting energies, but only doublets can be expected from these two models. Therefore, two or more Ar neighbors must be missing in order to account for the observed triplet. However, as Brith and Schnepf pointed out, either lattice distortion or missing neighbors must be highly regular throughout the matrix to account for the observed discrete lines. Neither of these can be explained by the authors. In addition, the reversible frequency shift of the triplets of many metals on warming up the matrix strongly opposes the missing neighbor mechanism.

Andrews and Pimentel¹ suggested the possible roles of nonnearest neighbor metal-metal interactions in determining the multiplet structure and the splitting energies. Li was trapped in Xe, Kr and Ar matrices, and Li_2 molecular potentials in the gas were used to obtain the energy shift at various nonnearest neighbor distances. Rough agreement with the experiment was obtained. However, the fact that the observed splitting persists even with extremely high M/R ratios led the authors to conclude that this cannot be the only cause of the splittings.

Brewer and King^{7,8} studied the possible contribution of metal-metal interaction in the splitting energies by codepositing Au and Ag in Kr matrix. The mixed metal matrix spectrum showed two triplets corresponding respectively to those of pure Au and Ag in Kr matrix. All the components had the same frequencies as in the pure metal spectra, with the same relative intensities and breadths of the absorption peaks, and no extra features appeared. This seems to eliminate the possibility that the metal-metal interaction could be responsible for the multiple structures,

because the interacting potential between Ag and Au is expected to be quite different from Ag-Ag and Au-Au potentials.

In addition, Brewer and coworkers^{3,8} studied the spectra of Cu, Ag and Au trapped in Xe, Kr and Ar matrices. The gas phase transitions $^2P_{3/2} \leftarrow ^2S_{1/2}$ and $^2P_{1/2} \leftarrow ^2S_{1/2}$ of Cu, Ag and Au are separated by 248 cm^{-1} , 921 cm^{-1} and 3813 cm^{-1} , respectively. The observed triplet for all three metals in the matrices has two components close in frequencies to that of $^2P_{3/2} \leftarrow ^2S_{1/2}$, and one to $^2P_{1/2} \leftarrow ^2S_{1/2}$ transitions. Because the $^2P_{3/2}$ and $^2P_{1/2}$ states split under Stark effect into two and one states, respectively, Brewer et al. suggested that the observed triplet could be due to Stark splittings caused by the matrix field.

Very recently McCarty⁹ proposed an explanation for the observed triplet of Hg in the matrices. One line was attributed to the completely isolated Hg atoms, and two lines due to resonance interaction between two Hg atoms being nearest neighbors to each other. In relating his work to the Ag-Au codeposition work by Brewer and King, McCarty argued¹⁰ that (1) the presence of a different metal atom as a nearest neighbor of Hg atom will not give two lines due to resonance interaction, but can only broaden the line which is due to completely isolated Hg atoms; (2) the distribution of solute atoms in the matrices is not random like, but being dependent on the energy differences associated with nearest neighbor solute atoms as opposed to nonnearest solute atoms. Therefore, even in matrices with small metal concentration, the metal monomer-dimer ratio does not change much from a concentrated matrix; (3) Hg-Hg has a relatively small interaction-potential well-depth compared to other metals like Na, Cu etc., therefore for the latter metals (a) the potential

combining relation should not hold, and (b) the distortion of the crystal in the neighborhood of either a metal monomer or dimer is likely to be qualitatively and quantitatively different from McCarty's expression for the Hg work.

As was mentioned earlier in this section there are static as well as dynamic matrix effects. All the above theories tried to interpret the possible origin of the multiplet structures observed in the matrices, but only by considering the static matrix effects. The possible relation between the dynamic matrix effect and the origin of the multiplet structures was mentioned only in the works by Brewer et. al. The work done in this thesis is therefore devoted to a better understanding of those matrix effects. Pb was trapped in a number of pure and mixed matrices and its absorption spectra were studied. The possibility of polymer formation on the target during the deposition is also studied. The Pb spectra observed were correlated with some theoretical considerations to try to understand both the static and dynamic matrix effects in a generalized way.

II. EXPERIMENTAL

A. General

In the experiments an atomic or molecular beam of the metal under study is generated by heating the metal in a furnace. The furnaces used in this thesis include resistance-heating cell, electron-bombardment-heating cell, and radiation-heating cell. The metal beam generated is then cocondensed with the matrix gas on a sapphire or cesium iodide target which has been cooled to 20°K by liquid hydrogen in a liquid hydrogen dewar, or the liquified hydrogen gas in a cryo-tip. The cryo-tip is mainly used to study the temperature dependence of the metal spectra in the matrices, while the L- H_2 dewar is mainly used for trapping metal species from furnace temperatures higher than 800°C . The spectral regions studied extend from IR, visible to the ultraviolet.

B. Cryostat

1. Liquid Hydrogen Dewar

The liquid hydrogen dewar used is shown in Figs. 1 and 2. Its detailed description has been given in B. King's thesis.⁸ The advantage of this dewar is its larger content of liquid hydrogen and thus better cooling efficiency which is useful in well isolating the metal species generated from temperatures higher than 800°C . On the other hand, it has the disadvantage of having to deal with the large quantity of liquid hydrogen both in the dewar and in the tank. Safety precaution therefore has to be taken into consideration in using this dewar. Also, target temperature can not be well controlled above 20°K to study the temperature dependence of the matrix spectra.

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Figure 1. Liquid hydrogen dewar and the set up.

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Figure 2. Cut-away drawing of liquid hydrogen dewar.

2. Cryo-tip

The cryo-tip used in this work is of the model number AC-21-110 built by Air Products and Chemical Inc. A general view of it is shown in Figs. 3 and 4. Detailed description of this cryo-tip can be found in J. L. Wang's thesis.⁴ Typically, it has the advantage that target temperature can be well controlled by monitoring the hydrogen gas pressure above the liquid gas at the bottom of the heat exchanger. Also, the absence of large quantity of liquid hydrogen in the cryo-tip and in the room causes less expensive precaution for safety concern.

C. Furnaces

1. Stainless Steel Knudsen Cell

The stainless steel Knudsen cell is mainly used to generate metal beam from 600°C to 800°C. The orifices of the cell used are 1.0 mm, 1.5 mm, 2.0 mm and 2.5 mm, with the 1.0 mm one used most often. It is believed that equilibrium state is obtained inside those cells because of the small orifices used relative to the surface area of the material under evaporation. The Knudsen cell is heated in a quartz tube which is wrapped with resistance heating wire. A tungsten foil is lined between the cell and the inner wall of the quartz tube to prevent the metal vapor from reaching the quartz tube. The temperature of the cell is measured with a Chromel Alumel thermocouple (Type K) which is spark-welded on the stainless steel Knudsen cell. The output is coupled to a Simplyrometer (API Instrument Company) with a temperature range from 0 to 1000°C. These are shown in Fig. 5.

XBB693-1633

Figure 3. The cryo-tip system.

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Figure 4. The cryo-tip system.

XBL 694-416

Figure 5. The stainless steel Knudsen cell and the optical system.

2. Resistance-Heating Graphite Cell

The resistance-heating graphite cell used is shown in Fig. 6. It has been described in B. King's thesis.⁸ This cell is used for Pb and for Cu. The furnace temperature needed to evaporate Cu is around 900°C. The temperature of the cell above 800°C is measured using a disappearing filament optical pyrometer.

3. Electron-Bombardment Heated Cell

The electron-bombardment heated cell is mainly used in the two metal codepositing experiments where one metal needs to be heated to above 900°C. The cell used is shown in Fig. 7, and the double furnace shown in Fig. 8. Those were constructed by B. King, and their detailed descriptions are also given in King's thesis.⁸ The cell temperature again is measured using a disappearing filament optical pyrometer.

D. Targets

Sapphire target is used in most of the experiments, while cesium iodide target is used in the IR region. The 3 mm thick sapphire plate used in both cryo-tip and liquid hydrogen dewar is clamped in a copper target holder between indium gaskets to ensure better thermal contact. Either quartz or sapphire windows are used along the optical path.

The temperature of the target is measured using a high thermoelectric power thermocouple made of copper versus alloy of gold-2.1 atomic % cobalt. The junction of the thermocouple is clamped between the target and indium gasket. The output is coupled to a potentiometer and the temperature changes be measured.

XBL 6810-6063

Figure 6. Resistance heating graphite cell

XBL 6810-6067

Figure 7. Electron bombardment heated graphite cell

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Figure 8. Double furnace of electron bombardment heated cells.

E. Gas Handling System

The matrix gas entering the liquid hydrogen dewar and the cryo-tip is handled by a dual channel system similar to the ones used by King⁸ and Wang.⁴ The flow rate of the gas is regulated by precision Nupro needle valves, and monitored by calibrated Fischer-Porter flowmeters equipped with sapphire floats. The flowrate used is normally 0.5 millimoles per hour. In some experiments it is varied over a range of 100.

The gas mixtures of rare gases, and rare gas - SF₆ mixtures are prepared by mixing the gases into an empty 1-liter bulb immersed in liquid N₂. The mixed gases are warmed up to room temperature and allowed to mixing for at least forty-eight hours before use.

Research grade purity rare gases (> 99.99%) and SF₆ gas (99.99%) are used without further purification.

The metals used in this work include Pb, Ag and Ca. The metallic Pb used in this work is provided by the American Smelting and Refining Co., with 99.999⁺% purity. The chemical and spectral analysis showed that the maximum impurity contents are: Mg < 1 ppm, Fe < 1 ppm and Cu < 1 ppm. Metallic Ag was provided by the Englehard Industries, Inc. with purity of 99.95%. The Ca in granules was provided by Gallard Schlesinger, Chemical Mfg. Corp., Carle Place, N.Y. The purity was 99.9%.

F. Typical Experimental Parameters

Before deposition the pressure in the vacuum system is $\leq 3 \times 10^{-6}$ torr, and rises during deposition. Target temperature used for deposition is 20°K in most experiments, and 18°K at cryo-tip when Ar is used as the

matrix gas. Because of the uncertainties of the amount of matrix gas that actually condensed on the target, the gas phase M/R ratio becomes unreliable in dealing with the degree of isolation of the metal atoms in the matrix film. A relative basis is therefore established by finding the minimum amount of Xe gas needed to isolate Pb at a fixed furnace temperature, and gives weak discrete atomic Pb spectrum in the matrix film. The M/R ratio in such a matrix film is approximated to be 30. Xe was chosen for this basis because it is believed that Xe has highest tendency to be condensed at 20°K than Kr and Ar. The M/R ratios for Kr, Ar and SF₆ are then estimated on this relative basis. It is emphasized that because of the different sticking coefficients and extents of diffusion on the target among the rare gases, the same M/R value in Kr and Xe would mean less efficient isolation in Kr than in Xe. The surface diffusion of matrix gases on the target were found¹¹ to take place at temperatures above 1/2 T_m of the gases. T_m being the melting points of the matrix gases. The actual difference due to these two factors is not known, however. The M/R ratios used in this work are varied from 30 to 4500 on the above basis.

G. Optical Systems

Spectra in the visible and ultraviolet regions are photographed with a 0.75 meter Jarrell-Ash plane grating spectrograph, model 75-000. It has a nominal exit aperture of f/6.3. A plane grating blazed at 7500Å is used for both visible and ultraviolet regions, which gives a dispersion of 20Å/mm in the first order. Another grating blazed at 3000Å is also used in the ultraviolet region, which gives a dispersion of 5Å/mm in the first order. The optical arrangement is shown in Fig. 9.

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Figure 9. Optical systems used

The light sources in the ultraviolet region are a 150 watt xenon-mercury arc lamp operating at 8 amp, and a 1-kilowatt hydrogen discharge lamp which is mostly used for the region below 2500Å. A high intensity tungsten lamp is used for the visible region. The reference source used for the whole spectral region is a low pressure Germicidal mercury lamp. Kodak 103a-O spectroscopic plates are used for the ultraviolet region, and 103a-F plates for both the ultraviolet and visible regions. Kodak 1-N plates are used for the region between 7000Å and 9000Å.

Spectra in the infrared region are made with a Perkin-Elmer 421 Spectrophotometer using Dual Grating Exchange with a spectral region covered from 4000 to 600 cm^{-1} .

III. RESULTS AND DISCUSSIONS

A. Matrix Work

Among the earlier matrix works reported in the literatures, atoms with $p \leftarrow s$ transitions have been studied very extensively. It is therefore interesting to study some atom which has ground-state P configuration and the first transition allowed excited state in S configuration. The observed spectra are expected to differ in certain aspects from atoms with $p \leftarrow s$ transitions. Pb was chosen for this purpose and was studied extensively.

Some of the lowest energy levels¹² of atomic Pb in the gas are tabulated in Table 1. Also included in the last column of Table 1 are the transition probabilities¹³ expressed in gA unit, where g is the statistical weight of the upper level, and A is the Einstein transition probability. Only those states are included which lie above the ground state within the energy differences covered by the spectral region studied here, i.e. with energies less than $50,000 \text{ cm}^{-1}$ above the ground state.

Pb_2 molecules are formed in the Pb vapor at higher temperatures, and its vapor pressure increases with increasing Pb vapor pressure. The Pb vapor pressure is 1×10^{-3} torr, 1.4×10^{-2} torr and 1×10^{-1} torr at 900° , 1000° and 1100°K , respectively. The vapor pressures of Pb_2 at the corresponding temperatures are estimated to be 1×10^{-8} torr, 1.3×10^{-6} torr and 2×10^{-5} torr, respectively.

Mass spectroscopic studies of Pb and Pb_2 by Drowart and Honig¹⁴ leads to a dissociation energy of $1.0 \pm 0.2 \text{ eV}$ for the ground state Pb_2 molecules. It is to be noted that this value is quite different from

TABLE 1. Energy levels of atomic Pb in the gas phase.

Config.	Desig.	J	Level	gA ($10^8/\text{sec}$)
$6s^2 6p^2$	$6p^2 \ ^3P$	0	0.00	
		1	7819.35	
		2	10650.47	
$6s^2 6p^2$	$6p^2 \ ^1D$	2	21457.90	
$6s^2 6p^2$	$6p^2 \ ^1S$	0	29466.81	
$6s^2 6p 7s$	$7s \ ^3P^\circ$	0	34959.90	
		1	35287.24	1.8
$6s^2 6p 7p$	$7p \ ^3P$	1	42918.68	
		0	44400.92	
$6s^2 6p 7p$	$7p \ ^3D$	1	44675.00	
		2	44809.41	
$6s^2 6p 6d$	$6d \ ^3F^\circ$	2	45443.26	
		3	46328.81	
$6s^2 6p 6d$	$6d \ ^3D^\circ$	2	46060.90	
		1	46068.57	0.68
$6s^2 6p 7s$	$7s \ ^3P^\circ$	2	48188.67	
		1	49439.57	
$6s^2 6p 8s$	$8s \ ^3P^\circ$	1	48686.87	0.44
		0	48726.16	

the value of 0.69 eV by the Birge-Sponer extrapolation from the spectroscopic data of Shawhan.¹⁵

The absorption and emission spectra of gaseous Pb_2 have been studied by Shawhan,¹⁵ and the absorption spectra by Weniger¹⁶ in more detail. Shawhan studied the transition between the ground state and the first excited state of Pb_2 . The transition has its band heads represented by the formula:

$$\nu = 19570.8 + 159.22(v'+1/2) - 0.882(v'+1/2)^2 + 0.00518(v'+1/2)^3 - 256.5(v''+1/2) + 2.96(v''+1/2)^2.$$

The first observed band is $v'=3$ and the band spectrum has its highest intensity at $v'=6$ and 7. This corresponds to an increase in r_e in going from the ground state to the excited state involved in this transition.

The observed band spectrum is attributed to diatomic based on the following reasons:

(1) The band system appeared only when Pb was present in the carbon or iron tube. This then clearly indicated that Pb must be one of the atoms of the diatomic molecule which gives rise to this band system.

(2) Since Pb was heated in tubes open to the air PbO is formed. However, although the observed band system is in the same region as that of PbO (with T_e at 19863.3 cm^{-1}), an assignment to any system of PbO is impossible because for the observed bands here $\omega_e'' = 255.6 \text{ cm}^{-1}$ while for PbO, $\omega_e'' = 722.5 \text{ cm}^{-1}$.

(3) The fact that $\omega_e'' = 255.6 \text{ cm}^{-1}$ for this system indicates that the molecule is heavier than PbS, the latter has ω_e'' of 428.14 cm^{-1} . This indicates that the second atom in the molecule must be heavier than S and cannot be any of the lighter elements like C, N, O or Si.

(4) The analysis of detailed spectrum is consistent with that expected from the isotope composition of the Pb used.

The fact that Pb_2 $\omega_e'' = 256.5 \text{ cm}^{-1}$ and $\omega_e' = 159.22 \text{ cm}^{-1}$ implies a change in force constant of about 2.6. This could mean a bond-order change of more than one-half in going from the ground state Pb_2 to the A state Pb_2 . Also, it means a larger r_e' than r_e'' , and a weaker bond in the A state Pb_2 .¹⁷

Weniger studied the absorption spectra of Pb_2 in more detail. In addition to the $A \leftarrow X$ transition, other transitions were found as described below:

$A \leftarrow X$

This is the same as Shawhan's observation. The vibrational spectra can be separated into three series of bands corresponding to P, Q, R branches. Thus, Weniger pointed out that $A \leftarrow X$ transition is of

$\Sigma - \pi$ type electronic transition. The intensity distribution is similar to that observed by Shawhan, and it again indicates a larger r_e value in the A state than in the X state.

$B \leftarrow X$

$$\nu = 34,202 + 110(\nu'+1/2) - 0.9(\nu'+1/2)^2 - 256.5(\nu''+1/2) + 2.96(\nu''+1/2)^2$$

D_e of B state is calculated to be 3361.1 cm^{-1} .

$E \leftarrow X$

$$\nu = 41965 + 110(\nu'+1/2) - 220(\nu''+1/2)$$

$a' \leftarrow A$

$$\nu = 15601 + 110(\nu'+1/2) - 164(\nu''+1/2)$$

$b' \leftarrow X$

This takes place between $31,000$ and $33,000 \text{ cm}^{-1}$, and b' state could be a repulsive state.

In addition, the resonance atomic transition at $2833.1\text{\AA}$ ($^3P_1 \leftarrow ^3P_0$)

is also observed at 1100°C. At higher temperatures, other atomic transitions are observed.

Lead was studied briefly by Duley¹⁸ in Xe, Kr and Ar matrices at 4°K and briefly by Wang⁴ in Xe and Kr matrices. In all three matrices a strong absorption band was observed at 2647A, 2617A and 2440A in Xe, Kr and Ar matrices, respectively. This band was assigned to the $6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition. In addition, one strong band and two weaker broad bands were observed in Xe, situated at 2349A, 2553A, and 2169A, respectively; two weak, broad bands in Kr, at 2787A and 2453A; one broad band at 2340A and many other bands at shorter wavelengths in Ar. The 2553A band in Xe, 2453A band in Kr, and 2340A band in Ar were temporarily assigned to the $6p6d\ ^3D_2^\circ \leftarrow 6p^2\ ^3P_0$ transition. However, no interpretation was given by Duley about the observed Pb spectra in these matrices.

Wang reported observing two bands in both Xe and Kr matrices. One strong band was observed at 2647A and 2613A in Xe and Kr matrices, respectively, and was assigned to the $Pb\ 6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition. In addition a broad band was observed at 2544A in Xe and at 2397A in Kr matrices.

In this work Pb has been trapped in the following matrices: Xe, Kr, Ar, Xe-Kr mixtures, Xe-Ar mixtures, SF₆, and Xe-SF₆ mixtures. Also, Pb was codeposited with Ag in the Kr matrix to study the solute-solute interactions and the diffusions on the target. The experimental results are shown and the implications discussed.

1. Xe

The absorption spectrum of Pb in Xe deposited at 20°K consists of two strong bands, situated at 2648A and 2259A, respectively. Two weak bands appear in thicker films deposited, situated at 2809A and 2402A, respectively. When a higher Pb evaporation temperature from the furnace was used

another band appeared centered at 2552A, which has a half-width of the order of 900 to 1000 cm^{-1} and showed blue-shaded structure. At still higher Pb evaporation temperatures while keeping the total Xe used the same, this band shows rapid intensity increase and increases its half-width as well as its blue-shaded structure. The spectra are shown in Fig. 10 with increasing Pb evaporation temperature. The temperatures used are 610°, 650°, 670° and 700°C for the spectra a -- d, respectively. The M/R used in these spectra are 1500, 500, 300, and 150 respectively. The film deposit time is one hour for the spectrum a, and 20 minutes each for the spectra b, c, and d. The microdensitometer tracings of the spectra c and d are shown in Fig. 11. In all the spectrum tracings reported in this thesis, the ordinates represent absorption intensities which increase from bottom to top in the figures shown. It is pointed out that because of the increasing background absorption below 2300A, the 2259A band does not show up except when longer exposure time is used at which the other longer wavelength bands appear very faint on the spectrum. Therefore, this band does not show in Figs. 10 and 11 where shorter exposure times are used in order to show up the bands around 2500A region for the comparison of their intensity changes when the Pb evaporation temperature is varied. The band wavelengths and frequencies of those bands are shown in Table 2. Also included is Duley's result of Pb in this matrix at 4°K.

