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Matrix Isolation of Pb and Pb₂

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ABSTRACT

Lead vapor trapped at 20°K in Ar, Kr, Xe, SF₆ and in mixtures of these matrix gases showed an atomic absorption line with no multiplet structure and molecular bands of Pb₂. Warming the matrices above 20°K shifted the atomic line reversibly to the red while the molecular features did not shift. Bulk diffusion of isolated Pb atoms to produce Pb₂ did not take place in Xe even after 2 hr. at 50°K. However, surface diffusion of Pb atoms to form Pb₂ can take place during the condensation process on a 20°K window under conditions of high heat load or poor thermal contact that cause high surface temperature.

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I. INTRODUCTION

It is well known that when metal atoms are trapped in inert gas matrices at low temperatures, new features appear in the spectra of the trapped species.¹ The absorption frequencies usually shift, either to the red or to the blue of the gaseous transitions; multiplet structures appear when transitions involving degenerate states are observed, and the lines are broadened in the matrices. In addition, upon warming the matrix, the components of the multiplets show different directions of shift. For most atoms involving $p \leftarrow s$ transitions, a triplet is observed with the highest frequency component of the triplet shifting reversibly to the blue, while the two lower frequency components reversibly shift to the red upon warming the matrix. Examples are Li,² Na,³ Ag,⁴ Ca,⁵ Cd,⁵ and Mg.⁵ Several groups of workers,^{4,6-10} have tried to interpret these matrix effects. Their results will be discussed in a second paper along with a proposed model to explain these effects. In this paper we report the experimental study of Pb and Pb₂ spectra in low temperature matrices.

Pb was chosen because it has a $6p^2 \ ^3P_0$ ground state configuration. The $6p^2 \ ^3P_1$ sublevel is excited by 7819 cm^{-1} and has a negligible population. The resonance transition is $6p7s \ ^3P_1 \leftarrow 6p^2 \ ^3P_0$. Since the $s \leftarrow p$ transition is the opposite of the transitions of most metal atoms studied in the past, it was hoped that Pb might offer some new insight into the effect of the matrix upon the spectra of trapped species. In addition, Pb offers the opportunity to study the formation of polymers and the diffusion mechanism of metal atoms in low temperature matrices.

Although light atoms such as Li are observed² to diffuse through the solid rare gas matrix at temperatures lower than 50°K, heavier atoms such as Mg, Ca, Pb, etc., do not diffuse through the matrix after deposition has been completed.⁵ For example, Mg can be cycled reversibly up to 65°K in Xe without polymerization of the trapped atoms.⁵ Similar results were observed for Pb in the present work. However, generally the degree of isolation of atoms and the extent of formation of polymers has not been reproducible between laboratories indicating that formation of polymers takes place during the condensation process under conditions of poor thermal contact or of relatively fast deposition. These conditions apparently provide a high enough surface temperature and mobility to allow polymerization of the atoms before they are frozen into the matrix. Pb offers an excellent opportunity to verify this mechanism of polymerization during the condensation process since beams of lead vapor can be produced from Knudsen cells at relatively low temperatures with negligible Pb₂. At higher temperatures Pb₂ molecules are present in substantial amounts; for example, at 1100°K, the partial pressures of Pb and Pb₂ are 10⁻¹ and 2x10⁻⁵ torr, respectively. The absorption and emission spectra of gaseous Pb₂ were studied by Shawhan,¹¹ and the absorption spectra by Weniger¹² in more detail. Duley¹³ studied briefly the absorption spectra of Pb in Xe, Kr, and Ar matrices at 4°K, and Wang⁵ briefly studied Pb spectra in Xe and Kr matrices at 20°K.

II. EXPERIMENTAL

The atomic or molecular beams of the metal under study were generated by heating the metal in Knudsen cells using resistance-heating, electron-bombardment-heating, and radiation-heating. The first two were described earlier,^{4,9} while in the last furnace a stainless steel Knudsen cell was mainly used to generate beams at 600-800°C. The temperature of the cell was measured with a Chromel Alumel thermocouple (Type K) which was spark-welded on the stainless steel cell. The output was coupled to a Simplyrometer (API Instrument Co.).

Both a metal cryostat and cryo-tip were used in this work. The cryostat using liquid hydrogen as refrigerant was described earlier.⁹ The cryo-tip was model AC-21-110 built by Air Products and Chemicals, Inc. It had the advantage that target temperature could be controlled closely by monitoring the hydrogen gas pressure.

A sapphire target was used in most of the experiments while a cesium iodide target was used in the IR spectral studies. The temperature of the target was measured using a high thermoelectric power thermocouple made of copper versus alloy of gold-2.1 at.% cobalt. The junction of the thermocouple was clamped between the target and indium gasket and the output was coupled to a recorder.

Research grade rare gases (> 99.99%) and SF₆ gas (99.99%) were used without further purification. The gas mixtures of rare gases, and of rare gas and SF₆ were prepared by mixing the gases and allowing to stand for at least 48 hours before use. All compositions are given

in at. %. The metals used in this work included Pb (99.999⁺% purity), Ag (99.95% purity) and Ca (99.9% purity).

Spectra were photographed in the region 2200-9000 Å using a Jarrell-Ash f/6.3 spectrograph with a grating blazed at 3000 Å giving a first order dispersion of 5Å/mm, and another grating blazed at 7500 Å giving a dispersion of 20Å/mm in the first order.

III. RESULTS

A. General

The longest wavelength resonance transition of gaseous atomic Pb is at 2883 Å ($35\,287\text{ cm}^{-1}$). The Pb₂ molecule has an A ← X transition in the 5000 Å region, and an E ← X transition in the 2500 Å region. At high M/R ratios (low metal concentration) a single strong absorption line in the region 2400-2700 Å appeared in all the pure and mixed rare gas matrices except in Xe where an additional strong line appeared at shorter wavelength. The frequency of the strong, single line common to these matrices increased in the order Xe < Kr < Ar. It shifted to lower frequencies on warming the matrices. The shift was reversible in all cases. This line was assigned to the Pb 6p7s ³P₁ ← 6p² ³P₀ transition in agreement with Duley¹³ and Wang.⁵ At lower M/R ratios, additional weak bands were observed. A broad band with blue-shaded structure was observed in the region 2330-2550 Å in all rare gas matrices, with the same increasing order of frequencies as the above mentioned strong line. It showed no shift on warming. Furthermore, this band was observed

to appear most easily in Ar, less in Kr and least in Xe matrices. As discussed below, this band is assigned to the $\text{Pb}_2 \text{E} \leftarrow \text{X}$ transition.