As the Pb evaporation temperature is increased a molecular band spectrum is observed around the 5000A region, along with a weak band at 6268A which has a half-width of 220 cm^{-1} . The molecular bands observed are assigned to the $\text{Pb}_2^A \leftarrow X$ transition for reasons to be shown later. The spectrum of this Pb_2 molecular band is shown in Fig. 12; and the band wavelengths

Figure 10. Absorption spectra of Pb/Xe vs Pb evaporation temperature used which increases in the order from a to d. See the text for the M/R's and temperatures used.

XBL 707-1357

Figure 11. Absorption spectra of Pb/Xe vs Pb evaporation temperature used. (a) from spectrum of Fig. 10c, (b) from spectrum of Fig. 10d. The absorption intensities increase upwardly.

TABLE 2. Absorption spectrum of Pb in Xe.

This work (at 20°K)			Assignment	Duley (at 4°K)		Assignment
$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$		$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	
2809(w)	35596	~570				
2648(s)	37770	~500	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$	26117(s)	37780	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
2552 (w blue shaded)	39187	> 900	$Pb_2(E \leftarrow X)$	2553(w)	39170	$6p6d \ ^3P_2^0 \leftarrow 6p^2 \ ^3P_1$
2402(w)	41630	~240				
2259(s)	44277	~550		2249(s)	44460	
				2169(w)	46100

XBL 707-1349

Figure 12. Absorption spectrum of Pb_2^+ ($A \leftarrow X$) in Xe

and frequency are tabulated in Table 3, along with the halfwidths measured as well as the relative intensities of the individual bands. The relative intensities are obtained by integrating the areas under the absorption peaks using a planimeter on a relative basis.

The Pb_2 spectrum shows no shift on warming up the matrix and disappears between 80° and 85°K . The 6268A band shows red shift on warming up and disappears at about the same temperature as Pb_2 bands. The warm up spectra of Pb_2 recorded on photographic plate are shown in Fig. 13.

The assignment of the observed molecular band system to $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ transition is based on the following facts:

1. The observed band frequencies are in the right region as those of the gas phase $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ transitions, observed by Shawhan and Weniger, except for some red shift which is usually expected for the matrix trapped molecular spectra.
2. The observed vibrational spacings of the upper state are all less than 100 cm^{-1} and close to the ω value 159.22 cm^{-1} of the gaseous $\text{Pb}_2 \text{ A}$ state. This eliminates the possibility that the molecular species could be PbO whose ω_e is 451.7 cm^{-1} . In addition, the absence of PbO vibrational mode at 722.5 cm^{-1} in the IR spectrum is a further evidence that PbO is not responsible for the molecular spectrum observed.

The assignment of the absolute vibrational number to the molecular band system observed is difficult in the absence of emission spectra despite numerous attempts using tungsten lamp as a light source to excite the molecular system. However, some information can be obtained about the relative vibrational numbers among Pb_2 spectra in different matrices, and hence the relative frequency shifts in the matrices. These will be discussed later in this chapter.

TABLE 3. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Xe.

$\lambda(A)$	νcm^{-1}	$\Delta G_{1/2} \text{cm}^{-1}$	$\nu_{1/2} \text{cm}^{-1}$	Relative Intensity
5211	19191	168	55	74
5166	19359	165	56	39
5122	19524	163	55	21
5080	19687	174	83	13
5035	19861	153	68	5
4997	20014	155	49	2
4985	20169			
6268*	15954		220	
* Unidentified

Figure 13. Warm-up spectrum of Pb_2 ($A \leftarrow X$) in Xe.

Among the bands observed in the region 2800Å to 2200Å, only the strong one at 2648Å shows strong temperature dependency of its frequency. On warming up the matrix, the 2648Å band shifts reversibly to longer wavelength and disappears between 80° and 85°K. The warm up spectrum of this band between 20° and 77°K is shown in Fig. 14, and the frequencies observed at each temperature recorded are shown in Table 4.

Because this band appears strongest in all rare gas and mixed rare gas matrices used in this work, and shows strong temperature dependence of its frequency, it is assigned to atomic Pb $6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition which takes place in gas phase at 2833.9Å (35287 cm^{-1}) and is the strongest transition from the ground state 3P_0 . If so assigned, the frequency shift in Xe at 20°K amounts to 2483 cm^{-1} to the blue. This is normally expected for the trapped metal atomic transition when there is large orbital expansion in going from lower to a higher state. More of the matrix shift and other matrix affects will be discussed in Chapter IV where the observed frequency shifts are compared with the calculated values from intermolecular force calculations. The half-width of this band in Xe is around 550 cm^{-1} , about twice as much as the absorption bands of other metals which range between 150 and 250 cm^{-1} for the multiplet components. Again, in Chapter IV it will be seen that this broader half width for the Pb atomic band is expected in the matrices.

The dependencies of this Pb atomic transition frequency on the experimental conditions are studied by varying the film deposit rate in the following ways: 1. The amount of Pb coming out from the furnace per unit time is kept constant and Xe gas is varied from $M/R = 30$ to 4500. No effect on the Pb 2648Å band frequency is observed.

Figure 14. Warm-up spectrum of Pb/Xe.

TABLE 4. Temperature dependence of the Pb/Xe $^3P_1^o \leftarrow ^3P_0$ Band

Temperature °K	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
20°	2648	37770
30°	2650	37744
40°	2655	37666
50°	2659	37604
60°	2663	37547
70°	2667	37497
77°	2671	37435

2. Pb evaporation temperature is kept constant while varying the Knudsen cell orifice size. The amount of Pb coming out per unit time is increased by a factor of 6.25. Again, no effect is seen on the 2648A band. 3. Pb vapor pressure in the Knudsen cell is varied between 3×10^{-4} torr and 6×10^{-2} torr while keeping M/R constant, i.e. to vary the deposit rate of the whole matrix. No effect is seen on the 2648A band.

Attempts have also been made to study the dependence of the absorption intensities of Pb 2648A band and the Pb₂ bands on the M/R used. Pb evaporation temperature is so chosen and kept constant that there is significant amount of Pb₂ in the vapor. The first deposit has a high M/R to ensure the efficient isolation of Pb and Pb₂ from the vapor. The second film is then deposited on top of the first one with less M/R. Several other films with decreasing M/R are then deposited on top of the first two. This is to keep the experimental conditions as well the photographic alignment, etc. constant to make the comparisons as reliable as possible. The relative absorption intensities of Pb and Pb₂ of each deposit are obtained by integrating their absorption bands from the microdensitometer tracings of the photographic plates. The intensities from spectra of same exposure time are compared for Pb and Pb₂ to try to see if decreasing M/R leads to less efficient Pb isolation while enhancing Pb₂ formation on the target. Unfortunately, the unsteadiness of the H₂-lamp intensity used makes the Pb comparison difficult and a meaningful conclusion from this study impossible.

Although the above test failed to work out, experimental results do show that some Pb₂ molecules are formed on the target, especially when the Pb evaporation temperature is increased and yet the Pb₂ in the vapor

still remains negligible. A clear idea about this will be obtained after results for all rare gas matrices have been discussed and compared.

The band at 2552A in Xe is rather difficult to assign. This band always appears broad and blue shaded. Both the breadth and blue shaded character increases as the film deposited becomes thicker, or when higher Pb evaporation temperature is used. Figure 10 shows that as higher Pb evaporation temperature is used, this band gains intensity more than the other bands and, in the last spectrum shown in Fig. 11, dominates all the other bands. Its broadness and blue shaded structure imply that this band has the similarity of a molecular band. It is therefore assigned to the $\text{Pb}_2\text{E} \leftarrow \text{X}$ transition, which has its T_e at 41965 cm^{-1} (2383A) in the gas phase, for the following reasons:

1. Its broadness and blue shaded structure, as mentioned above.
2. The appearance of this band strongly depends on the matrix gas used. It was found that at ordinary Pb evaporation temperature, this band does not show up in Xe matrix until a thick film is deposited. In Kr matrix, it appears very easily, while the ease of appearance in Xe-Kr mixed matrices increases with increasing Kr content in the mixed gases. In Ar, this band appears very strongly and dominates even the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ absorption band although very high M/R is used.

The above comparison of the ease of appearance of this band goes exactly as that of the molecular bands which are assigned to the $\text{Pb}_2\text{A} \leftarrow \text{X}$ transition. It was found that in Kr, when very high M/R is used, both $\text{Pb}_2\text{A} \leftarrow \text{X}$ and the broad band discussed here are absent in the matrix.

3. When this band is assigned to $\text{Pb}_2\text{E} \leftarrow \text{X}$ transition, the approximate red shift in T_e in all matrices compare very well with those of the $\text{PbA} \leftarrow \text{X}$ transition in the same matrices. An exact treatment is difficult

because of the lack of fine structure of this band.

4. It is rather insensitive to warming up the matrix, like that of $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ absorption bands. One way to prove this assignment would be to excite this band using a high power monochromatic beam and observe the fluorescence emitted. If the above assignment is correct, one would expect to see the fluorescence spectra of $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ transition. The matrix environment has long been known effectively to quench the excitation energy from higher excited states to the lowest excited state, from there the fluorescence is normally observed to the ground state. This would be of great value because it has three important contributions -- to confirm the above assignment, to help assigning the absolute vibrational levels of the bands observed in $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ absorption spectra and to gain information about the ground state of Pb_2 .

5. An indirect experimental proof about the molecular origin of this band comes from the work of codepositing Pb with Ag in Kr matrix. It is observed that when high concentration of Ag is used, the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band appears strong, while both the broad band discussed here and the Pb_2 spectrum are absent. More about this work will be shown later.

Duley,¹⁸ however tentatively assigned this band to the $\text{Pb } 6\text{p}^6\text{d } ^3\text{D}_2^\circ \leftarrow 6\text{p}^2 ^3\text{P}_1$ transition, based solely on the absorption frequencies observed in the matrices. The above observation of the behaviors of this band strongly conflicts with any assignment of it to atomic Pb transition. Furthermore, the population of $6\text{p}^2 ^3\text{P}_1$ state at 20°K is completely negligible because it is higher in energy than the ground state $^3\text{P}_0$ by 7819.4 cm^{-1} . One may argue that thermal excitation in the vapor may populate this state to some extent, and those Pb atoms are then trapped in their excited state. This can be checked by estimating the population at the

temperature used. The normal evaporation temperature used for Pb is between 600°C and 800°C , which gives Pb pressure between 5×10^{-4} and 5×10^{-2} torr. The population ratio of $^3\text{P}_1$ state to $^3\text{P}_0$ state would range between $\exp(-13)$ and $\exp(-10.5)$. Therefore, the negligible population of the $6p^2\ ^3\text{P}_1$ state in the temperature range used for evaporating Pb from the furnace rules out such possible transitions starting from the $^3\text{P}_1$ state.

Other possibilities like forbidden transitions, multiple site, etc. are also ruled out due to the behaviors of this band as well as the fact that it does not disappear on warming up the matrix and cooling back, as some alkali metals do in the matrices.

The possibility that this band could be due to PbO also suffers from the fact that the gas phase PbO $E \leftarrow X$ takes place at $T_e = 34900\text{ cm}^{-1}$. This would require a blue-shift of the order of 4000 cm^{-1} in Xe matrix, which normally is not observed for molecular transitions except in the Rydberg transition where an expansion of the orbital is involved during the excitation.^{19,20}

The strong band at 2259A is difficult to assign. Duley also reported seeing this band. The consistent appearing of this band and its persistence to warming the matrix to 77°K and cooling back seem to oppose the multiple site possibility. If one assumes a blue-shift from the gas phase transition, the absorption energy is close to the transition $6p7p\ ^3\text{P}_1 \leftarrow 6p^2\ ^3\text{P}_0$ which in the gas has a value of 42919 cm^{-1} , and is parity forbidden. This transition might gain some intensity through the heavy atom perturbing effect of the Xe matrix atoms. This seems to be consistent with the absence of a similar band in Kr matrix which is same as Duley's observation and in Xe-Kr (10%-90%) matrix. Only the Xe-Kr (75%-25%)

matrix shows a diffuse band in the same region. However, such an excitation would involve an even larger orbital expansion in the upper state than the $6p7s\ ^3P_1$ state, and the absorption frequency should be temperature dependent, like that of the 2648A band in Xe matrix. The fact that this 2260A band is rather insensitive to warm up the Xe matrix casts doubt on the above assignment.

On the other band, if one assumes a red shift from the gas phase transition, the rather insensitive temperature dependence brought up the possible transition $6p6d\ ^3D_1^\circ \leftarrow 6p^2\ ^3P_0$ with a gas phase frequency of 46069 cm^{-1} . The red shift could be from the pushing down effect due to perturbations by higher state with energies close to that of the $^3D_1^\circ$ state. Another contributing factor to the red shift could be a larger attractive interaction of the $^3D_1^\circ$ state with the Xe matrix than the ground state 3P_1 state. However, this suggestion must be tentative and the assignment still remains in question.

The two weak bands located at 2809A and 2402A, not observed by Duley, are also observed in Kr matrix with similar respective half-widths. The band at 2402A is more atomic transition like, with a half-width of 240 cm^{-1} , while that at 2809A is 570 cm^{-1} . Both bands are rather temperature insensitive. The broad band centered at 2809A could be related to $Pb_2\ B \leftarrow X$ transition which lies in the region 3000A to 2800A. The identification of the 2402A band remains unclear.

As was mentioned earlier, the appearance of the $Pb_2\ A \leftarrow X$ spectra in Xe matrix is accompanied by a weak single band at 6268A (15954 cm^{-1}). This band has a half-width of 220 cm^{-1} and shows red shift on warming up the matrix. In all the matrices studied in this work, a similar band

consistently accompanies the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ bands, even in the SF_6 matrix. Here it suffices to mention that no discrete Pb atomic band can be seen in SF_6 matrix in the region 2200A and up. This could imply interaction or reaction between the Pb atom and SF_6 molecules. The former could be of the charge transfer type, and the latter could be chemical reactions leading to fluorides or sulfides. In either case, the discrete bands attributed to free Pb atoms should be absent. However, at higher Pb evaporation temperature where Pb_2 becomes appreciable in the vapor, the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ spectrum is observed, again accompanied by a single band at 6054A (16519 cm^{-1}) which has a half-width of 135 cm^{-1} and shifts to the red on warming up the SF_6 matrix. This fact implies that the band observed at 6200A region in all the matrices studied here could not be attributed to the free Pb atoms. From the energy levels of Pb atoms in the gas in Table 1, one notices that there is no transition from the ground state that gives comparable transition energy to the ones observed at 6200A region in the matrices. Therefore, the possibility always remains that impurities in the matrices could be responsible for the bands observed at 6200A region.

It was observed that when the matrix film shows strong $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ absorption, the region below about 2600A becomes continuously opaque. At still stronger Pb_2 absorption, the film was opaque below 3100A. Pb_2 molecule in the gas has two repulsive e' and b' states, located at the region 2380A and 2930A, respectively. These states could be responsible for the continuous absorptions observed above. In some of the experiment, very weak molecular band spectra are observed at the edge of continuous absorption below 3000A. This could be $\text{Pb}_2 \text{ B} \leftarrow \text{X}$ transition which is located close to the $b' \leftarrow x$ transition for the gas.

The matrix work of Pb in Xe reveals some information about the Pb_2 formation on the target during the film deposition. It was noticed that when the amount of Pb coming out the furnace per unit time is kept about the same, the use of a radiation shield in front of the Knudsen cell helps to decrease significantly the amount of Pb_2 in the matrix film as shown from the absorption spectra. This indicates that some Pb_2 are formed on the target because of the radiation heat coming out constantly from the furnace. The radiation heat could cause a decreasing cooling efficiency of the target, which in turn increases the mobility of Xe gas, and enhances the chance of some Pb atoms to form Pb_2 because of poorer isolation and surface diffusion, in a way described latter.

It was also noticed that depositing Xe gas prior to depositing Pb/Xe film also helps to decrease the Pb_2 in the matrix film. This seems to be contradictory because prior deposit of a Xe thin film could cause larger temperature gradient from the target and cause poorer isolation of Pb atoms due to decreasing cooling efficiency of the target. One possibility is that prior deposit of pure rare gas could lead to a better thermal contact with the target due to a better sticking of the film on the target. This would help to cool the matrix film more efficiently and to decrease the Pb_2 formation on the target. Another contributing factor could be the penetration effect of the metal atoms during the film deposition. The Pb atoms coming out from the furnace, because of the thermal energies they carry, might knock off some Xe atoms on the target due to the quick releasing of its thermal energy. This would bring the Pb atoms penetrating several layers deep into the Xe film. Because of the heat released, Xe atoms in the neighborhood would gain mobility and fill the

vacancies knocked out by the Pb atoms and help dissipating the heat released by Pb. The Xe atoms coming afterward would strike on a film with slight temperature gradient from the target, and stick on the film easily. Thus, several layers of Xe atoms could be added on the old one before the next Pb atom arrives on the film. This process could lead to an efficient isolation of the Pb atoms. If, however, there are not enough layers of Xe atoms present before a Pb atom arrives on the target, the vacancies might not be filled enough, and the heat released by the Pb atom not dissipated enough. This could decrease the efficient sticking of the later Xe gas atoms because of a warmer film present. This would mean that the second Pb atom coming on the target had less layers of Xe atom to penetrate before it met the first Pb atom and formed a Pb_2 molecule. The idea here is that it is easier for the Xe atoms already in the film to be warmed up to a higher temperature and yet still remain sticking on the target than that of a Xe atom coming from the vapor. The higher the film temperature the smaller is the sticking coefficient for the Xe gas atoms. The presence of certain thickness of Xe layers prior to the matrix deposit might then lead to a better isolation of the Pb atoms.

The above idea of Pb_2 formation on the target is supported by the facts that:

1. Within a temperature range where Pb_2 in the vapor remains negligible, and keeping the M/R constant, increasing Pb evaporation temperature leads to easier Pb_2 formation on the target.

2. Since above idea is closely related to the sticking coefficient of the matrix gas used, Pb atoms should be isolated most efficiently in Xe, less in Kr, and least in Ar. This is just what is observed. In the

meantime, the appearance of Pb_2 in the spectra also is found to be easiest in Ar, less in Kr and least in Xe, when the same Pb evaporation temperature and same M/R are used.

The possibility of forming Pb_2 by diffusion on warming up the matrix is also tested. Xe film which shows only discrete Pb atomic spectrum is warmed up and traced at 5000A region. No Pb_2 spectrum is observed up to and above the temperature of the disappearance of atomic Pb spectrum. This could be due to several factors: 1) Pb atoms are too heavy to diffuse, unlike light atoms like Li, which forms dimer on warming up the matrix. 2) Pb interacts strongly with Xe atoms which could also keep the Pb atoms from diffusing around. 3) The time span involved on warming up the matrix may not be long enough to observe the diffusion taking place.

Another test of diffusion was done by allowing the matrix film which shows both Pb and Pb_2 spectra to stay at 50°K for two hours. The only effect seen is that the film becomes a little foggy, which causes the region below 2800A to be opaque and also makes the comparison of the Pb_2 absorption intensity difficult. This could be due to the higher evaporation rate of Xe gas from the matrix film at 50°K. Such evaporation from the upper layers would leave the Pb atoms behind in dimer or polymer forms. The nonuniform absorption could then cause the fog problem.

2. Kr

At ordinary M/R ratios the Pb in Kr matrix shows one strong band at 2614A, with a half width about 400 cm^{-1} and another band at 2440A with blue shaded structure and a half-width larger than 900 cm^{-1} . Two very weak bands situated at 2783A and 2360A, respectively. These are

shown in Table 5. The tracing of the spectrum is shown in Fig. 15. The M/R used here is 200.

At higher Pb evaporation temperature, a molecular band spectrum appears at 5000Å region which is assigned to Pb_2 A $\leftarrow$ X transition. A single band is seen at 6126Å (16323 cm^{-1}), which has a half width about 150 cm^{-1} and shifts to the red on warming. The Pb_2 spectrum is shown in Fig. 16, and the band wavelengths and frequencies are shown in Table 6. The Pb_2 bands and the 6126Å band persist to 65°K on warming the matrix. The plate of absorption spectrum is shown in Fig. 17.

The strong band at 2614Å is assigned to Pb $6p7s \ ^3P_1 \leftarrow 6p^2 \ ^3P_0$ transition, the shift from gas phase transition thus being 2972 cm^{-1} to the blue. It shifts reversibly to the red on warming up the matrix. The spectrum remains observable to 50°K. Around 60°K it becomes very weak and hard to observe, partly due to the poor transparency of the film due to quick evaporation of Kr from the target. The absorption frequencies of this band at various temperatures are shown in Table 7, and the warm-up spectrum in Fig. 18.

The band at 2440Å is very similar to the Pb/Xe 2552Å band in its band shape and broadness. Both the breadth and blue-shaded structure increase with thickness of deposit. There is one difference, however, the ease of appearance of this band between the two matrices. In Xe, it was recalled that the 2552Å band appears only in concentrated matrices or when high Pb evaporation temperature is used. In Kr, this band almost always accompanies the strong 2614Å band, and is absent only when very large M/R is used. Based on the previous discussion in Xe matrix work, this band is assigned to the Pb_2 E $\leftarrow$ X transition.

TABLE 5. Absorption spectrum of Pb in Kr.

This work (at 20°K)			Assignment	Duley (at 4°K)		Assignment
$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu_{1/2}\text{cm}^{-1}$		$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	
2783(w)	35927			2787 (broad)	35880	
2614(s)	38261	~400	$6p7s\ ^3P_1^0 \leftarrow 6p^2\ ^3P_0$	2617(s)	38210	$6p7s\ ^3P_1^0 \leftarrow 6p^2\ ^3P_0$
2440 (w blue shaded)	40987	> 900	$Pb_2\ (E \leftarrow X)$	2453 (broad)	40770	$6p6d\ ^3D_2^0 \leftarrow 6p^2\ ^3P_1$
2360(w)	42373

Figure 15. Absorption spectrum of Pb/Kr.

XBL 707-1352

Figure 16. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Kr.

XBL 707-1354

TABLE 6. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Kr.

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\Delta G_{1/2} \text{cm}^{-1}$	$\nu_{1/2} \text{cm}^{-1}$	Relative intensity
5083	19673		60	20
		173		
5039	19846		55	20
		161		
4998	20007		62	17
		157		
4959	20164		62	11
		159		
4921	20323		63	7
		147		
4885	20470		69	5
		163		
4847	20633		75	3
6126*	16323		150	
x Unidentified

Figure 17. Warm-up spectrum of Pb_2 ($A \leftarrow X$) in Kr.

TABLE 7. Temperature dependence of the Pb/Kr $^3P_1^o \leftarrow ^3P_0$ band

Temperature °K	$\lambda(A)$	$\nu \text{ cm}^{-1}$
20	2614	38261
30	2617	38215
40	2619	38183
50	2622	38145

XBB707-3013

Figure 18. Warm-up spectrum of Pb/Kr.

The strong band observed in Xe at 2259A finds no counterpart in Kr up to 2100A region. Duley did not report any such band either down to the vacuum UV region.

The two very weak bands at 2783A and 2360A correspond, respectively, to the 2809A and 2402A band in Xe.

The single band at 6126A (16323 cm^{-1}) corresponds to the 6268A (15954 cm^{-1}) band in Xe except with narrower half-width than the latter.

It was found that to observe Pb_2 spectrum in the Kr matrix, lower Pb evaporation temperature is needed than that for a Xe matrix. According to the previously proposed mechanism of dimer formation on the target, this is attributed to the lower sticking coefficient of Kr than that of Xe. This also explains the fact that the 2440A band in Kr appears more easily and strong than the 2552A band in Xe, which supports the assignment of these two bands to the $\text{Pb}_2\text{ E} \leftarrow \text{X}$ transition.

The effects of changing deposit conditions on the observed absorption frequencies of both Pb and Pb_2 are studied, in a way similar to those done in the Xe matrices. The same conclusion is drawn here, i.e. the observed frequencies of both Pb and Pb_2 in Kr do not depend on the deposition conditions.

3. Ar

Depositions of Pb in Ar were carried out in two ways. First the M/R ratio was about the same as in the Xe and Kr work. It normally takes seven hours of deposit to show up very weak absorption spectra, while one hour of deposit is enough for Xe and Kr matrices to show clear Pb spectra. Second, M/R as high as 3000 is used to get a stronger spectrum in less than an hour. The spectra obtained from both deposits show

the same absorption frequencies. This is in agreement with the observations in the Xe and Kr matrices. The band frequencies observed are shown in Table 8, and the spectrum from the $M/R = 3000$ deposit is shown in Fig. 19.

Pb_2 $A \leftarrow X$ molecular bands are also observed, accompanied by a single band at $6053A$ (16521 cm^{-1}). The Pb_2 bands show no frequency shift on warming up the matrix and stay to $45^\circ K$. The spectrum of Pb_2 and its warm up spectra are shown in Figs. 20 and 21, respectively, and the frequencies shown in Table 9.

The strong broad band at $2334A$ is similar in its blue-shaded structure to those bands in Xe and Kr which are assigned to the Pb_2 $E \leftarrow X$ absorption bands. It is therefore assigned to the same transition of Pb_2 . The medium intensity band at $2449A$ shifts to the red on warming up the matrix, and remains observable to $40^\circ K$. It is assigned to the Pb $6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition. The warm-up spectra are shown in Fig. 22. It is noticed that the $2449A$ band, although appears with medium intensity in the spectra in Fig. 22, appears only as a shoulder on the strong uv absorption edge in the spectrum tracing in Fig. 19. This makes it difficult to measure the exact frequency change of this band at higher temperatures.

The $2334A$ band appears much stronger than the $2440A$ band in all the Pb/Ar experiments. The sticking coefficients among rare gases lie in the order $Ar < Kr < Xe$, and this is just the reverse of that of the ease of appearance of the observed broad, blue-shaded band in the matrices.

TABLE 8. Absorption spectrum of Pb in Ar.

This work (at 20°K)		Assignment	Duley (at 4°K)		Assignment
$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$		$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$	
2503(w)	39960		2528(b)	39560	
2449(m)	40840	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$	2440(s)	40980	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
2334 (s broad)	42838	$Pb_2 \ (E \leftarrow X)$	2340(b)	42660	$6p6d \ ^3D_2^0 \leftarrow 6p^2 \ ^3P_1$
			2094	47760	
			2069	48330	
			2044	48920	$6p6d \ ^3D_1^0 \leftarrow 6p^2 \ ^3P_0$
			2002	49950	$6p6d \ ^3D_2^0 \leftarrow 6p^2 \ ^3P_0$
			1960	51020	
			1818	55000	
			1793	55770

XBL 707-1439

Figure 19. Absorption spectrum of Pb/Ar.

Figure 20. Absorption spectrum of Pb_2 ($\bar{A} \leftarrow X$) in Ar.

XBL 707-1350

Figure 21. Warm-up spectrum of $\text{Pb}_2(\text{A} \leftarrow \text{X})$ in Ar.

TABLE 9. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Ar.

$\lambda(A)$	$\nu \text{ cm}^{-1}$	$\Delta G_{1/2} \text{ cm}^{-1}$	$\nu_{1/2} \text{ cm}^{-1}$	Relative intensity
4992	20032		49	12
		167		
4951	20199		39	18
		162		
4911	20361		79	19
		166		
4872	20527		68	14
		166		
4833	20693		41	10
		155		
4797	20848		32	7
		153		
4762	21001		27	6
6053*	16521		130	
* Unidentified

Figure 22. Warm-up spectrum of Pb/Ar.

4. Xe-Kr Mixtures

Three Xe-Kr mixed matrices were used; 75%Xe-25%Kr, 38%Xe-62%Kr and 10%Xe-90%Kr. In all three matrices one set of Pb spectrum and one set of Pb₂ spectrum are observed, and are more diffuse than those in pure Xe and pure Kr matrices. The observed frequencies of Pb and Pb₂ in these three matrices are shown in Table 11, spectrum of Pb and Pb₂ are shown in Figs. 23 and 24, respectively. The M/R used are between 500 and 600.

In all three matrices, the band around 2650A appears strongest. It shifts reversibly to the red on warming up. The disappearance temperature of this band and the Pb₂ spectrum are about 70°K in 75%Xe-25%Kr, 70°K in 38%Xe-62%Kr, and 60°K in 10%Xe-90%Kr matrices. The strongest band around 2650A in the three matrices are assigned to the Pb 6p7s ³P₁ ← 6p² ³P₀ transition, and their frequencies at various temperature are shown in Table 12.

The broad band in the matrices between 2540A and 2460A are similar to the broad band observed in Xe and in Kr in the same wavelength region. It was observed that with increasing content of Kr in the mixed matrix, this band appears easier and easier. This is completely consistent with the trend found so far, i.e. easiest in Ar, less in Kr and least in Xe matrices.

All the bands observed appear more diffuse than the corresponding ones in the pure Xe or Kr matrices. This could be due to the less regular trapping site in those matrices. The most interesting feature is that in all three mixed matrices, only one set of Pb spectra and one set of Pb₂ spectra are observed, both being intermediate between those in the pure Xe and pure Kr matrices. This clearly shows that in those mixed

TABLE 10. Absorption spectra of Pb in Xe-Kr mixed matrices at 20°K.

	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	Assignment
75% Xe - 25% Kr	2660(s)	37590	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2530(w,b)	39526	$Pb_2 \ (E \leftarrow X)$
38% Xe - 62% Kr	2660(s)	37601	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2508(w,b)	39877	$Pb_2 \ (E \leftarrow X)$
10% Xe - 90% Kr	2635(s)	37946	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2467(w,b)	40540	$Pb_2 \ (E \leftarrow X)$

TABLE 11. Absorption spectra of Pb_2 ($A \leftarrow X$) in the Xe-Kr mixed matrices

	$\lambda(A)$	$\nu \text{ cm}^{-1}$	$\Delta G_{1/2} \text{ cm}^{-1}$	$\nu_{1/2} \text{ cm}^{-1}$	Relative intensity
75% Xe-25% Kr	5189	19272		100	18
			177		
	5142	19449		78	7
			141		
	5105	19590		79	4
			174		
	5060	19764		82	3
38% Xe-62% Kr			145		
	5023	19909		69	1
	6240*	16026		180	
	5166	19358		87	38
			184		
	5117	19542		95	17
			144		
10% Xe-90% Kr	5080	19686		91	11
			158		
	5039	19844		92	9
			147		
	5002	19991		94	8
	6224*	16066		175	
	5115	19550		89	49
			157		
	5074	19707		100	28
			147		
	5037	19854		83	18
			155		
	4998	20009		93	8
			167		

TABLE 11. (Continued)

$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$	$\Delta G_{1/2} \text{ cm}^{-1}$	$\nu_{1/2} \text{ cm}^{-1}$	Relative Intensity
4956	20176	156	86	7
4918	20332		66	5
4883	20480	148	50	2
6165 *	16221		204	

* Unidentified

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Figure 23. Absorption spectra of Pb in (a) 75% Xe-25% Kr, (b) 38% Xe-62% Kr, and (c) 10% Xe-90% Kr.

XBL 707 -1356

Figure 24. Absorption spectra of Pb_2 ($A \leftarrow X$) in (a) 75% Xe-25% Kr, (b) 38% Xe-62% Kr, and (c) 10% Xe-90% Kr.

TABLE 12. Temperature dependences of the $\text{Pb } ^3\text{P}_1^\circ \leftarrow ^3\text{P}_0$ band in the Xe-Kr mixed matrices.

Temp °K	75% Xe-25% Kr		38% Xe-62% Kr		10% Xe-90% Kr	
	$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$	$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$	$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$
20	2660	37590	2660	37601	2635	37946
30	2661	37580	2663	37559	2640	37885
40	2666	37504	2667	37502	2644	37819
50	2669	37473	2669	37470	2647	37779
60	2673	37411	2673	37418		

matrices, Xe and Kr cocondense on a microscopic scale, at least around the trapped Pb and Pb₂. The fact that the observed frequencies lies intermediate to those in pure Xe and pure Kr, and approach those in Kr as Kr content is increased in the matrix, gives very good hint about the origin of the frequency shift of the trapped species absorption spectra from their gas phase values. This will be discussed in more detail later in Chapter IV.

It is recalled that in Xe a strong band is observed at 2259A which is absent in Kr. Among the Xe-Kr mixed matrices, a similar but more diffuse band is observed only in the 75%Xe-25%Kr matrix. This band appears weakly upon longer exposures than the one used for Fig. 23b. This explains to some extent the absence of such a band in Kr matrix, but its actual cause as well as transition attributed to this band remain unclear. One possibility is that this band could be the same $^3P_1 \leftarrow ^3P_0$ transition of some Pb atoms trapped in an unstable site, or in an interstitial site. Such multiple site should occur most easily in the matrix with least mobility at the temperature of condensation, i.e. being easiest in Xe, less in Kr and least in Ar, because of their different melting points. The unstable site is expected to change into the stable one on annealing the matrix and to lead to disappearance of the observed spectra. However, the fact that the band observed in Xe persists on warming up the matrix to 77°K and cool back seems not to support this possibility. On the other hand, an interstitial trapping site is expected to lead to larger blue shift of spectral frequency than that from a Pb atom in a substitutional site, because of the smaller site space and larger squeezing effect on the Pb 7s orbital. This seems to be in agreement with the large energy difference of 6200 cm⁻¹ between

the two bands observed. However, one would expect a larger red shift in frequency of such a band on warming up the matrix due to relaxing the squeezing effect. The rather insensitive dependence of this band on the matrix temperature seems not to be in favor of this possibility.

Another possible interpretation is that the Pb/Xe 2259A band could be from transition other than $^3P_1 \leftarrow ^3P_0$. Its absence in Kr and Kr containing matrices could then be due to a different perturbing effect between Xe and Kr on the absorption intensity of this transition. Such intensity perturbing effect have been observed on some matrix trapped molecules. More works, both experimental and theoretical, have to be done to well understand the Pb band discussed here.

The work of Xe-Kr mixed matrices gives some information on the sticking coefficient difference between Xe and Kr at 20°K. Taking the 10%Xe-90%Kr matrix for example, the Pb $^3P_1 \leftarrow ^3P_0$ frequency is shifted from its gas phase value by 2660 cm^{-1} to the blue. The shifts in Xe and Kr matrices are, respectively, 2483 cm^{-1} and 2972 cm^{-1} . The rare gas crystal have face center cubic structure with twelve first nearest neighbors, twenty four next nearest neighbors etc. If one assumes only van der Waal type interaction between a Pb atom in a lattice site with the matrix gas neighbors, to a first approximation only the first twelve nearest neighbors are involved in the interactions. The observed blue shift in frequencies are then due to the twelve pairs of Pb-Xe or Pb-Kr interactions, if additive pairwise interaction is assumed. In this way one can find out the approximate numbers of Xe and Kr atoms around the trapped Pb atom in the 10%Xe-90%Kr matrix. The relation needed has the form

$$2483 (X/12) + 2972 ((12-X)/12) = 2660$$

Here X is the number of nearest Xe atoms around the Pb atom in the mixed Xe-Kr matrix. X is found to be 7.7. Therefore, the twelve nearest neighbors around the trapped Pb atom consist of about 8 Xe atoms and 4 Kr atoms. The Xe-Kr ratio is 1:8 in the gas, while in the solid at least around the trapped Pb atoms, it is about 2:1. This result can to a large extent be attributed to the difference of sticking coefficients between Xe and Kr atoms at 20°K used in this work.

5. Xe-Ar Mixtures

Two Xe-Ar mixed matrices were used, 4%~~Xe~~-96%~~Ar~~ and 16%~~Xe~~-84%~~Ar~~. Only a very fast deposit rate of matrix gas was used that gave M/R ratio between 2700 and 3100. This is to try to reproduce the situation in sputtering technique when Ar gas is used to sputter the solid species in study and Xe is used to trap the species being sputtered out. The Ar-Xe ratio could range from 10 to 1000. It is found that when 4%~~Xe~~-96%~~Ar~~ is used with a rate of Xe-Pb about 100, the spectrum observed is quite different from that in the pure Xe matrix and is shown in Fig. 25. Three broad bands are observed. One extends between 2875Å and 2672Å; the other two are narrower, centered at 2558Å (39096 cm^{-1}) and 2433Å (41102 cm^{-1}), respectively. These three bands are thought to correspond to the 2809Å, 2648Å and 2552Å band of Pb in Xe, respectively. This is based on the fact that these three bands are expected to fall between the corresponding ones in Xe and in Ar. The spectrum remain to about 40°K. No clear bands of Pb_2 A ← X are observed.

The spectrum of Pb in the 16%~~Xe~~-84%~~Ar~~ matrix shows two bands, one extending between 3326Å and 2848Å and the second one is narrower, centered at 2618Å (38194 cm^{-1}). The spectrum is shown in Fig. 25. The 2618Å band

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Figure 25. Absorption spectra of Pb in (a) 16% Xe-84% Ar, and (b) 4% Xe-96% Ar.

is assigned to $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ transition, while the first broad band corresponds to the ones in other matrices in the same wavelength region. It is to be noted that in this matrix, Xe content is high enough to predominate the nearest neighbors around the trapped Pb atom, and gives a $^3\text{P}_1 \leftarrow ^3\text{P}_0$ absorption close in energy to that in the pure Xe matrix; while the band in the 4%Xe-96%Ar matrix lies in even high energy and closer to that in the Ar matrix. If one estimates, in the same way as shown before, the number of Xe and Ar atoms that constitute the twelve nearest neighbors of the trapped Pb atom in the matrix, one comes out with seven Xe atoms and five Ar atoms in the 4%Xe-96%Ar matrix, and ten Xe atoms and two Ar atoms in the 16%Xe-84%Ar matrix. Again, the effect of sticking coefficients difference between the component rare gases shows up in the matrix composition.

The above estimated number of nearest Xe atoms around the trapped Pb atom support the assignment of the bands observed in these matrices. In the 16%Xe-84%Ar matrix, Xe atoms dominate in being nearest to Pb atom and the spectrum is more similar to that in pure Xe matrix. This means that the broad band, which is assigned to the $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ transition and is hard to observe in Xe, should also be hard to observe in this matrix when compared to that in the 16%Xe-84%Ar matrix. In the latter, the spectrum should be closer to that in an Ar matrix which gives a very strong $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ broad band. The clear broad band observed in this matrix is therefore consistent with the predicted feature.

6. SF₆

There is no discrete band in the spectrum of Pb in SF₆. Only two very weak and diffuse bands are observed between 2800Å and 2600Å

region. One band extends between 2848Å and 2816Å, the second band between 2709Å and 2655Å. The spectrum is shown in Fig. 26.

However, when high Pb evaporation temperature is used with significant Pb_2 in the vapor, a clear spectrum of the Pb_2 A $\leftarrow$ X transition is obtained. Also, one single band appears at 6054Å (16520 cm^{-1}) which shows red shift on warming up the matrix. In addition, a broad band appears which is centered at about 4580Å and extends between 4510Å and 4250Å. The spectrum remains to 90°K and disappears between 90° and 100°K. The spectrum is shown in Fig. 27, and the wavelengths tabulated in Table 13. The Pb_2 bands show no shift on warming up, and the warm up spectrum is shown in Fig. 28.

It is observed that when the Pb_2 spectrum becomes strong, the matrix absorbs continuously below 3250Å and gives a pale yellow color which deepens as the Pb_2 spectrum gets stronger. The color becomes grayish when the matrix is warmed up to above 100°K and has lost the Pb_2 spectrum.

The absence of discrete Pb bands in SF_6 could mean (1) an interaction between Pb atoms and SF_6 such as charge transfer type which leads to $Pb^+SF_6^-$, or (2) a chemical reaction between Pb and SF_6 . In both cases the discrete Pb bands observed in rare gas matrices would be absent. There is another possibility, however. The fluorine atoms in SF_6 molecules could be partially negative charged and interact strongly with the trapped Pb atoms. The field created by the fluorine atoms could be so strong that it did not fade away rapidly beyond the nearest neighbor SF_6 molecules. This quasi-continuous field could then smear out the Pb absorption bands normally observed in the rare gas matrices.

XBL 707-1438

Figure 26. Absorption spectrum of Pb/SF₆.

Figure 27. Absorption spectrum of Pb_2 ($A \leftarrow X$) in SF_6 .

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TABLE 13. Absorption spectrum of Pb_2 ($A \leftarrow X$) in SF_6 .

$\lambda(A)$	$\nu \text{ cm}^{-1}$	$\Delta G_{1/2} \text{ cm}^{-1}$	$\nu_{1/2} \text{ cm}^{-1}$	Relative intensity
5006	19976		96	25
		148		
4969	20124		85	53
		158		
4930	20282		98	60
		151		
4894	20433		87	48
		155		
4857	20588		74	32
		151		
4822	20739		76	18
		144		
4789	20883		70	8
		143		
4756	21026		53	5
6054 *	16520		130	
One broad band centered at 4380A, and extending between 4510A and 4250A.				
One broad shoulder between 4660A and 4580A.				