At higher furnace temperatures, molecular spectra were observed in all the matrices in the 5000 Å region. Again the ease of appearance of these bands increased from Xe to Kr to Ar. The bands showed no frequency shift on warming and disappeared upon warming at about the same temperatures as the Pb single lines in the 2400-2700 Å region. These bands are assigned to the $\text{Pb}_2 \text{A} \leftarrow \text{X}$ transition.

In all rare gas matrices it was observed that varying the M/R ratio by a factor of 100 had no effect on the frequencies of the Pb line spectrum in the 2400-2700 Å region. In the cases of Xe and Kr, which were studied most extensively, the molecular spectra could be intensified by removing the radiation shield in front of the furnace that minimized heat load on the target. A prior deposit of matrix gas before deposition of the metal-matrix gas mixture to provide better thermal contact offset the enhancement of molecular spectra.

B. Xenon

The absorption spectrum of Pb in Xe deposited at 20°K consisted of two strong lines, two very weak lines and a weak, broad band situated at 2648, 2259, 2809, 2402, and 2552 Å, respectively. The spectrum recorded on a photographic plate is shown in Fig. 1. The frequencies and half-widths of these lines are shown in Table I. Only the strong line at 2648 Å, which is assigned to the $\text{Pb } 6p7s \text{ } ^3\text{P}_1 \leftarrow 6p^2 \text{ } ^3\text{P}_0$ transition, showed temperature dependence of its frequency. It

shifted to lower frequencies on warming the matrix. The shift was reversible on cooling back to 20°K. The warm-up spectrum of this line is shown in Fig. 2 and the line frequencies at various temperatures shown in Table II. The spectrum persisted until about 82°K.

The broad band at 2552 Å had a half-width of about 900-1000 cm^{-1} and a blue-shaded structure both of which increased rapidly when higher Pb evaporation temperatures were used. Fig. 3 shows two such spectra for comparison. This band, which is assigned to the $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ transition, will be discussed in detail later.

As the Pb evaporation temperature was increased, a molecular band spectrum was observed around the 5000 Å region along with a weak line at 6268 Å. The spectrum of this band system, which is assigned to the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ transition, is shown in Fig. 4. The band wavelengths are tabulated in Table III along with the half-widths 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. The Pb_2 spectrum showed no shift while the 6268 Å line shifted to the red on warming the matrix. Both spectra disappeared around 82°K.

Because the strong 2648 Å line of Pb was easiest to observe, it was used to study the effects of varying the matrix deposition conditions on the Pb spectrum in this matrix. This was done in three ways:

1. The amount of Pb coming out from the furnace per unit time was kept constant and Xe gas was varied from $M/R = 30$ to 4500.

2. Pb evaporation temperature was kept constant while varying the Knudsen cell orifice size. The amount of Pb coming out per unit time was thus increased by a factor of 6.25.
3. Pb vapor pressure in the Knudsen cell was varied by a factor of 200 while keeping M/R constant, i.e., to vary the deposition rate of the whole matrix.

In all three cases no effect was seen on the Pb 2648 Å line.

The matrix work of Pb in Xe revealed some information about the Pb₂ formation on the target during the film deposition. It was noticed that when the amount of Pb coming out the furnace per unit time was kept about the same, the use of a radiation shield in front of the Knudsen cell helped to decrease significantly the amount of Pb₂ in the matrix film as shown from the absorption spectrum intensities. Also, prior deposit of Xe gas to that of the Pb/Xe mixture helped to decrease the Pb₂ in the matrix film.

The possibility of forming Pb₂ by diffusion of atoms on warming up the matrix was also tested. A Xe film which showed only discrete Pb atomic spectrum was warmed up and the 5000 Å region traced. However, no Pb₂ spectrum was observed up to and above the temperature at which the Pb atomic spectrum disappeared. This could be due to several factors: (1) Pb atoms were too heavy to diffuse, unlike light atoms like Li, which formed dimers on warming from the matrix;¹ (2) Pb interacted strongly with Xe atoms which could keep the Pb atoms from diffusing; (3) The time span involved on warming the matrix might not be long enough to observe the diffusion taking place.

To test the third possibility cited above, a matrix film which showed both Pb and Pb₂ spectra was warmed to 50°K and kept for 2 hr. The only effect seen, however, was that the film became a little foggy, which caused the region below 2800 Å to be opaque and also made the comparison of the Pb₂ absorption intensities difficult. This could be due to a higher evaporation rate of Xe gas from the matrix film at 50°K which would leave a surface layer of lead particles. The nonuniform absorption could then cause the fog problem.

C. Krypton

The spectrum of Pb in Kr deposited at 20°K consisted of one strong line, two very weak lines and one broad band, at 2614, 2783, 2360, and 2440 Å, respectively. These are shown in Fig. 5 and Table IV. The strong line at 2614 Å shifted reversibly to the red on warming the matrix. The line frequencies at various temperatures are shown in Table V. The broad band at 2440 Å was very similar to the Pb₂ E ← X broad band observed in Xe matrix in its half-width and blue-shaded structure. However, it appeared more easily and stronger in the Kr matrix under similar experimental conditions.

The Pb₂ A ← X molecular spectrum was also observed in Kr at higher Pb evaporation temperatures, along with a single line at 6126 Å. These are shown in Fig. 6 and Table VI. The molecular spectrum in this matrix persisted to about 65°K, while the region below 3000 Å became opaque above 50°K.

The matrix deposit conditions were changed in the ways similar to those used in Xe work to study their effects on the absorption frequencies of both Pb and Pb₂. Again no effect was observed in all cases.

D. Argon

The absorption spectrum of Pb in Ar deposited at 20°K consisted of one medium intensity line and one strong broad band at 2449 and 2334 Å, respectively. The former shifted slightly to the red on warming the matrix and is shown in Fig. 7. The broad band at 2334 Å was very similar to the Pb₂ E ← X bands in Xe and Kr matrices except that in Ar it appeared even stronger than the Pb single line at 2449 Å even when M/R was as high as 3000. The Pb₂ A ← X molecular spectrum was also observed and is shown in Fig. 8 and Table VII.