* Unidentified

XBB707-3008

Figure 28. Warm-up spectrum of Pb_2 ($A \leftarrow X$) in SF_6 .

Experimentally the charge-transfer interaction could be best tested using ESR technique. However, without information from ESR work on this problem, it is studied in several ways. First, because the Pb^+ ion absorbs in the vacuum uv region, Ca is trapped in SF_6 to try to observe the $4p\ ^2P_{1/2,3/2} \leftarrow 4s\ ^2S_{1/2}$ transition of the Ca^+ ion which are at 4000Å region in the gas. Second, the conductivity of the Pb/SF_6 film is checked in a hope to measure the excessive current carried by the electrons which are loosely bound to the SF_6 molecules and might hop from one SF_6 molecule to the next throughout the matrix film. The latter work is discussed in the next section, and the work with Ca is discussed here.

The spectra of Ca in rare gas matrices have been studied in detail by Wang.⁴ Therefore, Ca was first trapped in Xe at 20°K and the spectrum observed was compared to that by Wang, as are shown in Table 14. The results agree very well with Wang's work.

Next, Ca was trapped in SF_6 . The spectrum showed no absorption bands in the region 2200Å to 6000Å. The matrix film also shows pale yellow color, similar to the Pb/SF_6 film, while the Ca/Xe films shows red color.

Ca was then trapped in a 77%Xe-23% SF_6 matrix. Again, the pale yellow colored film showed no absorption band.

In addition, the IR spectrum of the Pb/SF_6 matrix is checked between 4000 cm^{-1} and 600 cm^{-1} . No absorption band other than those due to SF_6 vibrational modes is found. Because of the strong SF_6 absorption around 900 cm^{-1} region, SF_6 was trapped in thin Pb films while keeping the films transparent. The SF_6 concentration was about 5 atomic %. Again, only bands due to the SF_6 vibrational modes were seen. This could

TABLE 14. Absorption spectrum of Ca in Xe at 20°K.

$\lambda(\text{\AA})$	This work $\nu \text{ cm}^{-1}$	Assignment	Wang $\lambda(\text{\AA})$	Wang $\nu \text{ cm}^{-1}$	Assign- ment
4378	22844	$1P \leftarrow 1S$	4377	22840	$1P \leftarrow 1S$
4338	35052		4337	23052	
4310	23200		4311	23192	

mean either (1) no chemical reaction, or (2) SF_6 is not well isolated, or (3) the reaction products, if formed, have vibrational absorptions below 650 cm^{-1} and escaped observations. Therefore, no definite conclusion can be drawn here.

The most interesting feature about the Pb/SF_6 work is the appearance of strong $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ absorption spectra and yet an absence of the atomic Pb bands. The Pb_2 molecules are believed to come from the vapor because thick deposit using low Pb evaporation temperatures showed no Pb_2 spectra. In fact, this could be used to eliminate the possibility that the absence of Pb spectra could be due to faster diffusion of Pb atoms in the SF_6 matrix to form Pb_2 molecules. Therefore, one comes to the conclusion that the interaction or reaction between atomic Pb and SF_6 does not take place between the Pb_2 molecules and SF_6 in the matrix. If what takes place between the Pb atom and SF_6 is of charge-transfer type interaction, then the formation of molecular orbitals in Pb_2 would change the atomic nature of the valence electrons, and bound them more tightly to the molecule. No transfer to SF_6 is allowed. On the other hand, if chemical reaction is responsible for the absence of the Pb atomic band in SF_6 , one could use a similar argument to explain the different behavior of Pb_2 toward the SF_6 molecules. The initial stage of the chemical reaction, if taking place, between Pb and SF_6 could also involve transfer of the valence electrons of Pb to the surrounding SF_6 molecules. If this is true, the entering of those Pb valence electrons into the Pb_2 molecular orbitals might again prevent such reaction to take place.

Another interesting feature to notice is the appearance in the SF_6 matrix of a single band at 6054A , like those in all the rare gas matrices. However, this band remains unidentified, as was discussed in the Xe work section.

Because of the high melting point (218°K) of SF_6 and that the Pb_2 spectrum in SF_6 persists to between 90° and 100°K , deposition of Pb in SF_6 was also carried out at 77°K . However, no Pb_2 absorption spectrum could be seen. Instead, as will be shown later, the film deposited at 77°K shows a much better electrical conductivity than the films deposited at 20°K . This implies that the poor isolation of Pb at 77°K leads to cluster formation of Pb which is then responsible for the better electrical conductivity measured.

7. Xe- SF_6 Mixtures

Two Xe- SF_6 mixed matrices were used, 77%Xe-23% SF_6 and 64%Xe-36% SF_6 . No discrete Pb atomic bands were observed in both matrices, only two weak broad bands were seen, like those in the SF_6 matrix. At higher Pb evaporation temperature, bands correspond to Pb_2 spectrum appear. The vibrational bands can be resolved in the 77%Xe-23% SF_6 matrix, but only a broad band is seen in the 64%Xe-36% SF_6 . The wavelengths of the bands observed are included in Table 15, and the spectra shown in Fig. 29.

The most interesting result of this part of work is the absence of discrete Pb bands and the appearance of only one set of Pb_2 spectra in the mixed matrices. This implies (1) Xe and SF_6 crystallized together on a microscopic scale around the trapped Pb atoms and molecules; (2) it is necessary to have only a few SF_6 molecules around to cause the absence of discrete Pb atomic bands in the matrices. However, an estimation of the number of SF_6 molecules being nearest to the Pb atoms in the mixed matrices is difficult because of (1) lack of knowledge about the SF_6 crystal structure and (2) uncertainties in the vibrational numbers of the Pb_2 bands observed in pure Xe and SF_6 matrices. Some

TABLE 15. Absorption spectra of Pb_2 ($A \leftarrow X$) in the Xe-SF₆ mixed matrices.

77% Xe-23% SF ₆	$\lambda(A)$	νcm^{-1}	$\Delta G_{1/2} cm^{-1}$	$\nu_{1/2} cm^{-1}$	Relative intensity
	5208(?)	19203(?)			2
			254(?)		
	5140	19457			9
			170		
	5095	19627		82	12
			143		
	5058	19770		99	14
			162		
	5017	19932		94	9
			159		
	4977	20091		83	8
			153		
	4940	20244		67	4
			164		
	4900	20408		103	4
	6263*	15966		250	

One broad band centered at 4490A and extending between 4633A and 4345A.

One broad shoulder between 4806A and 4700A .

64% Xe-36% SF₆

No clear bands of Pb_2 spectrum, but one broad band centered at 4920A, and extending between 5152A and 4681A, with a shoulder between 4681A and 4571A.

One broad band centered at 4416A and extending between 4571A and 4200A.

One single band at 6211A (16400 cm^{-1}) with $\nu_{1/2} = 330 cm^{-1}$.

* Unidentified

Figure 29. Absorption spectra of Pb_2 ($A \Sigma$) in (a) 77% Xe-23% SF_6 , and (b) 64% Xe-36% SF_6 .

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qualitative discussion about Pb_2 spectra in the SF_6 matrix will be carried out later in Chapter V.

8. Codepositing Pb and Ag in the Kr Matrix

In order to confirm the possible dimerization of Pb on the target, Pb is codeposited with Ag using the double furnace constructed by King.⁸ Kr is chosen for the matrix gas because, from the previous work on Pb, it is better than Xe in allowing for the surface dimerization, and yet better than Ar in obtaining enough metal atoms in the isolated form in a shorter period of deposition time.

The spectra of Ag trapped in matrices were studied extensively by Brewer et. al.³ Therefore, Ag is trapped in Kr at 20°K and the observed spectral frequencies are listed in Table 16, along with those by Brewer et. al. The agreement is very good for the strong triplet in the 3000Å region. The additional doublet and a weak shoulder observed in this work were not observed in the earlier work, and could be due to impurities. When concentrated Ag/Kr films are deposited, a broad band is observed at 4000Å region and could be attributed to the Ag_2 molecules.²¹

Next Pb and Ag are codeposited in the Kr matrix. The Pb evaporation temperature is kept such that Pb_2 in the vapor is low but the Pb_2 band and the Pb 2440Å broad band appear in the matrix when only Pb is trapped in the Kr matrix. It is found that when the Ag concentration is comparable to that of Pb, no significant effect is seen on the Pb_2 and the Pb 2440Å band intensities. However, when high concentration of Ag (1 to 2 atomic %) is used, it greatly decreases the Pb_2 and the Pb 2440Å band intensities. One set of spectra and tracings are shown in Figs. 30 and 31. In Fig. 30 spectrum of (Ag + Pb)/Kr is shown along with those of pure Ag/Kr and pure

TABLE 16. Absorption spectrum of Ag in Kr at 20°K.

This work		Assign- ment*	Brewer et al.		Assign- ment
$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$		$\lambda(\text{\AA})$	$\nu \text{ cm}^{-1}$	
3226(s)	30995	$2P_{1/2} \leftarrow 2S_{1/2}$	3227(s)	30989	$2P_{1/2} \leftarrow 2S_{1/2}$
3135(s)	31900		3136(s)	31888	
3092(s)	32343		3094(s)	32321	
2819(shoulder)	35479				
2753(w)	36324				
2702(w)	37015				

* See text (Chapter IV) for the reasons

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Figure 30. Absorption spectra of (a) Pb/Kr, (b) Ag/Kr, and (c) (Pb + Ag)/Kr.

Figure 31. Absorption spectra of (a) Ag/Kr, from Fig. 30b, and
(b) (Pb+Ag)/Kr, from Fig. 30c.

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Pb/Kr, and the tracings of the last two spectra (b,c) shown in Fig. 31. It is clearly seen that the 2440Å broad band of Pb/Kr is absent when Ag concentration is high, the Pb₂ spectrum is also absent in this film, compared to that when only Pb is trapped in Kr. The tracing of the (Ag+Pb)/Kr spectrum shows a broadening of the Pb/Kr 2614Å atomic band. This could be due to the effect of some Ag atoms in the neighborhood of some of the trapped Pb atoms. The interaction between Ag and Pb therefore reinforces that between Pb and Kr, and broadens the Pb $^3P_1 \leftarrow ^3P_0$ absorption band. The same broadening effect should also be seen on the Ag absorption bands. However, because of the high concentration of Ag in the matrix, such effect is expected to be small compared with the natural breadth of concentrated Ag in the matrix.

No effect is seen on the Pb and Ag atomic absorption frequencies in all the (Ag+Pb)/Kr films deposited. This confirms the work on Ag and Au by Brewer and King^{7,8} in that the observed triplet of Ag is not caused by the metal-metal interaction in the matrices. The absence of clear spectra in the (Ag+Pb)/Kr films which could be attributed to the Pb-Ag species is not surprising. No information is known about the spectral region of such species in the gas phase, and the spectra could be broad up to escape observation due to various factors, like the nonuniform environments around such species, quenching effect by the matrix, etc. However what demonstrates in this work is the clear effect of concentrated Ag on the trapped Pb spectra. Two conclusions can be drawn from this work:

1. At lower concentration of Ag, the Pb atoms can be trapped in the isolated form. However, when high concentration of Ag is used, Ag and Pb atoms do intercept one another during the deposition of the matrix film. This confirms the earlier work on Pb about the possible Pb₂ formation

on the target.

2. When Ag concentration is high in the matrix films the simultaneous absence of the 2440 Å broad, blue-shaded band of Pb/Kr and the Pb_2 bands indicates strongly, although indirectly, that the former band is also of molecular origin. This supports the earlier assignment of this broad band the Pb_2 $E \leftarrow X$ transition.

B. Conductivity Measurements

1. Introduction

In a dilute rare gas matrix, the trapped metal atoms are well isolated and quite far from one another. The matrix film is therefore expected to behave like an insulator to an electric current, in a way similar to a dilute metal vapor. The latter, however, starts to become conductive as the vapor pressure is increased to a critical one.²² The same idea is here tested for the matrix trapped metal atoms when the metal concentration becomes high and yet the metal atoms are still isolated from one another. Whether most of the metal atoms are well isolated is checked spectroscopically.

Pb is used for this work. In the previous matrix works, Pb shows no atomic spectra in the SF_6 matrix. This could mean that either a charge transfer interaction is taking place to form Pb^+SF_6^- , or Pb reacts with SF_6 to form other products, like the Cs work in liquid NH_3 which is reported later in this thesis. The charge transfer interaction, if taken place, would be expected to show electric conductivity even when the Pb atoms are low in concentration in the SF_6 matrix. The electron which is transferred to SF_6 from the Pb atom might be further transferred to the next SF_6 and so on, and thus gave rise to a conducting film. The resis-

tance of the matrix film is expected to be very high at liquid hydrogen temperatures. But it is hoped that at higher temperatures the resistance might be low enough to give measurable conductance. Also, the larger evaporation rate of the matrix gas at higher temperatures might bring the Pb atoms closer to one another and enhanced the conductivity of the matrix film. By tracing the isolated Pb_2 spectrum as the temperature is increased, one might get information about the possibility of obtaining conductance and yet still keeping the Pb or Pb_2 in the isolated forms.

2. Experimental and Results

A chromel-constantan thermocouple wrapped on the cryo-tip by the company is indium soldered on the sapphire target. A commercial Triplet model 630 voltmeter is used which measures a minimum current of $60 \mu A$. From the soldering spots on the target to the outside leads, the residue resistances for chromel and constantan wires are, respectively, 22Ω and 16Ω .

a. Pb Thin Film A pure Pb film is deposited at $20^\circ K$ on the target until measurable conductance shows up. The film is then annealed at a higher temperature and cooled back to $20^\circ K$. On warming up again, the measured resistance vs temperature is shown in Table 17, which is reproducible on cooling down.

In all the later experiments of Pb in matrices, the total Pb amount deposited in the matrices are at least twice as much as that used in the pure Pb film. This is to assure that enough Pb is present in the matrix to offset for the insulating effect of the matrix gas atoms or molecules.

TABLE 17. Resistance vs temperature for the pure Pb film after annealing.

T°K	Resistance Ω
20	1.1×10^5
30	9.8×10^4
40	9.2×10^4
50	8.7×10^4
60	8.3×10^4
67	2.3×10^4
70	2.3×10^4
77	2.2×10^4
104	1.9×10^4

b. Pb in Xe Xe matrix containing 5% Pb is deposited at 20°K. The film shows strong Pb₂ spectrum. At 20°K, the film shows no measurable conductance. On warming up at a rate of 10 deg per 10 min., the film shows weak conductance of $2.5 \times 10^{-6} \Omega^{-1}$ at 79°K. At 79°K the film shows brown color and has lost the Pb₂ spectrum. The conductance decreases on cooling back, and becomes unmeasurable at 20°K. On warming up again, the film conductance increases and becomes $3 \times 10^{-5} \Omega^{-1}$ at 102°K.

Thinner Xe film containing 5% Pb is also deposited at 20°K. On warming up at the same rate, the film shows very weak conductance of $1.6 \times 10^{-6} \Omega^{-1}$ at 79°K. Again, the film becomes brown at this temperature, and has lost the Pb₂ spectrum. On cooling back the conductance decreases and becomes unmeasurable at 20°K. When warming again, a conductance of $1 \times 10^{-8} \Omega^{-1}$ shows up at 79°K. At 121°K, the conductance is $1 \times 10^{-6} \Omega^{-1}$.

In the above Pb/Xe experiments, the warm up rate is slower than that normally used for the Pb and Pb₂ warm up frequency shift studies. The latter rate is 10 deg per 4 min. and the Pb₂ spectrum in Xe remains to about 82°K. When the warm up rate becomes slower, more Xe gas is evaporated from the matrix film per 10 deg increase than that from a faster rate, although the exact evaporation amount is not known. Therefore, the discrete Pb₂ spectrum may disappear at temperatures lower than those from a faster warm up rate. However, what concerns us here is not the highest temperature the film can retain the Pb₂ spectrum, but that whether the Pb₂ spectrum is retained at the moment the film conductivity becomes measurable. The main reason of using the slow warm up rate is to allow us to follow the conductivity behavior more closely, and to cool the film back to 20°K as soon as very weak conductivity shows up. This

step is essential to tracing the Pb_2 spectrum because it minimizes further evaporation of the matrix gas, and keeps the film composition as close as possible to the composition at which conductivity becomes measurable.

c. Pb in SF_6 and Xe- SF_6 Mixture The Pb/SF_6 matrix film, which shows strong Pb_2 spectrum, shows no measurable conductance at $20^\circ K$. On warming up the Pb_2 spectrum disappears between 90° and $100^\circ K$. At $110^\circ K$ the film becomes grayish, and remains so at higher temperatures. At $120^\circ K$ a very weak conductance of $1 \times 10^{-8} \Omega^{-1}$ shows up. The conductance hardly increases at higher temperatures.

Pb/SF_6 matrix is also deposited at $77^\circ K$ to measure its conductance. A thick film containing 5% Pb is deposited. The film shows no Pb_2 spectrum, but is transparent, like the films deposited at $20^\circ K$. The film shows no measurable conductivity at $77^\circ K$. However, it starts to show conductivity at $120^\circ K$, and increases to $1.5 \times 10^{-4} \Omega^{-1}$ at $199^\circ K$, and $1 \times 10^{-3} \Omega^{-1}$ at $215^\circ K$. At $215^\circ K$ the film left on the target is blown with SF_6 gas. No effect on the measured conductance is seen.

Pb is also trapped in a 77%Xe-23% SF_6 matrix to a concentration of 5%. At $20^\circ K$ this film shows no conductance. It becomes grayish at $83^\circ K$, and shows no conductance even at $197^\circ K$.

3. Discussions

The Pb/Xe film conductivity experiments show that no conductance could be measured in the temperature region where discrete Pb_2 spectrum can be observed. By the time the matrix film starts to conduct, both Pb and Pb_2 spectra have been lost. This indicates that, within the experimental measurability, no electron jump from one isolated Pb to the next is observed.

In the 5% Pb containing SF_6 film deposited at 20°K , a large portion of Pb atoms from the vapor is expected to be trapped in the isolated form. The absence of atomic Pb spectrum implies that Pb atoms either form a charge transfer complexes with SF_6 , or react with SF_6 to give fluorides and sulfides. The Pb^+SF_6^- complex is expected to cause an increase of conductance of the film compared to that of a Pb/Xe film where Pb atoms are in the natural form. The latter reaction products will, however, behave like insulators and will lower the conductance of the film. The fact that much lower conductance is measured from Pb/ SF_6 film is in favor of the reaction possibility.

Pb in the Xe- SF_6 mixed matrix deposited at 20°K shows no measurable conductance up to 220°K is in agreement with the above discussion.

When Pb/ SF_6 film is deposited at 77°K , a much higher conductance is observed at higher temperatures. This is expected from the above discussion, because at 77°K the isolation of Pb in SF_6 is very poor, even for the Pb_2 molecules whose spectrum is absent in this film. The Pb exists in the film in the form of small aggregates which are expected to be inert to SF_6 molecules, like the Pb_2 molecules. After the SF_6 gas is evaporated at higher temperatures, these Pb aggregates connect to form a rather intact Pb film which is responsible for the high conductance observed.

C. Discussions

1. Pb Atomic Spectra

In all the rare gas matrices used here, one strong absorption band is observed and is assigned to the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ transition. Although some weak features appear in thick films deposited and might be due to

atomic transitions, only the $^3P_1 \leftarrow ^3P_0$ atomic feature was extensively studied in this work. In Chapter IV the observed frequency shift on this band as well as the warm up frequency changes in the rare gas matrices are correlated with some model calculations. The singlet structure and observed breadth of this band are also discussed.

2. Pb₂ Molecular Spectra

The Pb₂ A $\leftarrow$ X spectrum is observed in most of the matrices used in this work. The frequency of the first band observed is lowest in Xe, higher in Kr, and highest in Ar and SF₆. When mixed matrices are used, the first band frequency always lies between those in the pure matrices. However, the absolute frequency shifts from gas phase value are difficult to determine due to the lack of knowledge about the absolute vibrational numbers of the observed bands. In this section, the observed intensity distributions are used in an attempt to estimate the least relative frequency shifts among the matrices. The possible trapping site geometry of Pb in the matrices is discussed by considering the size ratio of Pb₂ to the various lattice sites. The effects of SF₆ lattice on the trapped Pb₂ molecule is briefly discussed by comparing the Pb₂ frequency shift in this matrix to those in the rare gas matrices.

a. Relative Vibrational Numbers and Frequency Shifts of the Pb₂ A $\leftarrow$ X

Spectra in the Matrices. According to Franck-Condon principle, the intensity distributions of the molecular absorption and emission spectra depend on the relative positions and the shapes of the potential curves of the upper and lower states involved. Pb₂ A $\leftarrow$ X absorption spectrum in matrices shows different intensity distribution, and this fact is used to try to obtain information about the relative vibrational levels involved

in the observed spectra. The information thus obtained is then used to approximate the relative frequency shifts of $Pb_2 A \leftarrow X$ transition in the various matrices.

The intensity distribution of Pb_2 shows the same trend in Xe and Xe-Kr mixed matrices. The first band has the maximum intensity which is most significant in pure Xe, and less so in the Xe-Kr mixed matrices as the Kr% is increased. This intensity distribution changes in pure Kr with the first two bands highest in intensities. In Ar, the second and third bands have maximum intensities. As will be shown, this maximum intensity distribution changes are expected from Xe to Kr to Ar. Let us consider the lattice size difference among these three matrices. At $20^\circ K$, the nearest neighbor distances in Xe, Kr and Ar lattices are $4.34\text{\AA}$, $3.999\text{\AA}$ and $3.761\text{\AA}$, respectively.²³ The attractive portion of the Pb_2 potential curves is therefore squeezed most in Ar and least in Xe lattices. Such squeezing has two effects on the potential curves: the internuclear distance may be shortened slightly, and the vibrational levels be pushed up in energy. Both effects are expected to be larger in the excited state than the groundstate when the former has a larger r_e . In the absorption spectra at $20^\circ K$, these effects on the ground state are at their minimum because transition starts from $v'' = 0$ level which has smallest r_e among all the vibrational levels considered. It can be seen easily that both effects mentioned above will tend to change the intensity distribution pattern as these two effects become larger, i.e. transition to the lower v' levels will start to appear in the absorption spectra. With a difference in intensity distribution of Pb_2 in Xe, Kr and Ar, it is easily expected that the first band observed in Kr has its vibrational

quantum number smaller than that of the first band in Xe by at least one. Same relation holds between Kr and Ar.

Next, the observed Pb_2 spectra are related to the Pb spectra to see if more information might be obtained. The Xe-Kr mixed matrices are used in this respect. It is recalled that in the Pb work discussed earlier the 10%Xe-90%Kr matrix was approximated to be composed of eight Xe atoms and four Kr atoms as the twelve nearest neighbors of the trapped Pb atoms. Here the same approximation is adopted by assuming that the nearest neighbors in this matrix of the trapped Pb_2 molecule consist of Xe and Kr atoms in the same 8 to 4 ratio. Random distribution of Xe and Kr atoms is assumed. Therefore, the observed frequency shift of Pb_2 $A \leftarrow X$ transition in this matrix is approximately equal to the sum of $8/12\Delta\nu$ (Xe) and $4/12\Delta\nu$ (Kr), here $\Delta\nu$'s are the frequency shifts of the molecular bands in the matrices.

To compare Pb_2 absorption frequency shifts, it is best to use the shifts of the electronic transition energy of the $A \leftarrow X$ transition. Pb_2 molecules at the zero points of the two states interact with the matrix environment, and the net difference between these two interaction magnitudes determines the net shift of the electronic transition energy T_e . Because of the difficulties in assigning the absolute vibrational numbers for the Pb_2 spectra observed in the matrices, all possible assignments are included to calculate the corresponding ΔT_e 's. The smallest possible v' value for the first observed band is 0, and the largest possible one is six. The upper limit of v' value is determined by the fact that the maximum intensity band in the gaseous phase is at $v' = 6$, and that the matrix environment can squeeze the A state potential curve to allow only the lower v' levels to become highest in intensity.

ΔT_e is calculated in the following way:

$$v_{\text{obs}}^{\text{matrix}} = T_e^{\text{matrix}} + \omega_e'(v'+1/2) - \omega_e'x_e'(v'+1/2)^2 - \omega_e''(v''+1/2) + \omega_e''x_e''(v''+1/2)^2$$

At 20°K one expects that only the $v''=0$ level is well populated, and that all the observed transitions start from this level. Therefore

$$v_{\text{obs}}^{\text{matrix}} = A^{\text{matrix}} + \omega_e'(v'+1/2) - \omega_e'x_e'(v'+1/2)^2$$

with

$$A^{\text{matrix}} = T_e^{\text{matrix}} - 1/2 \omega_e'' + 1/4 \omega_e''x_e''$$

To a first approximation, gas phase ω_e'' and $\omega_e''x_e''$ values are used in the matrix. This would introduce some error if the ground state is strongly perturbed in matrix. The effect in this case, however, is small enough to be neglected, as is seen later in this section. Here it is helpful to mention two such cases. The gas phase ω_e'' and $\omega_e''x_e''$ of S_2 are 722.8 and 2.85 cm^{-1} , respectively. In the matrices,²⁴ the changes in ω_e'' are less than 12 cm^{-1} , and in $\omega_e''x_e''$ less than 0.3 cm^{-1} . Another case is CO.²⁵ Its $\omega_e'' = 2169.8 \text{ cm}^{-1}$ and $\omega_e''x_e'' = 13.3 \text{ cm}^{-1}$ in the gas. In the solid, $\omega_e'' = 2160.8 \text{ cm}^{-1}$, and $\omega_e''x_e'' = 11.3 \text{ cm}^{-1}$. These can be used to support the approximation adopted in this work.

The first three observed band frequencies in each matrix are used to solve for A , ω_e' and $\omega_e'x_e'$ and therefore ΔT_e , which is equal to $(T_e^{\text{matrix}} - T_e^{\text{gas}})$. The calculated ΔT_e 's are shown in Table 18.

All combinations are tested, and the best suited ones with the observed ΔT_e 's in 10%Xe-90%Kr matrix are listed in the last column of Table 18, along with the corresponding v_1 values of Xe and Kr matrices

TABLE 18. Possible T_e shifts of the Pb_2 spectra in the matrices

v_1' assigned	$\Delta T_e^{obs}(Xe)$ cm^{-1}	$\Delta T_e^{obs}(Kr)$ cm^{-1}	$\Delta T_e^{obs}(10\% Xe-90\% Kr)$ cm^{-1}	$\Delta T_e^{calc.}(10\% Xe-90\% Kr)$ cm^{-1}
0	+593	-117	-202	
1	+765	-307	-401	
2	+940	-507	-582	
3	-1119	-719	-772	-785 ($Xe^{(3)}-Kr^{(0)}$)
4	-1300	-940	-972	-969 ($Xe^{(4)}-Kr^{(1)}$)
5	-1485	-1175	-1182	-1159 ($Xe^{(5)}-Kr^{(2)}$)
6	-1678	-1419	-1398	-1359 ($Xe^{(6)}-Kr^{(3)}$)

from which the ΔT_e 's are chosen. It is seen that based on the above assumption, the observed ΔT_e in the 10%Xe-90%Kr matrix for each v_1' assignment can only be obtained if it has the same vibrational number as v_1' (Xe) while that of v_1' (Kr) be smaller by three. This is in agreement with the previous deduction that v_1' (Xe) $\geq$ v_1' (Kr) + 1.

In calculating the T_e 's the assumption is made that ω_e and $\omega_e x_e$ for the X state are the same as those in the gas phase. The observed ω_e' values for the assignment of v_1' (Xe) = 6, v_1' (Kr) = 3, and v_1' (10%Xe-90%Kr) = 6 are, respectively, 189 cm^{-1} , 217 cm^{-1} and 224 cm^{-1} , with the corresponding $\omega_e' x_e'$ values 1.5, 5.5 and 4.75 cm^{-1} for Pb_2 in the three matrices. Compared to the gas phase $\omega_e' = 159.22 \text{ cm}^{-1}$, it clearly shows an increase of ω_e' values in the matrices. The actual ω_e'' values in the matrices are also expected to increase but to a less extent than that of ω_e' because of the smaller r_e in the ground state. In the limit, when 15 cm^{-1} increase in ω_e'' is used in Xe matrix, the T_e observed will be 15 cm^{-1} more to the red. This has very small effect on the discussions above.

The larger $\omega_e' x_e'$ values in all three matrices than that in the gas indicate an increase in the anharmonicities of the A state potential curve in the matrices.

In the calculations of ΔT_e , the observed frequencies of the first three bands are used to obtain ω_e' , $\omega_e' x_e'$, and Δv . These values are then used to calculate the frequencies for the other bands and compare with the observed ones. One set of calculated values is shown in Table 19 in which the first observed bands in Xe, Kr and 10% Xe-90% Kr matrices are assigned to v_1' values of 6, 3, 6, respectively.

TABLE 19. Calculated Δv 's of the Pb_2 (A_{∞}) bands in Xe, Kr and Xe-Kr matrices

v_1'	assigned	ν obs cm ⁻¹	ν calc cm ⁻¹	ν obs - ν calc cm ⁻¹
Xe	6	19191	19191	0
	7	19359	19359	0
	8	19524	19524	0
	9	19687	19686	1
	10	19861	19845	16
	11	20014	20001	13
	12	20169	20154	15
Kr	3	19673	19673	0
	4	19846	19846	0
	5	20007	20007	0
	6	20164	20158	6
	7	20323	20298	25
	8	20470	20427	43
	9	20633	20545	88
10% Xe-90%Kr	6	19550	19550	0
	7	19707	19707	0
	8	19854	19854	0
	9	20009	19992	17
	10	20176	20120	56
	11	20332	20239	93
	12	20480	20348	132

Pb_2 in Kr shows larger pushing-up effect of the higher v' levels than in Xe. However, the effect is even larger in the mixed matrix. This abnormally large effect in the latter matrix is reflected by its ω_e' value which is larger than those in Xe and Kr matrices. This could be due to the irregular vibrational spacings in the first three levels observed in this matrix. If effort is made to make ω_e' in this matrix fall between those in Xe and Kr, ΔT_e will change by 80 cm^{-1} . This would change the above relation to $v_1'(\text{Xe}) = v_1'(\text{Kr}) + 2(\text{or } 3)$, but is still in qualitative agreement with the relation $v_1'(\text{Xe}) \geq v_1'(\text{Kr}) + 1$.

The relative frequency shifts in T_e of $\text{Pb}_2 A \leftarrow X$ transition can now be approximated. With the relation that $v_1'(\text{Xe}) \geq v_1'(\text{Kr}) + 1 \geq v_1'(\text{Ar}) + 2$, the difference in ΔT_e is more than 500 cm^{-1} between Xe and Kr, and more than 400 cm^{-1} between Kr and Ar. If the assumption used in the above Xe-Kr mixed matrix work is adopted, the difference in ΔT_e between Xe and Kr could be as large as 740 to 960 cm^{-1} .

b. Possible Trapping Site Geometry of Pb_2 in the Matrices The discussions in the last section indicated large red shifts of T_e in Xe and possibly Kr matrices. This implies that the excited Pb_2 molecule in its equilibrium state must be stabilized more than the ground state by interacting with the matrix environment. The $v'=0$ level, therefore must be free from strong repulsive interaction with the environment due to orbital overlapping, although the higher v' levels might suffer great repulsive interactions. Bass and Broida²⁶ observed that the Schumann-Runge bands of O_2 in the matrices showed diverging increase of $\Delta G_{1/2}$ values above $v' = 14$. The absence of such diverging effect in all the

$\text{Pb}_2 \text{ A} \leftarrow \text{X}$ spectra in the matrices could be due to the failure of observing transitions to higher v' levels because of the rapid decrease in the absorption intensities toward the higher v' levels. The above information of Pb_2 is here used to try to get some idea about the possible trapping site geometry of Pb_2 molecules in the matrices.

The intensity distribution of the gas phase $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ absorption spectrum indicate that $r'_e > r''_e$, although no exact values were reported. The ground state r_e was reported to be 3.08Å.²⁷ This value is here used in comparing the sizes of Pb_2 and the lattice sites in the matrices. The ground state Pb_2 molecules correlates to two $6p^2 \text{ } ^3\text{P}_0$ Pb atoms. The atomic radius of the $6p^2 \text{ } ^3\text{P}_0$ Pb atom is reported to be 1.80Å.²⁸ Taking the above $r_e(\text{X})$ into consideration, the center-to-edge distance of $\text{Pb}_2(\text{X})$ is about 3.34Å. In a Xe matrix at 20°K, the nearest neighbor distance is 4.34Å and the σ value between two Xe atoms is 2.23Å. Because the rare gas atoms have closed valence shells, orbital overlapping between two such atoms will lead to large repulsion. Therefore, one can approximate the σ value between one Xe atom and one Pb $6p^2 \text{ } ^3\text{P}_0$ atom to be $(2.23+1.80) = 4.03\text{Å}$. Let the Pb_2 molecules lie in the center of a substitutional site of a Xe lattice. The internuclear distance between the Pb atom and its nearest Xe neighbor is 2.80Å or 3.10Å for an alignment of Pb_2 on the long or short axis, respectively, of the Xe hexagon in the same plane. In the former each Pb atom overlaps with one Xe atom, while in the latter with two Xe atoms. Both distances are smaller than the σ value between Pb and Xe. This implies that, for a Pb_2 molecule in a substitutional site in a Xe lattice, the repulsive interaction is very large even for the Pb_2 molecule in the ground state. The repulsive

interaction will be even larger in the excited A state when its $r_e > r_e(X)$ and makes the Pb-Xe distances even shorter. Such large increase in the repulsive interaction would cause a large blue shift of the $T_e (A \leftarrow X)$ value. However, red shift is instead observed in a Xe matrix. This implies that Pb_2 molecule cannot be in a perfect substitutional site in the Xe matrix. Some Xe atoms must be missing to remove the huge overlapping even with the ground state Pb_2 , e.g. the two nearest Xe neighbors on the hexagon long axis. The earlier discussion on the Pb_2 formation mechanism indicated that during deposition the matrix atoms in the neighborhood of trapped Pb atoms have high enough mobility due to the releasing heat from the Pb. In addition, as will be shown in Chapter IV, the reported thin film work indicated that under some conditions the rare gas atoms have high mobility even at a deposition temperature of $7^\circ K$. This could be used to support the proposal here that during deposition, the two nearest Xe atoms moved to the next positions to avoid orbital overlapping with the Pb_2 molecules. The new geometry would not only stabilize the ground state Pb_2 but also the A state Pb_2 due to the absence of orbital overlapping in both states.

It is emphasized, however, that this geometry is different from the one proposed by Brith and Schnepf for the Ar trapped Mn atoms. There, Ar atoms are thought to be missing to allow for the removal of Mn orbital degeneracy in order to account for the observed multiplet structure. On warming up such a Mn/Ar lattice, there is possibility that other Ar atoms could move in to fill the vacancies near the Mn atoms. This is allowed because no orbital overlapping exists between a Mn atom in the perfect substitutional Ar lattice site and the surrounding Ar atoms.

The Mn/Ar case is therefore an unstable state which will change to a stable one on warming up the matrix and allowing for annealing. The Pb_2 case, however, is in an equilibrium state, and would remain so on warming up the matrix film. Because of the absence of orbital overlapping, both ground and excited states Pb_2 interact with the environment attractively, with the excited state dominated in Xe and Kr matrices. It is this attractive interaction, which is less sensitive than a repulsive one to the lattice expansion at higher temperatures, that causes the observed temperature-independence of the Pb_2 absorption frequencies in all the matrices reported in this work.

c. Effects of SF_6 Matrix on the Trapped Pb_2 Molecules

Because of the lack of knowledge about the SF_6 crystal structure, a reliable comparison of its effects on the trapped Pb_2 molecules with other rare gas matrices is difficult. Therefore, only a brief discussion is made here.

The IR spectrum of solid SF_6 ²⁹ reveals that the center of symmetry is maintained at the site in the solid. This is based on the fact that solid SF_6 deposited at 77°K does not show any of the Raman active fundamentals in its IR spectrum. Both Raman³⁰ and IR²⁹ spectra of solid SF_6 show splitting possibly due both to site group and factor group splittings. This indicates that the symmetry at the site in the solid is lower than O_h which is the point group of SF_6 molecule. If one assumes that SF_6 , because of its spherical symmetry and nonpolarity, crystallized into closed pack structure,³¹ one would expect that hexagonal close-packed lattice (site group D_{6h}) be more probable than cubic close-packed lattice (site group O_h) based on the IR and Raman works cited above.

In the discussions of Pb_2 spectra in the rare gas matrices, the lattice geometry used is the same for both hcp and ccp (fcc) lattices because only pair interactions are included, and the orientational effect is neglected which distinguished hcp from fcc lattices. The values for σ and ϵ at the potential well minima of a L-J 6-12 potential for Ar, Kr, Xe and SF_6 are compared in Table 20.

Table 20 implies that, if solid SF_6 had a hcp structure and with a similar geometry for the trapped Pb_2 molecules as in the rare gas matrices, the predicted red shift in SF_6 matrix of the T_e of Pb_2 $X \leftarrow A$ transition would be smaller than that in Xe, but could be of comparable magnitude with those in Ar and Kr. This comparison would be invalid if Pb_2 in SF_6 has a rather different trapping site geometry as that in the rare gas matrices.

In the proposed geometry model for Pb_2 in the rare gas matrices, two of the nearest neighbors have to be missed to remove the huge repulsion with X state Pb_2 molecules. Similarly, if hcp structure is assumed for a SF_6 lattice, with the r_e value about 6.0A, the same two nearest neighbor SF_6 molecules have to be missed as in Xe, Kr and Ar. The distance between the Pb atomic center and one of these two SF_6 molecules is $(6.0-1.54) = 4.46\text{A}$, compared to $\sigma_{\text{Pb-SF}_6} (1.8+3.2) = 5.0\text{A}$.

In addition, the observed smaller vibrational spacings of the Pb_2 spectrum in SF_6 than those in the rare gas matrices implies that Pb_2 in the SF_6 matrix is more gas phase like than in the other matrices. This could be expected if SF_6 matrix had similar structure as the rare gas matrices, and with the larger trapping site in this matrix.

TABLE 20. Comparisons of σ and ϵ values among the matrix gases

	σ (Å)	$\epsilon/k(\text{deg K})$
Ar ^a	3.87	119.3
Kr ^a	4.04	159
Xe ^a	4.46	228
SF ₆ ^b	6.19	200.9

a. Reference 20.

b. Reference 26.

IV. DISCUSSIONS OF MATRIX EFFECTS ON THE TRAPPED METAL ATOMIC SPECTRA

A. Matrix Effects on the Pb $^3P_1 \leftarrow ^3P_0$ Absorption Band

It is recalled that the Pb absorption spectra in all the rare gas matrices contains a single strong band, which is assigned to the Pb $6p7s\ ^3P_1 \leftarrow 6p^2\ ^3P_0$ transition. This band has a half-width around 400 cm^{-1} , and is blue-shifted from the gas phase value by several thousand cm^{-1} . On warming up the matrix, a reversible red shift is observed for this band. These observed matrix effects are discussed in this section.

The reversible red shift of the atomic Pb band on warming up the matrix suggests that the absorption frequency of Pb may be closely related to the interaction between Pb atom and the surrounding matrix atoms. This is based on the facts that 1) the rare gas crystals expand reversibly as the temperature is increased,^{23,33} and 2) The rare gas atoms are expected to interact differently with the ground and excited states of the Pb atom; the net difference between these two interactions is very possibly responsible for the observed frequency shift in the matrices. The latter is very similar to the cases of pressure-effect studies of rare gases on the alkali metal atoms.³⁴ To test the possible relation cited, calculations are carried out using Lennard-Jones 6-12 potential. The Lennard-Jones potential, although physically less plausible than, say Buckingham (6, exp) potential, is more convenient to use. In addition, the calculated values of the various properties of the rare gas crystals using the Lennard-Jones potential are very close to those obtained by using other potentials.^{23,35} Therefore, this type of potential is used in this work.

The Lennard-Jones 6-12 potential has the form

$$v(r) = \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where σ is the equilibrium distance between the two interacting molecules, ϵ is the well depth of the potential at σ . Since both the ground and excited states are concerned in the absorption frequency shifts, two equations are needed, one for each state. The surrounding matrix atoms are in the ground state in both cases, while only the trapped species changes its state. The observed shift in absorption frequency is then the difference between the two $v(r)$'s involved. A positive value for $\Delta\nu$ implies a blue shift, and a negative value a red shift relative to the free atom transition.

The pure rare gas crystals are found to be in cubic close-packed (face-centered cubic) structures. The interaction of the trapped species with the nonnearest neighbor matrix atoms should also be included in the calculation. The potential constants were calculated by Kihara³⁶ to be $C_6 = 14.45$ and $C_{12} = 12.13$. These constants were obtained by assuming an infinite crystal as well as an additive pairwise potential. The repulsive part of the interaction quickly fades away as one goes to the next nearest neighbor and beyond, but the attractive part persists to larger distance.