E. Xe-Kr Mixtures and Xe-Ar Mixtures

Three Xe-Kr mixtures were used: 75% Xe - 25% Kr, 38% Xe - 62% Kr and 10% Xe - 90% Kr. All spectra were more diffuse than in pure Xe or Kr. In all three matrices one strong line and a broad band were observed in the 2500 Å region. These are shown in Fig. 9 and Table VIII. The strong single line shifted to the red on warming the matrices. The frequencies at various temperatures are shown in Table IX. It is worth noticing that the broad band observed appeared with increasing intensity as the Kr content was increased in the mixture. The Pb₂ A ← X molecular spectrum was also observed in each matrix, and is shown in Fig. 10 and Table X.

Two Xe-Ar mixed matrices were used: 4% Xe - 96% Ar and 16% Xe - 84% Ar. A very fast deposit rate was used which gave M/R ratios between 2700 and 1300. The spectra observed are shown in Fig. 11. The bands near 2600 Å are believed to correspond to the Pb atomic lines at 2648 Å in Xe and 2449 Å in Ar.

F. SF₆ and Xe-SF₆ Mixtures

Contrary to the rare gas matrices, the Pb/SF₆ matrix showed no discrete Pb atomic lines in the 2400-3000 Å region. Only two very weak, diffuse bands were observed between 2600 and 2800 Å.

At higher Pb evaporation temperatures a clear molecular spectrum was observed in the 4900 Å region, along with a single line at 6054 Å which shifted to the red on warming the matrix, and a broad band at 4300 Å region. The spectra are shown in Fig. 12 and the band frequencies are shown in Table XI. The molecular bands showed no frequency shift on warming the matrix, and disappeared between 90 and 100°K.

When the molecular bands appeared strongly, the matrix film absorbed continuously below 3250 Å and gave a pale yellow color. The film became grayish above 100°K where the molecular spectrum had disappeared.

The absence of discrete Pb lines in SF₆ could mean¹⁴ (1) an interaction between Pb atoms and SF₆ such as charge-transfer type which led to Pb⁺SF₆⁻, or (2) a chemical reaction between Pb and SF₆. In both cases, the discrete Pb lines observed in rare gas matrices would be

absent. Because the Pb^+ ion, if formed, absorbed in the vacuum uv region, Ca was trapped in SF_6 to try to observe the $4p\ ^2P_{1/2,3/2} \leftarrow 4s\ ^2S_{1/2}$ transitions of Ca^+ ion which are at the 4000 Å region in the gas.

The spectra of Ca in rare gas matrices were studied in detail by Wang.⁵ Therefore, Ca was first trapped in Xe at 20°K and the observed spectrum is compared to that by Wang in Table XII. The agreement was very good. Ca was then trapped in SF_6 . However, the Ca/SF_6 film showed no absorption lines in the region 2200 - 6000 Å. The film also showed a pale yellow color, similar to the Pb/SF_6 film, while the Ca/Xe film showed a red color.

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

The IR spectrum of the Pb/SF_6 film was also checked between 4000 cm^{-1} and 600 cm^{-1} . No absorption band other than those due to SF_6 vibrational modes were found. Because of interference by the strong SF_6 absorption around the 900 cm^{-1} region, SF_6 was trapped in a thin Pb film while keeping the film transparent. The SF_6 concentration was about 5 at.%. Again, only bands due to the SF_6 vibrational modes were seen. This could mean (1) no chemical reaction, (2) SF_6 was not well isolated, or (3) the reaction products, if formed, had vibrational absorptions below 650 cm^{-1} and escaped observation. No definite conclusion could be drawn here.

The fate of Pb atoms in the SF_6 matrix was further studied by measuring the electric conductivity of such films. The work is reported in a separate paper.¹⁵ No enhancement of conductivity over that of the rare gas films was found for the SF_6 films.

Pb was also trapped in a 77% Xe - 23% SF₆ matrix and a 64% Xe - 36% SF₆ matrix. Again, no discrete Pb atomic lines were observed in both matrices, but only two weak broad bands were seen, like those in the SF₆ matrix. At higher Pb evaporation temperatures, molecular bands were observed and are shown in Fig. 13 and Table XIII.

G. Co-depositing Pb and Ag in Kr Matrix

Pb and Ag were co-deposited in Kr matrix to study surface diffusion. Kr was chosen because it was better than Xe in allowing surface dimerization, and yet better than Ar in providing enough metal atoms in isolated form in a short period of deposition.

A strong triplet was observed in the 3000 Å region for Ag alone in Kr at 20°K in excellent agreement with the extensive work reported by Brewer et al.⁴ An additional doublet at 2753 and 2702 Å and a weak shoulder at 2819 Å, not reported in earlier work, could be due to impurities. When concentrated Ag/Kr films were deposited, a broad band was observed in the 4000 Å region and could be attributed to the Ag₂ molecule.¹⁶

Pb and Ag were co-deposited in Kr using the double-furnace constructed by King.⁹ The Pb evaporation temperature was kept low enough to insure that the Pb₂ concentration in the vapor was low, but the Pb₂ A ← X and E ← X bands appeared when Pb was trapped in Kr at 20°K. When the Ag concentration was comparable to that of Pb, around 0.2 at.%, no significant effect was seen on any spectral features. However, when

high concentrations of Ag (1-2 at.%) were used, both the Pb_2 A $\leftarrow$ X and E $\leftarrow$ X band intensities were greatly decreased. One set of spectra is shown in Fig. 14, which shows clearly that the $2440 \text{ \AA}$ Pb_2 E $\leftarrow$ X band was absent when the Ag concentration was high; the Pb A $\leftarrow$ X spectra were also absent. In addition, the Pb line at $2614 \text{ \AA}$ was broadened at high Ag concentrations.

IV. DISCUSSION

A. Assignment of the Observed Spectra

1. One strong Pb absorption line was observed in the $2400\text{-}2700 \text{ \AA}$ region in all rare gas matrices, which shifted reversibly to the red on warming. This line is assigned to the atomic Pb $6p7s \text{ } ^3\text{P}_1 \leftarrow 6p^2 \text{ } ^3\text{P}_0$ transition. With this assignment, the frequency shifts to the blue of the gaseous line are 2480 , 2970 , and 5550 cm^{-1} in Xe, Kr and Ar, respectively. This is consistent with the orbital expansion upon transition from $6p$ to $7s$. Such transitions should then be sensitive to the matrix expansion at higher temperatures that would reduce the blue shift, thus accounting for the observed red shift of the absorption lines at higher temperatures. More of the matrix shifts and other matrix effects will be discussed in detail in the second paper of this study.

2. A broad band was also observed in all rare gas matrices at a shorter wavelength than that of the Pb atomic line. This broad band had a blue shaded structure and a half-width of around 900 cm^{-1} .

Although no fine structure could be resolved, this band was assigned to the $\text{Pb}_2 \text{E} \leftarrow \text{X}$ transition, which has its origin at $2386 \text{ \AA}$ in the gas for the following reasons:

- (1) The broadness and blue-shaded structure implied that it was similar to a molecular band.
- (2) Deposition conditions that promoted surface diffusion during the condensation process enhanced this band as well as the $\text{Pb}_2 \text{A} \leftarrow \text{X}$ bands. Also the ease of production of the band increased as the melting or boiling point of the matrix was reduced from Xe to Ar.
- (3) The band was rather insensitive to warming the matrices as were $\text{Pb}_2 \text{A} \leftarrow \text{X}$ bands.
- (4) With this assignment, the shifts relative to the gas are 2720 and 920 cm^{-1} to the red for Xe and Kr, respectively, with intermediate shifts for the mixed Xe-Kr matrices, while in argon, the shift was 930 cm^{-1} to the blue. These shifts are larger than but in the same order as the shifts for the $\text{Pb}_2 \text{A} \leftarrow \text{X}$ bands in the same matrices.
- (5) The results of co-depositing Pb and Ag provide an indirect proof to the molecular origin of this band.

Duley,¹³ however, tentatively assigned this band to the $\text{Pb } 6p6d \text{ } ^3\text{D}_2 \leftarrow 6p^2 \text{ } ^3\text{P}_1$ atomic transition, based solely on the frequency observed.

This possibility can be eliminated because of the negligible population of the $^3\text{P}_1$ level at the Pb evaporation temperatures used.

3. In Xe an additional strong line was observed at 2259 Å, which found no counterpart in the other rare gas matrices in the optical region investigated. It showed no frequency shift on warming and persisted after annealing. The $6p6d\ ^3D_1^0 \leftarrow 6p^2\ ^3P_0$ transition at 46 069 cm^{-1} is the closest allowed transition, but a red shift of 1792 cm^{-1} seems too large. No definitive assignments could be made for this line.

4. Several very weak lines showed up in the thick rare gas matrix films. No frequency shifts were observed on warming, and their origins remained unclear.

5. A molecular band system was observed in the 5000 Å region in most of the matrices. It was assigned to the $\text{Pb}_2\ A \leftarrow X$ transition for the following reasons:

- (1) The observed frequencies were in the same region as those of the gaseous $\text{Pb}_2\ A \leftarrow X$ transition, except for a 330 cm^{-1} shift to the red in Xe and small shifts to the blue for the other matrices of the order commonly found for diatomic species in these matrices.¹
- (2) The observed vibrational spacings of the upper state ranged from 143 to 184 cm^{-1} with the $\Delta G'$ values the same within experimental error in Xe, Kr, Ar, or their mixtures. In SF_6 , $\Delta G'$ was about 10% smaller. The decrease in $\Delta G'$ with v' was only apparent after the fourth band. These values compare well with the ω' value of 159.22 cm^{-1} and $x'\omega'$ value of 0.882 cm^{-1} for the gaseous $\text{Pb}_2\ A$ state.^{11,12} PbO with

$\omega' = 451.7 \text{ cm}^{-1}$ is eliminated as the source of these bands.

In addition, the absence of $\omega'' = 722.5 \text{ cm}^{-1}$ in the IR spectrum further supports the conclusion that PbO could not be responsible for the observed molecular spectrum.

6. A weak narrow line around $6000 \text{ \AA}$ always appeared when the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ were observed. No transitions from the ground state of Pb take place in this wavelength region. Furthermore, the line appeared in SF_6 where the discrete Pb line in the $2600 \text{ \AA}$ region was absent. Therefore, it is likely due to impurities from the furnace.

B. Diffusion in Matrices

The following evidence for surface diffusion during condensation was obtained:

1. Although it was demonstrated that no bulk diffusion of atoms took place, the intensities of both the $\text{Pb}_2 \text{ A} \leftarrow \text{X}$ and $\text{E} \leftarrow \text{X}$ bands varied inversely with the melting points of the matrices. Isolation of Pb atoms was best in Xe and poorest in Ar where the intensity of the $\text{Pb}_2 \text{ E} \leftarrow \text{X}$ band was greater than that of the Pb atomic line.

2. The results of co-depositing Pb and Ag in Kr showed that, at high concentrations of Ag, the Ag did intercept the Pb atoms during the deposition of the matrix film leading to absence of both Pb_2 band systems.

3. The use of a radiation shield in front of the furnace and a prior deposit of pure matrix gas decreased significantly the intensity

of the Pb_2 A $\leftarrow$ X bands. The former indicates that some Pb_2 was formed on the target because of the radiation from the furnace. This would increase the surface temperature and surface mobility and thus enhance the chance of some Pb atoms meeting to form Pb_2 .

The prior deposit of matrix gas could lead to a better condensation of the later matrix gas atoms because of the self-depositing effect and to better thermal contact with the window. Such effect was encountered in many cases of thin film depositions and was attributed to a better sticking of the gases on the surface composed of the same species than those of different ones. This would give better isolation of Pb atoms due to better sticking of the matrix gases and lower surface temperatures during deposition.

C. Effects of Using Mixed Matrices

In the mixed matrices, all the lines or bands observed were more diffuse than those in the pure matrices. This could be due to less regular trapping sites in those matrices.