In the calculations here the combining relations

$$\epsilon_{12} = (\epsilon_{11} \times \epsilon_{22})^{1/2} \quad \text{and} \quad \sigma_{12} = 1/2(\sigma_{11} + \sigma_{22}) \quad (2)$$

are adopted. The values needed for the rare gases are²⁰

$$\begin{array}{ll}
 \epsilon_{\text{Xe}} = 158.5 \text{ cm}^{-1} & \sigma_{\text{Xe}} = 4.46\text{\AA} \\
 \epsilon_{\text{Kr}} = 110.5 \text{ cm}^{-1} & \sigma_{\text{Kr}} = 4.04\text{\AA} \\
 \epsilon_{\text{Ar}} = 82.9 \text{ cm}^{-1} & \sigma_{\text{Ar}} = 3.87\text{\AA}
 \end{array}$$

The ϵ value between two ground state Pb atoms is approximated by the dissociation energy value of the ground state Pb_2 molecule which correlates to two $6p^2 \text{ } ^3\text{P}_0$ Pb atoms. The σ value of the ground state Pb atom is approximated by its atomic radius which is $1.80\text{\AA}$.²⁸ The idea of using this atomic radius is to forbid orbital overlap between a Pb atom and a rare gas atom. The atomic radius of Pb in the $6p7s \text{ } ^3\text{P}_1$ state is not known, and is approximated by that of the ground state Ra, $2.15\text{\AA}$, in a state of $6p^2 7s$. This is a lower limit for the $6p7s \text{ } ^3\text{P}_1$ state Pb atom. The ϵ value between two $6p7s \text{ } ^3\text{P}_1$ Pb atoms is treated as a parameter and obtained empirically.

The observed frequency shift of Pb in Xe matrix is used to obtain $\epsilon_{\text{Pb(A)}-\text{Pb(A)}}$, here A denotes the excited $^3\text{P}_1$ state, while the X ground $^3\text{P}_0$ state. The predicted frequency shifts in Kr and Ar matrices are then compared with the observed ones.

The ϵ value between the two $^3\text{P}_1$ Pb atoms is found to be 3602 cm^{-1} . The frequency shifts in Kr and Ar are calculated to be 3300 cm^{-1} and 5480 cm^{-1} , respectively, while the corresponding observed values are 2974 and 5553 cm^{-1} , respectively.

The calculated frequency shifts in Kr and Ar, as mentioned before, are lower limits. As the actual atomic radius of the excited Pb atom becomes larger than the one used here, the calculated frequency shifts will

increase and deviate more from the observed values. However, the fair agreement in the Kr matrix offers some insight about the origin of the absorption frequency shift observed in the matrices. The calculated ϵ values indicate that when the Pb atom is at equilibrium distance from the matrix gas atom, the stabilization energy is larger for the ground state Pb atom than that for the excited Pb atom. The observed frequency shift is determined by the position of the Pb atom on the two interaction potential curves. From the set of σ values used one notices that the observed blue shift of the Pb absorption frequencies is mainly due to the larger ground state stabilization energy created by the matrix gas atoms.

A similar calculation is carried out including only the interactions of Pb with its twelve nearest neighbor matrix gas atoms. The calculated frequency shift is 3545 cm^{-1} in Kr, and 5940 cm^{-1} in Ar. The agreement with the experiment is poorer than that when all the neighbors are included in the calculations. Here it suffices to mention that the observed frequency shift in Ar is abnormally high, as will be seen in the later calculations. This explains why the two calculated values for Ar lie on the different sides of the experimental value, while those of Kr are both higher than the observed value. Taking the Kr case for example, it is found that when the σ values are changed to give a calculated frequency shift lower than the observed one, again the calculated value with all neighbor interactions included is superior to that with only twelve nearest neighbors included. This suggests that all neighbors should be included in such type of calculations to get better agreement with the experiment. The abnormally high value in Ar is explained later in the proposed model for the matrix effects observed.

In the above calculations, the σ value between the ground state Pb atom and the rare gas atom is taken to be the sum of the atomic radius of Pb and half of the σ value between two pure rare gas atoms. This is based on the fact that the orbital overlapping between the interacting species involving closed shell atom leads to huge repulsive interactions. The uncertainty in choosing the Pb excited state atomic radius makes the quantitative correlations difficult. Therefore, the frequency change on warming up the matrix is not checked using this method. Instead the method by McCarty and Robinson is adopted in serving this purpose.

McCarty and Robinson⁵ used the Lennard-Jones 6-12 equation in the form

$$v_{ab} = 4 \epsilon_{ab} [12.13 (\sigma_{ab}/d_{ab})^{12} - 14.45 (\sigma_{ab}/d_{ab})^6] \quad (3)$$

here σ_{ab} is the distance between species a and b at which the attractive interaction balances the repulsive interaction. Its relation with the equilibrium r_0 is that $\sigma_{ab} = r_0/2^{1/6}$. The coefficients in the bracket are potential constants, same as those used in the earlier calculations. McCarty and Robinson then made the assumption

$$\epsilon_{ab} \sigma_{ab}^6 \approx (\epsilon_a \sigma_a^6)^{1/2} (\epsilon_b \sigma_b^6)^{1/2} \quad (4)$$

based on perturbation derivation. The difference Δv between excited state and ground state v 's has the form after rearrangement

$$\Delta v_{ab} d_{ab}^6 / 57.8 \sqrt{\epsilon_a \sigma_a^6} \approx \frac{0.84 \sigma_a^3}{d_{ab}^6} (\Delta \sqrt{\epsilon_b \sigma_b^{12}}) - \Delta (\sqrt{\epsilon_b \sigma_b^6}) \quad (5)$$

here

$$\begin{aligned} \Delta \sqrt{\epsilon_b \sigma_b^{12}} &= \sqrt{\epsilon_b' \sigma_b'^{12}} - \sqrt{\epsilon_b'' \sigma_b''^{12}} \\ \Delta \sqrt{\epsilon_b \sigma_b^6} &= \sqrt{\epsilon_b' \sigma_b'^6} - \sqrt{\epsilon_b'' \sigma_b''^6} \end{aligned}$$

the single prime refers to the excited state while the double prime to the ground state. For convenience, $\Delta \sqrt{\epsilon_b \sigma_b^{12}}$ and $\Delta \sqrt{\epsilon_b \sigma_b^6}$ are denoted to be Δ_{12} and Δ_6 , respectively. The final form to be used is

$$\Delta \nu_{ab} d_{ab}^6 / 57.8 \sqrt{\epsilon_a \sigma_a^6} \approx \frac{0.84 \sigma_a^3}{d_{ab}^6} \Delta_{12} - \Delta_6 \quad (6)$$

The advantage of using the Lennard-Jones 6-12 equation in the form of Eq. 6 is that the empirical values of the trapped species, i.e., σ , ϵ are all included in Δ_6 and Δ_{12} . Therefore, only Δ_6 and Δ_{12} need to be solved from two different experimental values of $\Delta \nu$. The equation can then be applied to a different matrix involving the same trapping species.

The observed frequency shifts of Pb in Xe and Kr at 20°K are used to solve for the parameters Δ_6 and Δ_{12} , and lead to the values $\Delta_6 = -65.9 \text{ cm}^{-1/2} \text{ \AA}^3$, and $\Delta_{12} = 3.796 \times 10^4 \text{ cm}^{1/2} \text{ \AA}^6$. The equations used have the general forms

$$\Delta \nu_{ab} d_{ab}^6 / 45420 \approx \frac{52.7}{d_{ab}^6} \Delta_{12} - \Delta_6 \quad (7)$$

for Pb/Xe.

$$\text{for Pb/Kr} \quad \Delta \nu_{ab} d_{ab}^6 / 28333 \approx \frac{39.2}{d_{ab}^6} \Delta_{12} - \Delta_6 \quad (8)$$

Therefore, after plugging in the values for Δ_6 and Δ_{12} into Eqs. 7 and 8, the only variable left is d_{ab} that can affect the $\Delta \nu$ values observed. Equations 7 and 8 are now used to calculate the $\Delta \nu$'s at various temperatures higher than 20°K. The lattice parameters of Xe and Kr are taken from Pollack's paper.²⁰ So far it has been assumed that the trapped species is at the substitutional site in the matrix gas crystal lattice, so the rare gas lattice distance at each temperature is directly used for the d_{ab} needed.

The results of the calculations of $\Delta\nu$ in Xe and Kr at various temperatures are shown in Table 21, along with the observed values.

The calculated blue shifts in Xe parallel those of the observed ones, but being larger than the latter at all temperatures. This means that on warming up the Xe matrix, the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band decreases in frequency faster than are predicted from the calculations. However, the opposite is found for Pb/Kr. The $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band shows less and less red shift at higher temperatures than are predicted from calculations. It is to be noted that better agreement in Xe and Kr are expected because values from these two matrices are used to determine the Δ_6 and Δ_{12} values. When the set of Δ_6 and Δ_{12} obtained above are used to calculate frequency shift in Ar at 20°K, a value of 4017 cm^{-1} is obtained. The observed shift in Ar is 5553 cm^{-1} . Again, the calculations fail to predict a right frequency shift in Ar. As will be seen later, this failure in Ar case as well as the negative deviation in Kr are expected after a model is proposed to explain the observed spectra of various metal atoms in the matrices.

It is interesting to see how the correlation is in the Xe-Kr mixed matrices. The 10%Xe-90%Kr matrix, as noted in Chapter III, is assumed to consist of eight Xe atoms and four Kr atoms around each Pb atom trapped. It is therefore interesting to see how this relation holds at higher temperatures. compared to the calculated values using the same relation. The frequency shifts in Xe and Kr at each temperature are summed proportionately according to this composition relation, and compared with the observed ones in Table 22.

The agreement is fairly good in this case. It seems that the two opposite effects in Xe and Kr mentioned cancel each other and leads to

TABLE 21. Calculated and observed warm-up shifts of the Pb $^3P_1^o \leftarrow ^3P_0$ band in Xe and Kr matrices.

	Temp. °K	$d_{ab}(A)$	$\Delta\nu_{-1}^{calc}$ cm	$\Delta\nu_{-1}^{obs}$ cm
Xe	20	4.34	2483	2483
	30	4.345	2451	2437
	40	4.352	2408	2379
	50	4.361	2355	2317
	60	4.371	2296	2260
	70	4.380	2245	2210
	77	4.389	2196	2148
Kr	20	3.999	2974	2974
	30	4.005	2930	2928
	40	4.014	2860	2896
	50	4.025	2771	2858

TABLE 22. Calculated and observed warm-up shifts of the Pb $^3P_1 \leftarrow ^3P_0$ band in the 10% Xe-90% Kr matrix.

Temp °K	$\Delta\nu_{\text{cm}^{-1}}^{\text{calc}*}$	$\Delta\nu_{\text{cm}^{-1}}^{\text{obs}*}$	$\Delta\nu_{\text{cm}^{-1}}^{\text{obs} \dagger}$
20	2646	2659	2659
30	2601	2590	2598
40	2551	2551	2532
50	2498	2492	2492

* Those are the values from the corresponding ones in the Xe and Kr matrices from Table 21, using the approximation that

$$\Delta\nu_{\text{Xe-Kr}} \approx \frac{8}{12} \Delta\nu_{\text{Xe}} + \frac{4}{12} \Delta\nu_{\text{Kr}}.$$

† The experimental values.

better agreement obtained here.

Because the frequency shift of the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ transition in Xe and Kr matrices could be fairly well correlated with the calculated values, it is interesting to see whether one can apply this method to other metals to check for the assignment of the bands observed. In other words, the observed frequencies in Xe and Kr matrices are used to check the gas phase frequency they correspond to. Pb is here checked for this possibility.

It is noted that in the calculations using Eq. 5 there are two such equations one for Xe and one for Kr. The two parameters Δ_6 and Δ_{12} can be solved provided that the $\Delta\nu$'s are known. The frequency shift $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{gas}}$, and ν_{gas} is the corresponding gas phase transition frequency. If ν_{gas} is treated as unknown, one more equation is needed. This could be another equation containing Ar as the matrix gas. However, since the deviation in Ar is very large, an alternative way is used as described below.

The boundary condition of the 6-12 potential is that as $r \rightarrow \infty$, $\nu \rightarrow 0$. In real case, we can always find a limit r beyond which ν becomes negligible. This limiting r value can be plugged into Eq. 5 with $\Delta\nu \rightarrow 0$. In this way, there will be three equations for the three unknowns and ν_{gas} can be solved approximately. If, instead of using a finite value of r , one uses $r \rightarrow \infty$, the whole equation will vanish and no information can be obtained.

To find the limit r for $\Delta\nu \rightarrow 0$, the frequencies for the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band are used. It is calculated that in Xe at $r = 10\text{\AA}$, $\Delta\nu = 0.143 \text{ cm}^{-1}$, and at $r = 20\text{\AA}$, $\Delta\nu = 0.002 \text{ cm}^{-1}$. Apparently $r = 10\text{\AA}$ is a good choice.

The three equations needed are

$$\text{in Xe} \quad (\nu_{\text{obs}} - \nu_{\text{gas}}) (d_{\text{ab}})^6 / 45420 \approx \frac{52.7}{d_{\text{ab}}^6} \Delta_{12} - \Delta_6$$

$$\text{in Kr} \quad (\nu_{\text{obs}} - \nu_{\text{gas}}) (d_{\text{ab}})^6 / 28333 \approx \frac{39.2}{d_{\text{ab}}^6} \Delta_{12} - \Delta_6$$

$$\text{and} \quad (0.143) (10)^6 / 45420 \approx \frac{52.7}{10^6} \Delta_{12} - \Delta_6$$

the last one reduces to

$$2 \approx \frac{52.7}{10^6} \Delta_{12} - \Delta_6$$

When the values of the observed frequencies of Pb in Xe and Kr are plugged into these three equations, the ν_{gas} is found to be 35490 cm^{-1} , compared with the true ν_{gas} of 35287 cm^{-1} for the Pb $6p7s \ ^3P_1 \leftarrow 6p^2 \ ^3P_0$ transition.

Here, it is important to point out that the calculated ν_{gas} is an upper limit for the true ν_{gas} . If 10A separation is not enough to eliminate the $\Delta\nu$, and one has to go to, say, 20A the calculated value would be lower than the first one by about 1600 cm^{-1} .

The agreement with the true gas phase $^3P_1 \leftarrow ^3P_0$ value is very good. The same method of approximating gas phase ν will be used later for the other metals to check for the reported assignments of the bands observed.

B. The Predicted Dynamic Matrix Effect From the Earlier Theories

It was mentioned in the "Introduction" section that multiplet structures were observed for many matrix trapped metals with $p \leftarrow s$ resonance transitions. Various theories have been proposed to explain this fact. It was also pointed out that only the static frequency shifts were used

in those theories to explain the multiplet structures. However, on warming up the matrix, the two lower frequency components shift to the red while the highest frequency component to the blue, all being reversible on cooling back to original temperature. This experimental fact is closely related to the real cause of the multiplet structures observed. Therefore, any model proposed to account for the multiplet structures must also be able to predict correctly the observed different temperature dependence of the multiplet components. The earlier theories are now checked individually in this respect.

Brith and Schnepf⁶ proposed neighbor-missing or distortion model to explain the observed triplet of Mn in Ar. The neighbor-missing model can not give a reversible frequency shift of the bands observed, irrespective of the shift directions. The warming up process would anneal the matrix film and fill and vacancies in the neighborhood of the trapped Mn. This would cause disappearance of two of the triplet components on cooling back, in contradiction to the observed reversible shift. The distortion model, although giving the right order of magnitude of the splitting energies, predicts only two bands instead of three. Therefore, these two models could not explain the facts observed.

Andrews and Pimental¹ suggested the role of nonnearest metal neighbor interaction in the appearance of multiplet structures of Li in the matrices. If one assumes no mobility of the metal atoms at higher temperatures, i.e. the distances between the Li atoms remain the same, all multiplet components should not show any frequency shift on warming up the matrix. On the other hand, if the metal atoms move while the matrix film expands with increasing temperature, the metal atoms are expected to move toward

one another because of the attractions among them at the distances they are separated, as proposed by the authors. This would give blue shifts for all components according to the potential curves they used. Also, it is doubtful that on cooling back the Li atoms would move back to their original positions against the attractive force among them. Therefore, the observed multiplet structures of Li could not be explained using the nonnearest metal-metal interaction mechanism.

Brewer et al.^{3,7} suggested Stark splitting as a possible cause of the triplet structures of Au, Ag and Cu in the matrices. In order to check this model for its predicted temperature dependencies of the triplet components, one has to go in some detail about the nature of the Stark splitting. This is discussed later in a separate section. Here it suffices to mention that this model also fails to predict the correct temperature dependencies observed.

McCarty⁹ discussed the Hg triplet spectra in the matrices. One component is attributed to the completely isolated Hg atoms, and two to the two Hg atoms being nearest neighbors to each other. On warming up, the line due to isolated Hg atoms would give a red shift due to crystal expansion, while the other two lines would also shift to the red if the two Hg atoms remain the same distance apart. Even if these two Hg atoms do move closer yet without forming a Hg₂ molecule, the two lines they give rise to should show the same sign of frequency shift. In short, this model predicts either red shift for all three lines, or one red shift and two blue shifts. Neither prediction matches the observations.

None of these theories accounts satisfactorily for the observed frequency shifts of those metals in the matrices. Therefore, a different approach is taken to try to solve this problem.

The problem is tackled by considering the formation and structure of the matrix thin films. For a pure rare gas thin film, all the atoms are identical, the main factor determining the structure of the film is the mobility of the atoms on the target. This is determined by the vapor temperature, target temperature, deposit rate and the attractions among the gas atoms. If the first three are constant, the mobilities on the target among different gases will depend upon their melting points T_m relative to the target temperature.¹¹ Chopra³⁷ reported in his book that metal films, when deposited at or below the temperature of $1/3 T_m$, have disordered or amorphous structure. This $1/3 T_m$ can therefore be treated as the annealing temperature for the individual metal films. Rare gas atoms are similar to many metal atoms in that they are single atoms and spherical like, the deposited film structure is therefore not complicated by the orientational problems of many molecules. For the matrix-trapped alkali metals,² multiple trapping sites are formed because the deposit temperature is too low (4°K) for the matrix gases. After annealing at a higher temperature, the spectra corresponded to those metal atoms in the "abnormal" site disappear, while the main spectra remain. For the Pb spectra, since the films are deposited at 20°K and the spectrum persists after annealing, conclusions can be drawn about the stability of the trapping site formed at 20°K .

When the metal vapor is cocondensed on the target with the matrix gas, the much higher T_m of the metal greatly reduces its mobility on the target. Because of this, it is not unreasonable to expect that each metal atom is not in the center of the substitutional site, but penetrates

to a certain extent toward the inner layer matrix atoms. If there is further asymmetry in the other two directions (the two mutually perpendicular directions both parallel to the target surface), this can completely destroy the three-fold degeneracy of the p orbital. The p suborbital which is normal to the target suffers greatest distortion and accounts for the highest frequency line in the triplet. On warming up the matrix, the metal atom, because of its high T_m , can not obtain the same mobility as the rare gas atoms. The mobility of the metal is therefore negligible compared to that of the matrix gas atoms. The matrix film will expand three-dimensionally on warming up. However, because of the blocking effect of the target, the normal-to-target direction expansion will be completely outward from the target. This increases the distortion between the metal atom and the inner layer matrix gas atoms and causes a blue shift of the transition line. The other two directions, however expand without being blocked. This lowers the energies in these two directions and causes red shifts for both. On cooling back, the reverse takes place.

It is emphasized that in the $p \leftarrow s$ transitions the ground state is spherically symmetric while the upper state is strongly oriental-sensitive because of the three p orbitals involved that are mutually perpendicular to one another. It is this strong orientation sensitivity toward the matrix environment that causes that splitting when the symmetry is removed.

In the Pb work here only one strong band is observed in all rare gas matrices that can be assigned to the $6p7s \ ^3P_1 \leftarrow 6p^2 \ ^3P_0$ transition. This is also expected from the proposed model. The $\ ^3P_1$ state consists of

one 6p and one 7s electrons. The 7s electron has a larger orbital size than that of a 6p electron. Therefore, in the excited state, the 7s electron is expected to interact with the matrix environment much more strongly than the 6p electron which lies in an inner orbital. The 6p electron can be in one of the three sublevels of 6p state, therefore giving rise to three fold degeneracy. The penetration of the Pb atom toward the inner layer does affect this degeneracy. But the net difference among the interactions involving 6p electrons with the matrix environment is expected to be small due to the much larger interaction involving the 7s electron. Therefore, the excited state has only negligible splitting and is included in the breadth of the absorption band. The ground state contains two 6p electrons and is also three fold degenerate. The penetration again destroys this degeneracy, but one expects only a small difference in energy among the three nondegenerate states created. Again this only shows up in broadening the absorption band. Because the 7s orbital has a spherical structure and interacts with matrix environment much stronger than the inner 6p electron, the net absorption from $6p^2\ ^3P_0$ to $6p7s\ ^3P_1$ gives one single band. The breadth of this band is therefore expected to be twice or more than those of the triplet components for the metals with $p \leftarrow s$ transitions.