For the Xe-Kr mixed matrices, only one set of Pb spectra and one set of Pb_2 spectra were observed. This clearly indicated that in those mixed matrices, Xe and Kr co-condensed on a microscopic scale, at least around the trapped Pb and Pb_2 . Take 10% Xe - 90% Kr matrix for example; its Pb frequency was intermediate to those in Xe and in Kr. If one assumed that only van der Waals type interaction existed between Pb and the matrix atoms, one could estimate the nearest neighbor composition around the trapped Pb atom in this matrix. When only the first twelve nearest neighbor interactions were considered, and additive pairwise interaction was assumed, the twelve nearest neighbors in this

matrix around the Pb atom were found to consist of about 3 Xe atoms and 4 Kr atoms. The Xe-Kr ratio was 1 to 9 in the gas, while in the solid, at least around the Pb atoms, these calculations indicate about 2 to 1. This could be attributed in part to the difference of sticking coefficients of Xe and Kr atoms at 20°K and in part to stronger interaction between Pb and Xe which would tend to concentrate Xe in the vicinity of Pb or Pb₂.

The observed spectra in the mixed Xe-SF₆ matrices also showed similar correlation with their parent spectra. The absence of the Pb discrete spectrum and the presence of only one set of Pb₂ A ← X spectrum indicated again that Xe and SF₆ co-condensed on a microscopic scale around the trapped lead; and that the SF₆ molecules were responsible for the absence of the discrete Pb spectrum in those mixed matrices.

D. Co-depositing Pb and Ag

Other than studying surface diffusion, co-depositing Pb and Ag in Kr was also aimed at the study of long-range metal-metal interactions. Such metal-metal interaction was observable when the Ag concentration was above 1 at.%. This was based on the observed significant broadening of the Pb $^3P_1 \leftarrow ^3P_0$ line in such matrices. However, the center frequencies of both Pb and Ag absorption lines were not affected by varying the Ag concentration used. These indicated that the Pb-Ag interaction differed enough from that of Pb-Pb to cause the observed broadening effect with 1-2 at.% Ag, and yet not enough to give any new features other than broadening the Pb $^3P_1 \leftarrow ^3P_0$ line. On the other hand increasing

the Pb content in Xe to 3 at.% produced no broadening of the Pb line although Pb₂ bands were enhanced. Apparently when Pb atoms are close enough to interact, they interact strongly enough to produce Pb₂ spectra at a different wavelength and the remaining Pb atoms responsible for the atomic line absorption are well isolated.

E. Effect of Using SF₆ Matrix

The most interesting feature was the absence of any discrete Pb spectrum in the SF₆-containing matrices and yet the appearance of the Pb₂ spectrum when higher Pb evaporation temperatures were used.

As was mentioned, the possibility of forming charge transfer complex was checked by trapping Ca in SF₆ to try to observe transitions of Ca⁺ ion. No absorption spectrum was observed. Work was also done to measure the electric conductivity of Pb/SF₆ films. If Pb⁺SF₆⁻ were formed, the extra electron which was loosely bound to SF₆ molecule might, by applying an electric field, hop from one SF₆ molecule to the next throughout the matrix film. The excess current could then show up in the conductivity measurement. This is reported in a separate paper, and we only mention that no excess current over that of a Pb/Xe film was measured. Instead, the film showed rather low conductivity even at higher temperatures where SF₆ should have evaporated from the target. If charge transfer is involved, the charge must be well localized in a Pb⁺SF₆⁻ pair. The observations seem to indicate a chemical reaction between Pb and SF₆, but additional experiments would be necessary to clarify the behavior of metallic atoms in SF₆.

Whatever happened to Pb atoms, Pb₂ molecules seemed to behave very differently. Both the charge-transfer complex formation and chemical reaction would involve the valence electrons of the Pb atom. In Pb₂ molecules, the Pb valence electrons are in molecular orbitals and are less free to be transferred to SF₆. The conductivity measurement further showed that higher polymers of lead also seemed to be immune to SF₆ molecules. The same interpretation given above for Pb₂ could be applied to account for this.

F. Pb₂ Molecular Spectra in Matrices

The assignment of the Pb₂ A ← X and E ← X bands has been discussed above. It was observed that when the matrix film showed strong Pb₂ A ← X absorption, the region below about 2600 Å became continuously opaque. At still stronger Pb₂ absorption, the film was opaque below 3100 Å. Gaseous Pb₂ shows absorption to two repulsive states at 2380 and 2930 Å. These states could be responsible for the continuous absorption in the matrix. In some of the experiments, very weak molecular band spectra are observed at the edge of the continuous absorption below 3000 Å. This could be due to Pb₂ B ← X which is close to the 2930 Å continuous absorption in the gas.

The calculation of matrix spectral shifts for the Pb₂ A ← X bands requires fixing of the vibrational numbering of the bands. The high intensity of the first band in both Xe and Kr with no sign of another band to the red indicates that the first band is the 0-0 band. It was

also assumed that the first bands in Ar and SF₆ were also 0-0 bands. On this basis, the shift in Xe was 330 cm⁻¹ to the red of the gaseous origin, while the shifts in Kr, Ar, and SF₆ were 150, 510, and 450 cm⁻¹, respectively, to the blue. These shifts are similar to those tabulated¹ for SiO and SnS. The distribution of intensities is most gas-like for Ar and SF₆ with the maximum for the 3-0 band compared to 6-0 for the gaseous maximum while for Kr and Xe the maximum shifts to lower ν' . On the basis of the Franck-Condon principle, this would indicate that the upper state is squeezed more in Xe than in Ar. To explain this, it is necessary to postulate that Pb₂ replaces more rare gas atoms in an Ar matrix than in Xe.

At 20°K, the nearest neighbor distances in Xe, Kr, and Ar lattices¹⁷ are 4.34, 4.00 and 3.76 Å, respectively. By comparing the lattice size of Xe with the molecular size of Pb₂, it could be shown¹⁸ that orbital overlapping between Pb₂ and Xe existed for an alignment of the Pb₂ internuclear axis either on the long or short axis of the Xe hexagon in a plane of the Xe lattice. This implies that a Pb₂ molecule in a single substitutional site in the Xe lattice would experience a large repulsive interaction even in the ground state and an even larger repulsion for the excited A state. This should cause a blue shift instead of the observed red shift. Thus even in Xe, Pb₂ must occupy at least two adjoining sites of the Xe lattice and even more sites in Kr and Ar, so that attractive forces predominate over repulsive forces in contrast to atomic Pb which presumably occupies one atomic site in the rare gas lattice. Since the attractive interaction would be less sensitive

than the repulsive interaction to lattice expansion with increase of temperature, this interpretation is consistent with the lack of shift of the Pb_2 frequencies upon heating the matrix compared to the red shift for the Pb atomic line upon expansion of the lattice.