It is interesting to note that Duley¹⁸ reported a similar strong, single band in matrix-trapped Bi atoms absorption spectrum which is assigned to the resonance transition $6p^27s\ ^4S_{1/2} \leftarrow 6p^3\ ^4S_{3/2}^o$. The frequency shift from gas is 3400 cm^{-1} in Xe, 3800 cm^{-1} in Kr and 6000 cm^{-1} in Ar. It also shows red shift on warming up. It is obvious that the same idea for Pb can be applied to explain this band of Bi in the matrices.

As was mentioned, the penetration of metal atoms toward inner layer matrix atoms destroys the degeneracy between the normal-to-target axis, z , with the other two axes x and y . x and y axes will remain degenerate in a fcc lattice but not so in a hcp lattice. A knowledge about the impurity-containing matrix film structure is therefore essential to a conclusive interpretation of the observed multiplet structures. Although such a knowledge is lacking at present some understanding of it can be obtained by knowing the structures of both pure and impurity-containing crystals and thin films of the rare gases. This is discussed in the next section.

C. Structures of Pure and Impure Rare Gas Crystals

Experimentally only the cubic close-packed structure (ccp) is found for the crystals of pure Xe, Kr, Ar and Ne. The unit cell in this lattice is face-centered cubic (fcc) and therefore possesses cubic symmetry. Most of the theoretical calculations,³⁴ however, predicted that the rare gases should crystallize in the hexagonal close-packed form (hcp). The hcp structure is calculated to be more stable than the ccp structure by about 0.01% of the cohesive energy of the crystal. In those calculations the Lennard-Jones type potential was used with the assumption of additive pairwise interactions. Let us compare these two structures in the number of neighbors and their distances from the atom at the origin.²³ If R is the radius for the rigid sphere atom, both ccp and hcp structures have twelve first nearest neighbors, with distance $2R$; and six second nearest neighbors, with distance $2R\sqrt{2}$. However, the number of the third nearest neighbors in fcc is twenty-four, with distance $2R(3)^{1/2}$, and that in hcp is two with distance $2R(8/3)^{1/2}$.

Jansen and coworkers³⁸ included the three body interactions in their calculation of the crystal energies. They used Gaussian charge distribution and only considered the exchange interaction. Only the first nearest neighbors were included. The fcc was calculated to be lower in energy than hcp by about 4% of the cohesive energy. However, the difference in energy between the two types of structures was estimated by Meyer³⁹ to be at best 0.1% of the lattice energy, the latter being approximately the heat of sublimation. Using Trouton's rule the difference in energy between fcc and hcp near the melting point was at best of the order of 1% of the sublimation energy. Therefore, Jansen's work, although predicting the right sign of stability, overestimated the three body interactions. However, it is interesting to notice that when Jansen applied the same idea of three-body interactions to alkali halides,⁴⁰ he could correctly predict the cesium chloride structure for cesium chloride, bromide and iodide. Also, the calculated transformation pressure of the alkali halides from sodium chloride structure into cesium chloride structure agreed better with the experimental values than those calculated using the old Born-Meyer model which predicted sodium chloride structure for all alkali halides.

Alder and coworkers,⁴¹ however, pointed out that the failure of the previous pair-potentials in predicting the higher stability of the fcc crystals could be due to the restrictions imposed on the analytical forms of those potentials. Since fcc and hcp have the same set of first and second neighbors and the same over-all density, the energies for the two crystals differ only due to the different lattice sum for the intermediate neighbors. Therefore, Alder et al. constructed a numerical pair-potential

for the Ar gas to fit with all the available dilute gas equilibrium and transport data. This potential differs from the Lennard-Jones 6-12 potential in that: 1) the bowl of this potential is wider and deeper than that of the L-J potential, and the repulsive side is less steep, and 2) at large atomic separations, the attraction of this potential is weaker than that of the L-J potential.

Using this numerically tabulated pair-potential for Ar, Alder et al. obtained calculated values in satisfactory agreement with all data on gas phase viscosity, thermal diffusion, and second virial coefficients.

It is also interesting to notice that Burton⁴² applied the potential by Alder et al. to the solid Ar. The calculated heat of sublimation and equilibrium nearest neighbor separation in solid Ar agreed very well with experiment. This is particularly striking since the potential by Alder et al was determined exclusively from gas phase data. Burton also found that the static binding energy of fcc phase Ar was 0.15% greater than that of the hcp phase. The zero point energies of the two phases, however, were neglected in this comparison, which might affect their relative stability.

The structures of the mixed Ar-Kr and of mixed Ar-Ne thin films were studied by Curzon and Mascall.⁴³ The films were deposited both at 7°K and 4°K. For Ar-Kr mixed crystals, only the fcc structure was observed and the lattice constant was intermediate yet nonlinear to those of the pure components. In Ar-Ne mixed crystals, two phases were observed, one due to pure Ne and the other being very disordered and probably consisting mainly of Ar. Pure Kr and pure Ar films were also deposited at 7°K and

were both found to be single phase fcc structure.

Barrett and Meyer studied the structures and phase diagrams of N_2 in Ar,⁴⁴ CO in Ar,⁴⁵ O_2 in Ar⁴⁶, and CF_4 in Ar.⁴⁷ The x-ray determination of the phase diagrams showed that in Ar- N_2 the solid phase in equilibrium with the liquid is hcp from 1% to 100% nitrogen. This hcp phase is stable at all temperatures for compositions in the range from 55% to 77% N_2 . A martensitic transformation from hcp to fcc takes place at the Ar-rich end of the diagram.

The phase diagram of Ar-CO indicates that a solid solution of hcp form extends over almost the entire range of concentration at temperature just below the solidus. The hcp phase, however, eutectoidally decomposes at 53°K into an Ar-rich fcc phase and a CO rich primitive cubic phase. The eutectoid point is at 66% CO. The miscibility gap at 53°K extends from 5% to 85% CO and is probably complete at 0°K.

Pure N_2 and pure CO both crystallized in hcp forms. However the high temperature (γ) phase of O_2 is cubic and the addition of no more than 1% O_2 to fcc Ar produces a stable hcp structure. The phase diagram of Ar- O_2 shows that on the Ar-rich side, a phase having hcp structure exists under the solidus. This phase undergoes a strained-induced transformation at low temperature to fcc in mixtures from 1% to 20% O_2 . From 20% to 50% O_2 the hcp persists to 0°K.

In all three cases, the temperature-composition line of the hcp-fcc transformation, when extrapolated to pure Ar, led Meyer and Barnett to conclude that Ar should be stable in the hcp form at higher temperatures with the hypothetical equilibrium temperature between hcp and fcc being a few degrees above the melting point.

D. Comparison Between Observed and Predicted Multiplet Structures Using fcc and hcp Trapping Site Geometries

From the review of rare gas crystal structures we know that impurity-containing Ar crystals have a stable hcp structure over wide ranges of the impurity composition. This equilibrium phase forms when the mixed liquid are solidified and annealed. Also, the work on pure Ar and pure Kr films deposited at 7°K showed only one fcc phase. Because the x-ray diffraction patterns have sharp rings in both films this indicates that the mobilities of the Ar and Kr at 7°K are still high enough to give a well ordered crystal, at least on a microscopic scale. Macroscopically the films might be amorphous, as is the case in many metals when deposited at a temperature less than one-third of the metal melting point.³⁷ Therefore, the possibility always remains that the matrices with trapped species have hcp structures. In this section the relation of the matrix structures to the spectra of the trapped species is discussed.

As is seen, hcp differs from fcc only in the number and distances of the third nearest neighbors, and beyond. The potential constants of Lennard-Jones 6-12 equation for the two structures are³⁶ for hcp: $C_6 = 14.45489$, $C_{12} = 12.13229$; for fcc: $C_6 = 14.45392$, $C_{12} = 12.13188$. The differences between the corresponding pairs are very small. This is why the calculated crystal energies are very close for the two structures when such type of intermolecular potentials are used. The calculations for the Pb $^3P_1 \leftarrow ^3P_0$ band are therefore valid for both fcc and hcp structures. This is true because for this transition of Pb the upper state

is spherically symmetric and is only sensitive to the distances between the interacting atoms. A substitutional site in fcc crystal has the cubic symmetry if all the first few layer neighbors are identical species. However, as was discussed before, a penetration of the metal toward the inner layer matrix atoms is expected. This is now investigated to see whether the three fold degeneracy of the p orbitals can be lifted after such a penetration takes place.

When the rare gas atoms deposited on a target, the layers of spheres parallel to the target surface are in closed pack arrangement. An atom in any of the layers after first one will have six nearest neighbors in the same plane in a hexagonal arrangement. There are three nearest neighbors each in the inner and outer layer. In a cubic closed pack crystal the two triangles in these two planes are in inverse alignment. The unit cell of the ccp matrix film, however, is face center cubic, and the layers of atoms parallel to the target surfaces constitute the $[111]$ planes of the fcc crystal.⁴⁸ The relations can be seen in Fig. 32. The twelve nearest neighbors of the central atom labelled M are thus seen to come from three parallel planes. If the coordinate is taken to be along the cube edges, the interaction between the central atom at M with its twelve nearest neighbors can be represented as shown in Fig. 33(a). Here each sphere represents the summation of the fields of the four neighbors in the same directions, e.g. sphere A totals the neighbors 1, 2, 3, 4, in Fig. 33(a) etc. Because of the cubic symmetry of the crystal, the distances as well as the interaction magnitudes between M and all sum-field spheres are the same. This implies that the p orbitals of the atom M sitting in a substitutional site of ccp crystals is three-fold degenerate.

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Figure 32. A ccp lattice with fcc symmetry

(a)

(b)

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Figure 33. Force field representation in a ccp lattice,
(a) before penetration, and (b) after penetration along
the $[\bar{1}\bar{1}\bar{1}]$ axis of the fcc lattice.

If during the deposition M penetrates into the inner layer, it would penetrate along the $[111]$ axis of the fcc crystal. The figure symmetry of the interactions is now shown in Fig.33(b). Again the spheres in the drawing represents the sum-fields as before, except that their magnitudes of interaction and distances from the M are no longer the same. However, because the penetration is along the $[111]$ axis, it symmetrically changes the distances and the magnitudes of interactions in such a way that the representing spheres are two sets of three equivalent ones. The cubic symmetry is destroyed but the interactions between the sum-fields and the p orbitals of M atom still give the same interaction magnitude. Each p orbital has one of its lobes distorted to the same extent and the other one less distorted than before, again to the same extent. Therefore, the penetration in a fcc crystal does not split the three fold degeneracy of the p orbitals involved in the transition. However, as will be seen in the next section, this penetration does create a net asymmetric field on M along the $[111]$ axis which is interesting in the discussion of the Stark effect in the matrices.

The above discussion showed that the observed triplets of the metal $p \leftarrow s$ transitions in the matrices cannot be accounted for from a fcc structure either in a substitutional site or when the penetration is taken into account. On the other hand, since it has been reported that impurity-containing Ar crystals showed a stable hcp structure, it is worthwhile to see what effect the hcp structure may have on the trapped metal spectra.

A metal atom at the substitutional site of a hcp lattice cannot maintain its three-fold degeneracy of the p-orbitals. This is shown in Fig.34. We are mainly interested in the difference in interactions between

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Figure 34. Overlapping between the metal p-orbitals and the matrix atoms in a hcp lattice.

the metal and its nearest neighbors along x and y directions. From the diagram we see that for an s orbital of M the interaction is spherically symmetric with all the twelve nearest neighbors. The p orbitals, however do not interact the same in the x and y directions. As the orbital size becomes large, the overlap will set in with the neighbors on x axis while being much less so in the y axis. The coordinate can be rotated as one wishes, but the interactions along any two mutually perpendicular axis in the x and y plane are not the same. When penetration along inner z axis is taken into account, the interaction with the inner neighbors due largely to the repulsive interaction will always make the interaction along z axis the largest of the three. When the matrix film is warmed up, the whole film expands outward from the target surface and increases the distortion between the p_z orbital and the inner matrix atoms. Expansion along x and y axes, however relieves the repulsion. This explains why it is always the absorption line highest in frequency that shifts to the blue when the film is warmed up, and the two lower frequency components to the red. For the Pb atom $^3P_1 \leftarrow ^3P_0$ transition the upper state consists of one 7s electron and one 6p electron. The 7s orbital extends further out than the 6p inner orbital, one therefore expects that the interaction of the excited Pb atom with its surroundings is dominated by the 7s electron. This implies that only one band is observed because of the spherical symmetric nature of the s orbital. There is distortion of the inner layer matrix atoms due to -z penetration. The repulsive interaction due to this distortion is expected to increase from Xe to Kr to Ar. In fact, the repulsive interaction in Ar could be so large that the frequency shift in Ar could deviate by a large amount from the value based on a perfect

substitutional site geometry. The previous calculations indicate that the predicted shift in Ar is larger than that in Kr by 1100 cm^{-1} , if only the size effect is taken into account for a Pb atom in a substitutional site. However, the observed value is even larger than the predicted one by 1600 cm^{-1} which can not be explained by merely considering the size effect between Kr and Ar lattices, but can be explained at least qualitatively using the model proposed here.

In addition, this model predicts increasing distortion from the inner layer which offsets some of the relaxation effect along the x and y axes on warming up the matrix. The increase in distortion is expected to be largest in Ar, less in Kr and least in Xe. This might explain the increasing negative deviation observed in Kr matrix at higher temperatures from the calculated values. The deviation in Xe is however much less. Therefore, within the accuracies of the experimental measurements and the calculations used in this work, the different deviations in Xe and Kr between the calculated and the observed frequency shifts at higher temperatures could be explained using the model proposed above.

The above discussion on hcp trapping site also implies that for $p \leftarrow s$ transitions the larger the trapped metal p-orbitals involved in the transition, the larger the observed frequency difference between transitions to p_x and p_y , and the smaller the difference between transitions to p_x and p_z orbitals. Let the observed triplets of those metals be denoted as ν_1, ν_2, ν_3 in increasing frequency order, and corresponded to the transitions involving p_y, p_x and p_z orbitals, respectively, referring to Fig. 34. If $\Delta_{1,2}$ is for the difference in frequency between ν_1 and ν_2 etc., this model predicts that for a large trapped atom, or atoms with

large increase of orbital size in the transition, $\Delta_{1,2} > \Delta_{2,3}$; and this difference decreases from Ar to Kr to Xe. The experimental observations from various literatures are shown in Table 23.

The observed changes in $\Delta_{1,2}$ and $\Delta_{2,3}$ except for K and Ca, follow exactly as was predicted using the above model. These facts therefore support the possibility of having hcp structure in the matrices. X-ray works about the matrix structures are therefore very urgent in confirming this proposal.

One theory remaining to be considered is the Stark splitting in determining the multiplet structures observed. This is discussed in the next section.

E. Stark Effect - Its Possible Role in Causing the Multiplet Structure of the Trapped Atoms in the Matrices

As was mentioned before, the Stark splitting of the transition lines of the trapped metal by the matrix environment is a very promising possibility. This is based mainly on the following facts:

1. For most metals with $p \leftarrow s$ transitions, Stark splitting does lead to three lines, in agreement with the experiment. There are exceptions, however. Ca and Mg, with $^1P_1 \leftarrow ^1S_0$ transition would give only two lines with a Stark effect while a triplet is observed in both cases in the matrices.⁴ When the matrix is warmed up, both triplets have their highest frequency components shifted to the blue and the lower frequency components to the red. The shifts are reversible on cooling back.

2. For metals like Au and Ag with large splitting in the upper state $^2P_{3/2}$ and $^2P_{1/2}$ in the gas phase (3815 cm^{-1} in Au and 921 cm^{-1} in Ag), the observed spectra in the matrices have two of the triplet

TABLE 23

Metal [†]	Observed differences between $\Delta_{1,2}$ and $\Delta_{2,3}$	dependence of $(\Delta_{1,2} - \Delta_{2,3})$ on matrix gas
Li, Na, K*, Rb	$\Delta_{1,2} < \Delta_{2,3}$	not reported
Cs	$\Delta_{1,2} > \Delta_{2,3}$	in Ar > in Kr > in Xe
Au	$\Delta_{1,2} > \Delta_{2,3}$	in Kr > in Xe
Ag	$\Delta_{1,2} > \Delta_{2,3}$	in Ar > in Kr > in Xe
Cu	$\Delta_{1,2} < \Delta_{2,3}$ in Xe	
but	$\Delta_{1,2} \sim \Delta_{2,3}$ in Kr	
Mg [‡]	$\Delta_{1,2} > \Delta_{2,3}$	in Kr > in Xe

[†] Metals in the same series should be compared to eliminate complexities other than the orbital size change and interactions involved.

* K does not follow this trend too well

[‡] Ca shows just the opposite with $\Delta_{1,2} < \Delta_{2,3}$ in Kr and $\Delta_{1,2} > \Delta_{2,3}$ in Xe

components close in frequency to that of gas phase $^2P_{3/2} \leftarrow ^2S_{1/2}$ and one to that of $^2P_{1/2} \leftarrow ^2S_{1/2}$ transitions.

Other than the exceptions of Ca and Mg, the idea seems to be prominent in being able to account for the multiplet structure and the splittings in many cases. Therefore, it is helpful to study this possibility in more detail. This is done by considering the following questions:

1. Is the electric field created by the matrix environment large enough to cause the usual splittings of the order of 200 cm^{-1} ?
2. Using Stark splitting idea, how does the assignment of the components check with the calculations similar to that used for Pb discussion?
3. Does Stark splitting predict the correct sign of the warm up shift of the multiplet components?

These are discussed below.

1. Magnitude of the Electric Field Created by the Matrix Environment

Before estimating the magnitude of the electric field created by the matrix environment it is helpful first to review briefly the important aspects of the Stark effect theory.⁴⁹

When an electric field E is applied to an atom with an electric moment $\vec{P}_0$ the Hamiltonian for the atom in the applied field is

$$H = H_0 - \vec{E} \cdot \vec{P}$$

where H_0 is the unperturbed Hamiltonian. Therefore, the alteration of energy levels and proper states is governed by the matrix components of $\vec{P}$. Since the only component of $\vec{P}$ that is effective is that along $\vec{E}$, the axis can be chosen such that it is z-component. P_z is the same quantity that governs that part of the dipole radiation of atoms which is polarized with its electric vector parallel to the z-axis. If the matrix component

of P_z which connects two unperturbed energy states A and B is written as $\langle A|P|B\rangle$, the selection rules for $\langle A|P|B\rangle$ not to vanish are:

1. A and B are of odd parity.
 2. $J_B = J_A$ or $J_A \pm 1$, where J_B and J_A are the resultant angular momentum quantum numbers of B and A, respectively.
 3. $M_{JA} = M_{JB}$, where M_{JA} and M_{JB} are the z-components of resultant angular momentum of the atom in the two states measured in $h/2\pi$ units.
- These three rules are rigorous. In addition,
4. Configuration A may differ from configuration B at most by one unit of electronic n and l values.

In an electric field the shift of an energy state due to the coupling with another state allowed by the above selection rules is

$$\frac{|\langle A|EP|B\rangle|^2}{|W_A - W_B|} \quad (1)$$

from the second-order perturbation theory. Here, W_A and W_B are the unperturbed energies of states A and B, respectively. The matrix $|\langle A|EP|B\rangle|$ has the value of the order 6.4^2 cm^{-1} for a field of 10^5 volt/cm, n being the principal quantum number. The calculated energy shifts for the individual atoms in various strengths of the electric field showed good agreement with experiment.⁵⁰ This supports the theory described above in treating the energy shift of an atom in an electric field. Because of the selection rules different sublevels of an energy states usually are perturbed to different extents by the neighboring energy levels. The differences in the energy shift among the sublevels then give the splitting energies observed.

In Eq. (1) the energy shift is proportional to second power of the electric field magnitude and inversely proportional to the energy difference between the two states A and B. For atoms other than hydrogen, the energy levels are usually widely separated and the splitting energy is expected to be small when compared to that of hydrogen atom in the field of same strength. In Pb the nearest state which can perturb $6p^2\ ^3P_0$ is $6p7s\ ^3P_0$ separated by about $35,000\text{ cm}^{-1}$. Therefore, the field created by the matrix must be large enough to compensate for this huge difference in energy.

Take Pb for example, it is reasonable to estimate, from the previous calculations on Pb absorption spectra, the interaction energy of Pb and Xe at the normal separation in a matrix to be about $10^3\text{ cm}^{-1}/3.90\text{\AA}$. This is of the order of 10^6 volt/cm . Using this estimated field magnitude and Eq. (1), the expected shift in energy is calculated to be about 150 cm^{-1} for an energy difference $35,000\text{ cm}^{-1}$ between the two states.