V. SUMMARY

1. In contrast to the triplet structure observed for $p \leftarrow s$ transitions of other metallic atoms in rare gas matrices, the $s \leftarrow p$ transition of atomic Pb in Xe, Kr, and Ar yields a single line although somewhat more broadened. Variation of the Pb concentration in Xe from 0.02 to 3 at.% produced no change in line position or breadth. The presence of up to 2 at.% Ag in the matrix causes no splitting or shifting of the Pb line although additional broadening is observed with 1-2 at.% Ag.

2. The matrix spectra of Pb_2 can be produced either by isolation of Pb_2 from the vapor or by synthesis from the atoms by a surface diffusion mechanism.

3. The atomic line of Pb shifts reversibly to the red upon warming the matrix while the bands of Pb_2 show no shifts.

4. Pb like most metallic atoms shows no appreciable bulk diffusion through the rare gas matrix after isolation even when heated almost to the temperature at which the matrix gas evaporates and Pb from a low temperature source of Pb vapor can be isolated in Xe with virtually no Pb_2 formation when the heat load and thermal contact are optimized to minimize the matrix surface temperature.

5. During the condensation process on a 20°K window, surface diffusion of Pb can take place especially when the surface temperature is increased due to furnace radiation or poor thermal contact of the matrix or with high Pb concentrations. The surface diffusion of Pb to produce Pb₂ can be intercepted by co-deposition with the matrix gas of 1-2 at.% Ag.

ACKNOWLEDGMENTS

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TABLE I. Absorption Spectrum of Pb in Xe

$\lambda(\text{\AA})$	This work (at 20°K)		Assignment
	$\nu(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	
2809(w)	35 600	~ 570	
2648(s)	37 760	~ 500	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
2552 (w, blue shaded)	39 190	> 900	$\text{Pb}_2 \ (E \leftarrow X)$
2402(w)	41 630	~ 240	
2259(s)	44 280	~ 550	

TABLE II. Temperature Dependence of the Pb/Xe $^3P_1^0 \leftarrow ^3P_0$ Line

Temperature °K	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
20°	2648	37 760
30°	2650	37 740
40°	2655	37 670
50°	2659	37 610
60°	2663	37 550
70°	2667	37 500
77°	2671	37 440

TABLE III. Absorption Spectrum of Pb_2 ($A \leftarrow X$) in Xe

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\Delta G_{1/2}(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	Relative Intensity
5211	19 191	168	55	74
5166	19 359	165	56	39
5122	19 524	163	55	21
5080	19 687	174	83	13
5035	19 861	153	68	5
4997	20 014	155	49	2
4985	20 169			
6268 ^a	15 954		220	

^a Unidentified

TABLE IV. Absorption Spectrum of Pb in Kr

This work (at 20°K)			
$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	Assignment
2783(w)	35 927		
2614(s)	28 260	~ 400	$6p7s\ ^3P_1^0 \leftarrow 6p^2\ ^3P_0$
2440(w, blue shaded)	40 980	> 900	$Pb_2\ (E \leftarrow X)$
2360(w)	42 373		

TABLE V. Temperature Dependence of the Pb/Kr $^3P_1^0 \leftarrow ^3P_0$ Line

Temperature °K	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
20	2614	38 260
30	2617	38 210
40	2619	38 180
50	2622	38 140

TABLE VI. 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	19 673		60	20
		173		
5039	19 846		55	20
		161		
4998	20 007		62	17
		157		
4959	20 164		62	11
		159		
4921	20 323		63	7
		147		
4885	20 470		69	5
		163		
4867	20 633		75	3
6126 ^a	16 323		150	

^a Unidentified

TABLE VII. Absorption Spectrum of Pb_2 ($A \leftarrow X$) in Ar

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\Delta G_{1/2}(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	Relative Intensity
4992	20 032		49	12
		167		
4951	20 199		39	18
		162		
4911	20 361		79	19
		166		
4872	20 527		68	14
		166		
4833	20 693		41	10
		155		
4797	20 848		32	7
		153		
4762	21 001		27	6
6053 ^a	16 521		130	

^a Unidentified

TABLE VIII. 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)	37 590	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2530(w,b)	39 530	$\text{Pb}_2 \ (\text{E} \leftarrow \text{X})$
38% Xe - 62% Kr	2660(s)	37 590	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2508(w,b)	39 870	$\text{Pb}_2 \ (\text{E} \leftarrow \text{X})$
10% Xe - 90% Kr	2655(s)	37 950	$6p7s \ ^3P_1^0 \leftarrow 6p^2 \ ^3P_0$
	2467(w,b)	40 540	$\text{Pb}_2 \ (\text{E} \leftarrow \text{X})$

TABLE IX. Temperature Dependences of the Pb $^3P_1^0 \leftarrow ^3P_0$ Line
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	37 590	2660	37 590	2635	37 950
30	2661	37 580	2663	37 550	2640	37 880
40	2666	37 510	2667	37 500	2644	37 820
50	2669	37 470	2669	37 470	2647	37 780
60	2673	37 410	2673	37 410		

TABLE X. Absorption Spectra of Pb_2 ($A \leftarrow X$) in the Xe-Kr Mixed Matrices

	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\Delta G_{1/2}(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	Relative Intensity
75% Xe-25% Kr	5189	19 272		100	18
			177		
	5142	19 449		78	7
			141		
	5105	19 590		79	4
			174		
	5060	19 764		82	3
38% Xe-62% Kr			145		
	5023	19 909		69	1
	6240 ^a	16 026		180	
	5166	19 358		87	38
			184		
	5117	19 542		95	17
			144		
10% Xe-90% Kr	5080	19 686		91	11
			158		
	5039	19 844		92	9
			147		
	5002	19 991		94	8
	6224 ^a	16 066		175	
	5115	19 550		89	49
			157		
	5074	19 707		100	28
			147		
	5037	19 854		83	18
			155		

Table X (continued)

4998	20 009		93	8
		167		
4956	20 176		86	7
		156		
4918	20 332		66	5
		148		
4883	20 480		50	2
6165 ^a	16 221		204	

^a Unidentified

TABLE XI. Absorption Spectrum of Pb_2 ($A \leftarrow X$) in SF_6

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\Delta G_{1/2}(\text{cm}^{-1})$	$\nu_{1/2}(\text{cm}^{-1})$	Relative Intensity
5006	19 976		96	25
		148		
4969	20 124		85	53
		158		
4930	20 282		98	60
		151		
4894	20 433		87	48
		155		
4857	20 588		74	32
		151		
4822	20 739		76	18
		144		
4789	20 883		70	8
		143		
4756	21 026		53	5
6054 ^a	16 520		130	

One broad band centered at 4380 $\text{\AA}$, and extending between 4510 and 4250 $\text{\AA}$.