If the trapped metal atom is at a substitutional site, with no distortion the symmetric environment cannot cause any splitting of the above type, because no unilateral field exists. However, an asymmetric field can be introduced by the matrix as soon as the trapped metal is distorted nonuniformly. As was discussed in the last section, a matrix of fcc structure with metal penetration can create an asymmetric field along the $[111]$ axis. Also, the hcp structure with penetration creates an asymmetric field. Such field is expected to approximate that for a single Pb-Xe pair interaction in its order of magnitude. For metals like Au, the interaction with Xe and Kr could be larger than those for Pb as will be shown later. A splitting of several hundred cm^{-1} from $^2P_{3/2}$ state is therefore quite

possible to be accounted for by the field created in this matrix.

In most cases, in addition to the splittings observed all the triplet components of the trapped metals shift from the gas phase absorption frequencies. This can be explained on the basis of calculations for Pb frequencies. There, the shift is mainly due to the difference in the interactions of the ground and excited states Pb with the surrounding matrix atoms. Such shift still exists even for Pb in a perfect substitutional site. Further splitting of the sublevels of metals with $p \leftarrow s$ transition comes in only when there is a net asymmetric field in the matrix, caused by distortion, for example. In this way, one can explain the observed shift and splitting of the multiplet components in the matrices. Because the estimated field is large enough to cause this further splitting to match the observed values, the discussion so far is in favor of Stark splitting as a possible cause for the multiplet structures of the trapped metal atoms.

2. Investigation by Calculations to Correlate the Observed Multiplet Frequencies

As was mentioned before, Au has very large energy separation between its $6p\ ^2P_{3/2}$ and $6p\ ^2P_{1/2}$ states. In Xe and Kr matrices two of the triplet components of Au lie close to the gas phase $^2P_{3/2}$ level while the third one close to the $^2P_{1/2}$ level. All the other metals which can give triplet under Stark effect consideration have their $^2P_{1/2}$ and $^2P_{3/2}$ levels much less separated in gas phase and so are the separations among the triplet components in the matrices. Au therefore represents an extreme case in concerning the role of the Stark effect in the multiplet structures. It is for this reason Au is treated in more detail in the following calculations to try to generalize to the other cases.

The data needed for Au is summarized in Table 24.⁸ The same assignment of the observed lines is adopted here to compare with the predicted assignment from calculations.

Calculations like that for Pb can also be done for the Au spectral lines by first finding the $\epsilon_{\text{Au(A)}-\text{Au(A)}}$ from empirical values in Xe and then applying it to the Au in Kr. It is emphasized that in using the L-J 6-12 potential the only two parameters important in determining the interactions are ϵ and σ . Here assumption is made that the only difference between $^2P_{1/2}$ and $^2P_{3/2}$ states in their interactions with the matrix atoms is in ϵ . This is not unreasonable because both states have the same principal quantum number, and orbital sizes, the only difference is in their couplings between orbital and spin angular momenta. The difference in this L-S coupling is assumed to have its effect mainly on the well depth and width of the interaction potential curve; and the σ values of the two curves are expected to be approximately the same. Bearing this in mind, and using the atomic radius for Au ground state from Slater's book²⁶ and estimating the excited state Au atomic radius in the same way as for Pb, the parameters needed for the calculations are

in Xe A state $r_0 = 2.23 + 2.10 = 4.33\text{\AA}$

$$\epsilon_{\text{Au(A)}-\text{Xe}} \text{ unknown}$$

$$\text{X state } r_0 = 2.23 + 1.35 = 3.58\text{\AA}$$

$$\begin{aligned} \epsilon_{\text{Xe-Au(x)}} &= (158.5 \times 17991)^{1/2} \\ &= 1689 \text{ cm}^{-1} \end{aligned}$$

in Kr

$$\text{A state } r_0 = 2.02 + 2.10 = 4.12\text{\AA}$$

$$\epsilon_{\text{Au(A)}-\text{Kr}} \text{ unknown}$$

TABLE 24. Absorption spectra of gold in the matrices by King

Matrix	$\nu(\text{cm}^{-1})$	Assignment	Gas Phase Frequency cm^{-1}	$\nu-\nu_0(\text{cm}^{-1})$
Xe	36860	$^2P_{1/2} \leftarrow ^2S_{1/2}$	(37359)	-499
	40355	$^2P_{3/2} \leftarrow ^2S_{1/2}$	(41174)	-819
	40969			-205
Kr	38300	$^2P_{1/2} \leftarrow ^2S_{1/2}$	(37359)	+941
	42499	$^2P_{3/2} \leftarrow ^2S_{1/2}$	(41174)	+1325
	43011			+1837

$$X \text{ state } r_0 = 2.02 + 1.35 = 3.37 \text{ \AA}$$

$$\epsilon_{\text{Kr-Au}(x)} = (110.5 \times 17991)^{1/2} = 1410 \text{ cm}^{-1}$$

The ϵ values for Au ground state is taken from Ref. 51. Using the Au 36860 cm^{-1} line and the value for $\nu - \nu_0$ the calculated $\epsilon_{\text{Au(A)}-\text{Au(A)}} = 5110 \text{ cm}^{-1}$. This leads to a calculated frequency shift for Au/Kr of -560 cm^{-1} i.e. a red shift, compared with the observed blue shift of 941 cm^{-1} .

The agreement is rather poor which can probably be attributed to:

1. The uncertainties in estimating the Au excited state atomic radius.
2. The deviation of the actual trapping site configuration from a perfect substitutional one. For Pb, it is found that a decrease of r of 0.1 \AA in Kr from the normal r_0 value at 20°K led to an increase of about 1000 cm^{-1} .
3. Failure of the L-J potential calculations in dealing with excited states involving p orbitals.

However, it is interesting to see how the calculated values compared with the experimental ones.

The same calculation for the Au/Xe 40355 cm^{-1} line and the value of -819 cm^{-1} for the $\nu - \nu_0$ leads to about 5270 cm^{-1} for the $\epsilon_{\text{Au(A)}-\text{Au(A)}}$ and a predicted shift in Kr of -760 cm^{-1} , compared to the observed $+1325 \text{ cm}^{-1}$.

The agreement is even worse than the first line of Au. Since the same errors, if any, in using L-J potentials in the Au work are involved in both calculations, the results imply that either the idea is wrong to treat the interactions between the $^2P_{3/2}$ and $^2P_{1/2}$ states with the matrix atoms in the same way, or the assignment of the $\Delta\nu$'s is wrong, i.e. the

Au/Xe 40355 cm^{-1} line does not originate from $^2P_{3/2} \leftarrow ^2S_{1/2}$ transition. Between these two alternatives the latter seems more probably to be the case. This is justified by the approximate validity of the idea in treating the $^2P_{3/2}$ and $^2P_{1/2}$ states the same way, and that when all three lines are attributed to originating from the same $^2P_{1/2} \leftarrow ^2S_{1/2}$ transition the calculated frequency shifts in Kr are in better qualitative agreement with experiment under this new assignment.

Next, the same calculation for Pb in finding ν_{gas}° is applied to all the multiplet components of Au, Ag, Cu and some alkali metals where reliable experimental data can be found in the literature.^{8,52} The absorption frequencies in Xe and Kr matrices are used here, and the calculated results are shown in Table 25.

All the calculated ν_{gas}° values are lower than the experimental ones. The validity of this calculation therefore needs to be discussed to some length before one considers the significance shown by these calculated results.

The validity of this calculation was checked before for the Pb $^3P_1 \leftarrow ^3P_0$ transition band and the agreement with experiment was found to be satisfactory. The different behavior of all the metals included in the above calculations is attributed to the directional sensitivity of the excited p orbitals involved when there is an accompanying large increase in orbital size during the electronic excitation. The individual p orbital interacts with strong orientational dependence and cannot be treated as point or sphere charges. The use of the L-J 6-12 potential is therefore no longer justified as for a spherical electronic distribution. The excited state of Pb, $6p7s^3P_1$, however is almost spherical symmetric and can be treated well with L-J 6-12 potential.

TABLE 25. Calculated ν_{gas} values of the various metals

Metal	$\nu(\text{M/Xe}) \text{ cm}^{-1}$	$\nu(\text{M/Kr}) \text{ cm}^{-1}$	$\nu_{\text{calc.}}^{\text{gas}} \text{ cm}^{-1}$	$\nu_{\text{expt}}^{\text{gas}} \text{ cm}^{-1}$
Au	36860	38300	30832	37359 ($^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$)
	(3495)	(4199)	(501)	(3815)
	40355	42499	31333	
	(615)	(512)	(1067)	41174 ($^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$)
	40969	43011	32400	
Ag	29886	30989	25313	29552 ($^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$)
	(667)	(899)	(-313)	(921)
	30553	31888	25003	
	(445)	(433)	(493)	30473 ($^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$)
	30998	32321	25496	
Cu	30647	31766	26002	30535 ($^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$)
	(246)	(378)	(-309)	(248)
	30893	32144	25693	
	(347)	(376)	(224)	30783 ($^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$)
	31240	32520	25917	
K	12424	12623	11741	12989 ($^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$)
	(263)	(315)	(43)	(58)
	12687	12938	11784	
	(265)	(277)	(214)	13047 ($^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$)
	12952	13215	11998	
Cs	10807	11036	10008	11181 ($^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$)
	(433)	(497)	(162)	
	11240	11533	10170	(555)
	(403)	(403)	(277)	
	11643	11936	10347	11736 ($^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$)

* The numbers in the parenthesis are the differences between the two consecutive values.

To support this, matrix work by Duley on Bi atoms is tested here. Duley¹⁸ trapped Bi in Xe, Kr and Ar. One strong absorption line is observed at 35971 cm^{-1} , 36363 cm^{-1} and 38610 cm^{-1} in Xe, Kr and Ar, respectively. They are assigned to $6p^2 7s\ ^4S_{1/2} \leftarrow 6p^3\ ^4S_{3/2}$ transition which is at 32605 cm^{-1} in the gas phase. Here the excited state is also spherical symmetric like, similar to the Pb $6p7s$ state. Using the values in Xe and Kr for Bi the calculated ν_{gas}° is 34330 cm^{-1} . This is an upper limit because of the assumption that at 10A separation the interaction between Bi and a matrix gas atom becomes negligibly small as is the case of Pb. For Bi, the frequency shift is 3366 cm^{-1} and 3758 cm^{-1} in Xe and Kr respectively which are larger than those for Pb, and 10A separation may not be far enough to eliminate the interaction between Bi and Xe or Kr. When 20A is used, which should be more than enough, ν_{gas}° is found to be 32600 cm^{-1} . This agrees very well with the gas phase value for the assigned transition. The large red shift on warm up for the above absorption line of Bi led Duley to the above assignment. The good agreement between calculated and experimental ν_{gas}° values further supports the correctness of this method for the atoms involving spherically symmetric excited states.

Although the method of locating ν_{gas}° works well for Pb and Bi, it does not work at all for the metals with $p \leftarrow s$ transition. This might served as an example that one should be cautious in using the calculated values when an excited p electron is involved in the L-J type calculations.

Therefore no conclusion can be drawn from this part of the Stark splitting analysis due to the uncertainties in the calculations involving excited p electrons.

3. The Predicted Warm-Up Frequency Shift of the Multiplet Components by the Stark Effect

As was emphasized before, both the static and dynamic matrix effects should be considered in explaining the multiplet structures observed. In this part the predicted warm up shift by Stark effect is investigated.

With the Stark effect, the $^2P_{3/2}$ state of Au, Ag and Cu and alkali metals are splitted into two substates with $M_J = \pm 3/2$ and $\pm 1/2$, respectively. According to the theory both substates are shifted to the same direction with increasing strength of the electric field. Since the local field strength on a trapped atom changes on warm up the matrix this implies that the transitions to these two states should shift to the same direction with increasing matrix temperatures. Another effect in the absorption frequencies upon warming the matrix is the decreasing interaction between the metal and the matrix atoms. The sum of these two effects again would in most cases predict that the two components of the $^2P_{3/2}$ state shift to the same direction. This is in clear contradiction with experiment.

Next with a Stark effect the $^2P_{1/2}$ state gives only one component with $M_J = \pm 1/2$. This state should behave very similarly to the $M_J = \pm 1/2$ component from the $^2P_{3/2}$ state. The latter should be lower in energy than the component with $M_J = \pm 3/2$ because, taking Au for example, the perturbations from the higher levels are larger than that from the lower levels due to the closer spacing in energies in the former. All the higher states having substates with $J = 3/2$ also have $J = 1/2$ substates, but the reverse is not necessarily true. This means every state which perturbs $M_J = \pm 3/2$ level also perturbs $M_J = \pm 1/2$ but not the reverse way. The $M_J = \pm 1/2$ level is therefore pushed down more than the $M_J = \pm 3/2$ level. From Eq. (1) one notices that as $\Delta E (^2P_{1/2} \rightarrow ^2P_{3/2})$ approaches zero,

so is the difference in energy between the two levels with $M_J = \pm 1/2$. Again the triplet components are labelled as ν_1, ν_2, ν_3 , in increasing energy order, and correspond to the components $^2P_{1/2}(M_J = \pm 1/2)$, $^2P_{3/2}(M_J = \pm 1/2)$ and $^2P_{3/2}(M_J = \pm 3/2)$, respectively. When ΔE ($^2P_{1/2} \rightarrow ^2P_{3/2}$) is not too large, $(\nu_2 - \nu_1)$ should approach ΔE , and should be quite independent of the field change from Xe to Kr. The latter should be a more reliable criterion because the former depends on the relative importance of ΔE to $(W_A - W_B)$ in the calculations using Eq. (1). However, after taking this correction into account the criterion that $(\nu_2 - \nu_1)$ be temperature independent should be more rigorous.

From Table 24 one notices that this is not what is observed. The change for $(\nu_2 - \nu_1)$ in going from Xe to Kr matrices is rather large for the metals, being 700 cm^{-1} in Au, 230 cm^{-1} in Ag and 130 cm^{-1} in Cu. Furthermore, it is interesting to notice the rather small change in $(\nu_3 - \nu_2)$ which is 98 cm^{-1} , 12 cm^{-1} , and 30 cm^{-1} in Au, Ag, Cu, respectively. The small $(\nu_3 - \nu_2)$ change between Xe and Kr matrices is again in contrast to what is predicted from the Stark theory. The field is expected to change quite significantly from Xe to Kr, this would cause large changes in the splitting energy for the $\pm 3/2$ and $\pm 1/2$ substates from the same $^2P_{3/2}$ state.

Summarizing the discussions in this section, the Stark splitting accounts well for the very large splitting energies observed for Au in Xe and Kr matrices, but has difficulties in predicting some other behaviors of the triplet components at increasing matrix temperature. On the other hand the model suggested in the earlier sections could also be used to explain the large splitting in Au which is an extreme case. The work on Pb showed that large energy shifts can be expected. If the predicted hcp

structure. is proved to be true, the larger orbital expansion of Au during the excitation will give a large distortion on the p_x orbital which could approximate in energy to that of P_z , the latter suffers large distortion from the inner layer matrix atoms due to the metal penetration. However, this must be proved by reliable calculations. The L-J 6-12 equation is not suitable for interactions involving strong overlap with the p orbitals. Quantum mechanical calculations are needed to properly take into consideration the orientation effect and the correct trapping site geometry. The main point here is that at least qualitatively the large splitting in Au can be expected, in addition to the successful interpretation of many other experimental facts using the model proposed in this thesis.

V. REACTION BETWEEN CESIUM AND SF_6 IN LIQUID NH_3

See appendix A.

VI. CONCLUSIONS

Pb has been trapped in various matrices to study the matrix effects on the absorption spectra of both Pb and Pb_2 . The observation of discrete Pb_2 spectra is used to study the dimerization mechanism of Pb on the target during the deposition. The matrix effects are studied in detail to find a suitable model for the observed facts. The conclusions from this work are shown below.

1. It is observed that surface diffusion on the target is controllable to certain extent by varying the experimental conditions. Two factors which help to decrease such diffusion are the use of a radiation shield in front of the furnace, and prior deposit of matrix gas before depositing the metal-matrix gas mixture.

2. Ag is codeposited with Pb in the Kr matrix to study (a) surface diffusion, (b) metal-metal interaction, and (c) possible origin of the broad band which is assigned to the Pb_2 $E \leftarrow X$ absorption. The results show that (a) Surface diffusion does occur under some experimental conditions. The use of high Ag concentrations provides direct experimental demonstration of surface diffusion by the interference with Pb_2 formation. (b) The metal-metal interaction is observable when the Ag concentration is high enough. This is based on the observed significant broadening of the Pb $^3P_1 \leftarrow ^3P_0$ band in such matrices. However, the center frequencies of both Pb and Ag absorption bands are not affected by varying the Ag concentration used. These facts indicate that the Pb-Ag interaction differs enough from that of Pb-Pb to cause the observable broadening effect, but not enough to give any new features other than broadening the Pb $^3P_1 \leftarrow ^3P_0$ band.

(c) The absence of both the broad band, assigned to the $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ transition, and the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ bands when Ag concentration is high in the Kr matrices supports the molecular origin of the broad band which is assigned to the $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ absorption spectrum.

3. The observed frequencies of the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band in Xe, Kr and Ar matrices are correlated with model calculations. The calculated frequency shifts in Ar are always too low compared to the observed value. The observed frequency shifts of the $\text{Pb } ^3\text{P}_1 \leftarrow ^3\text{P}_0$ band in Xe and Kr matrices at higher temperatures are also compared with the calculated values. The values of $(\Delta\nu_{\text{calc}} - \Delta\nu_{\text{obs}})$ are all positive in Xe matrix, but negative at higher temperatures in Kr matrix. This as well as the deviation observed in Ar matrix are then explained by the model proposed in this thesis.

4. A method is demonstrated to relate the gas phase transition frequency to the observed frequencies in Xe and Kr matrices. The purpose is two fold: (a) to predict the frequency shift in Kr when the frequency shift is known in Xe, and (b) to predict the gas phase ν_0 using the band frequencies observed in Xe and Kr matrices. The latter is especially valuable in identifying the absorbing species in the gas by locating its resonance transition in the gas phase spectrum using the data in the matrices.

The results of this work show that both purposes can be accomplished for the metal atoms with $s \leftarrow p$ resonance transitions, but not so for the metal atoms with $p \leftarrow s$ resonance transition. This is explained as due to the validity of using the Lennard-Jones potential calculation in the former case but not so in the latter. The work indicates that if one observes a single, strong absorption band in the Xe and Kr matrices, which shifts to

lower frequencies on warming the matrix, one may approximate with some confidence the gas phase ν_0 of this transition using the method shown in this work. On the other hand, when multiplet bands are observed, one should be cautious in doing so, and should keep in mind that the calculated gas phase ν_0 is lower than the true ν_0^{gas} . It is hoped, however that this calculated value can sometimes be used as the lower limit of the real ν_0^{gas} and offers some helpful information one needs.

5. The earlier theories on the observed matrix effects on various metal atoms have been compared and discussed. It is found that none of them accounts for the observed temperature dependencies of the absorption frequencies of the multiplet components. A model is proposed to try to account for both the static and dynamic matrix effects for those metal atomic spectra. The proposed model is based on an assumed hcp structure of the trapping site in the matrices which is based on various indirect experimental observations. Direct structure determination is needed to confirm this assumption. However, the analysis in this thesis clearly indicates that the trapping site geometry must be playing a central role in the observed static and dynamic matrix effects on the trapped atomic spectra in the matrices.

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APPENDIX A

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CONTRIBUTION FROM THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY
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Sulfur Hexafluoride. Its Reaction with Ammoniated Electrons and Its Use as a Matrix for Isolated Gold, Silver, and Copper Atoms

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The reactivity of SF_6 with reactive metals was studied to explore the use of SF_6 as a matrix material for low-temperature isolation of metallic atoms. At 212°K SF_6 rapidly decolorized the blue liquid ammonia solutions of alkali metals to produce white precipitates of alkali fluorides and sulfides. The codeposition of Au vapor with SF_6 at 20°K gave well-isolated matrices with very sharp atomic spectra comparable to those obtained with inert-gas matrices, but Cu and Ag spectra in SF_6 were very broad. *n*-Perfluoroheptane was also examined as a matrix material, but Ag and Au gave very complex spectra.

Introduction

The rare gases, which have been widely used¹ for matrix isolation of reactive species, are restricted to very low temperatures because of their low melting points. SF_6 with a melting point of 218°K is an attractive non-polar molecule for matrix studies that could be extended

to above liquid nitrogen temperatures. It is known to be chemically inert toward aqueous or fused alkali, ammonia, and oxygen and does not react appreciably with sodium metal² below 200° or with CF_3 or CH_3 radicals³ up to 365° . The high electron affinity⁴ and

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