One broad shoulder between 4660 and 4580 $\text{\AA}$.

^a Unidentified

TABLE XII. Absorption Spectrum of Ca $^1P \leftarrow ^1S$ in Xe at 20°K

This Work		Wang ⁵	
$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
4378	22 840	4377	22 850
4338	35 050	4337	23 060
4310	23 200	4311	23 200

TABLE XIII. Absorption Spectra of Pb_2 ($A \leftarrow X$) in the Xe-SF₆ Mixed Matrices

	$\lambda(A)$	$\nu(cm^{-1})$	$\Delta G_{1/2}(cm^{-1})$	$\nu_{1/2}(cm^{-1})$	Relative Intensity
77% Xe-23% SF ₆	5208(?)	19 203 (?)			2
			254(?)		
	5140	19 457			9
			170		
	5095	19 627		82	12
			143		
	5058	19 770		99	14
			162		
	5017	19 932		94	9
			159		
	4977	20 091		83	8
			153		
	4940	20 244		67	4
			164		
	4900	20 408		103	4
	6263 ^a	15 966		250	

One broad band centered at 4490 Å and extending between 4633 and 4345 Å.
One broad shoulder between 4806 and 4700 Å.

64% Xe-36% SF₆

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

One broad band centered at 4416 Å and extending between 4571 and 4200 Å.
One single band^a at 6211 Å (16 400 cm⁻¹) with $\nu_{1/2} = 330$ cm⁻¹.

^a Unidentified

FIGURE CAPTIONS

Fig. 1. Absorption spectrum of Pb/Xe.

Fig. 2. Warm up spectrum of Pb/Xe.

Fig. 3. Absorption spectrum of Pb/Xe

a) at normal Pb evaporation temperature of 670°C , $M/R = 300$

b) at high Pb evaporation temperature of 700°C , $M/R = 150$.

In all the spectrum tracings of this paper, the ordinates represent absorption intensities which increase from bottom to top.

Fig. 4. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Xe.

Fig. 5. Absorption spectrum of Pb/Kr, $M/R = 200$.

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

Fig. 7. Warm up spectrum of Pb/Ar.

Fig. 8. Absorption spectrum of Pb_2 ($A \leftarrow X$) in Ar.

Fig. 9. Absorption spectra of Pb in

a) 75% Xe - 25% Kr,

b) 38% Xe - 62% Kr, and

c) 10% Xe - 90% Kr.

$M/R = 500-600$.

Fig. 10. 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.

$M/R = 500-600$.

Fig. 11. Absorption spectra of Pb in

a) 16% Xe - 84% Ar, and

b) 4% Xe - 96% Ar.

M/R = 2700-3100.

Fig. 12. Absorption spectrum of Pb_2 ($A \leftarrow X$) in SF_6 .

Fig. 13. Absorption spectra of Pb_2 ($A \leftarrow X$) in

a) 77% Xe - 23% SF_6 and

b) 64% Xe - 36% SF_6 .

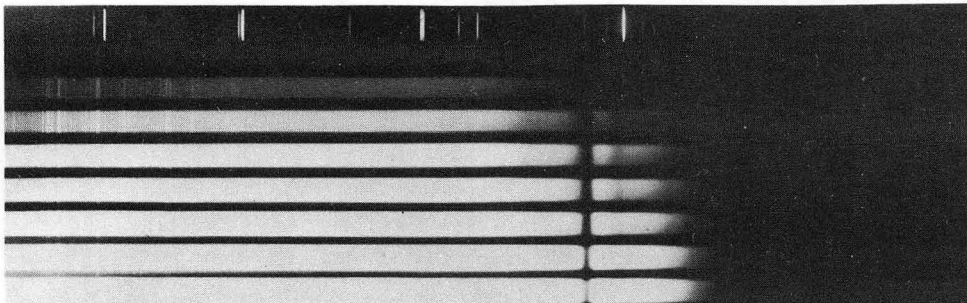
Fig. 14. Absorption spectra of

a) Pb/Kr, 0.2 at.%,

b) Ag/Kr, 0.2 at.%, and

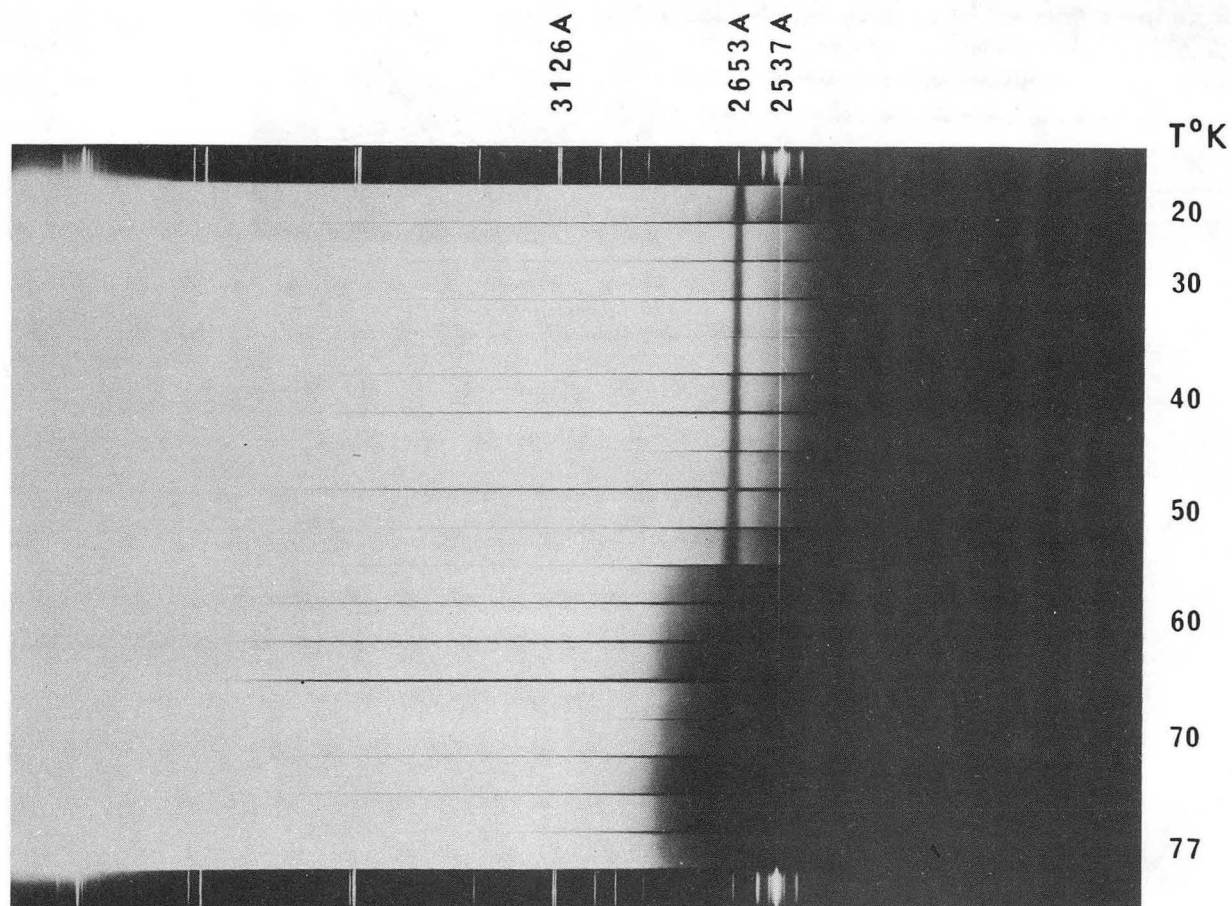
c) (Pb + Ag)/Kr; 0.2 at.% Pb, 2 at.% Ag.

The unidentified doublet at 2702 and 2753 Å to the red of the Pb line is associated with high Ag concentrations.



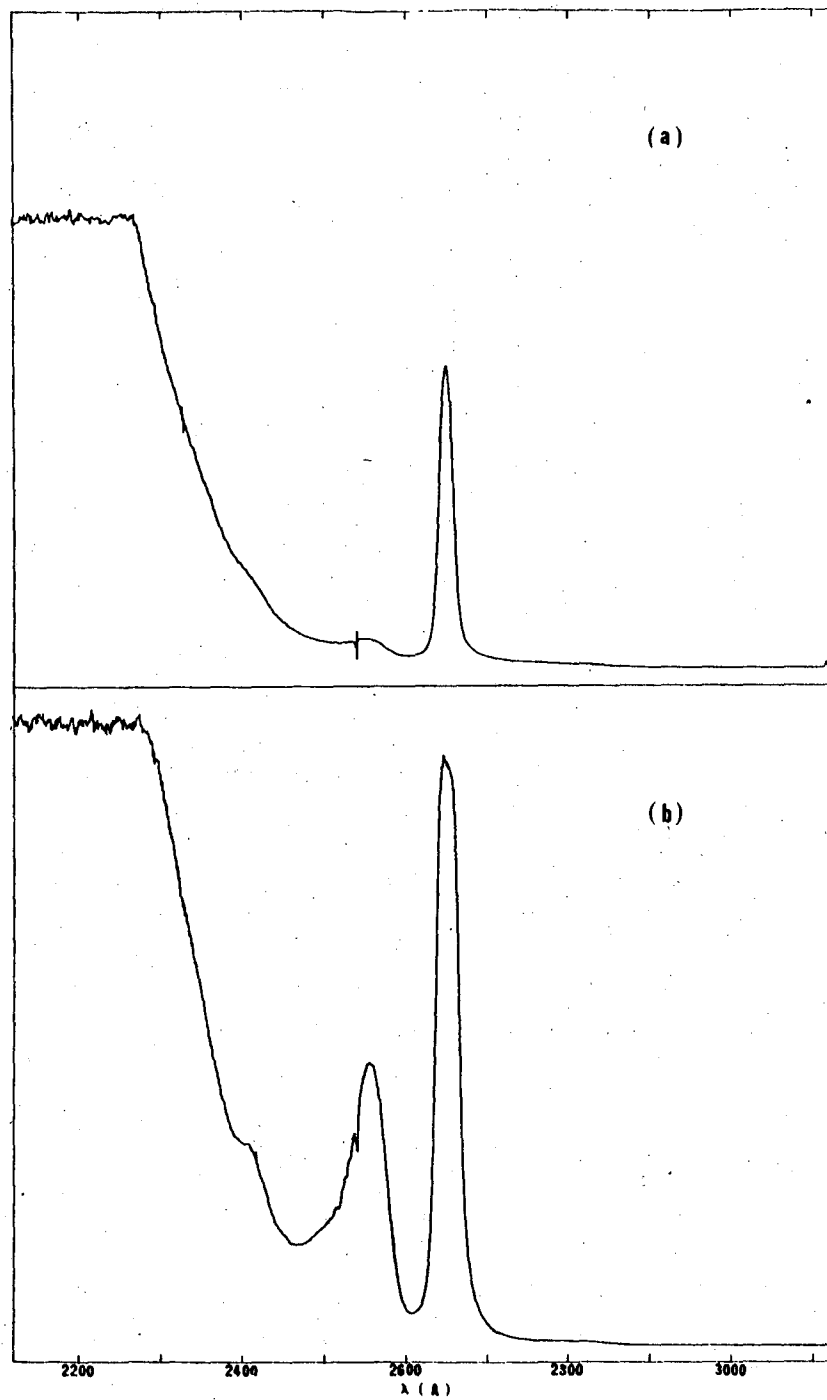
XBB 707-3039 (C only)

Fig. 1



XBB 707-3012

Fig. 2



XBL 707-1357

Fig. 3

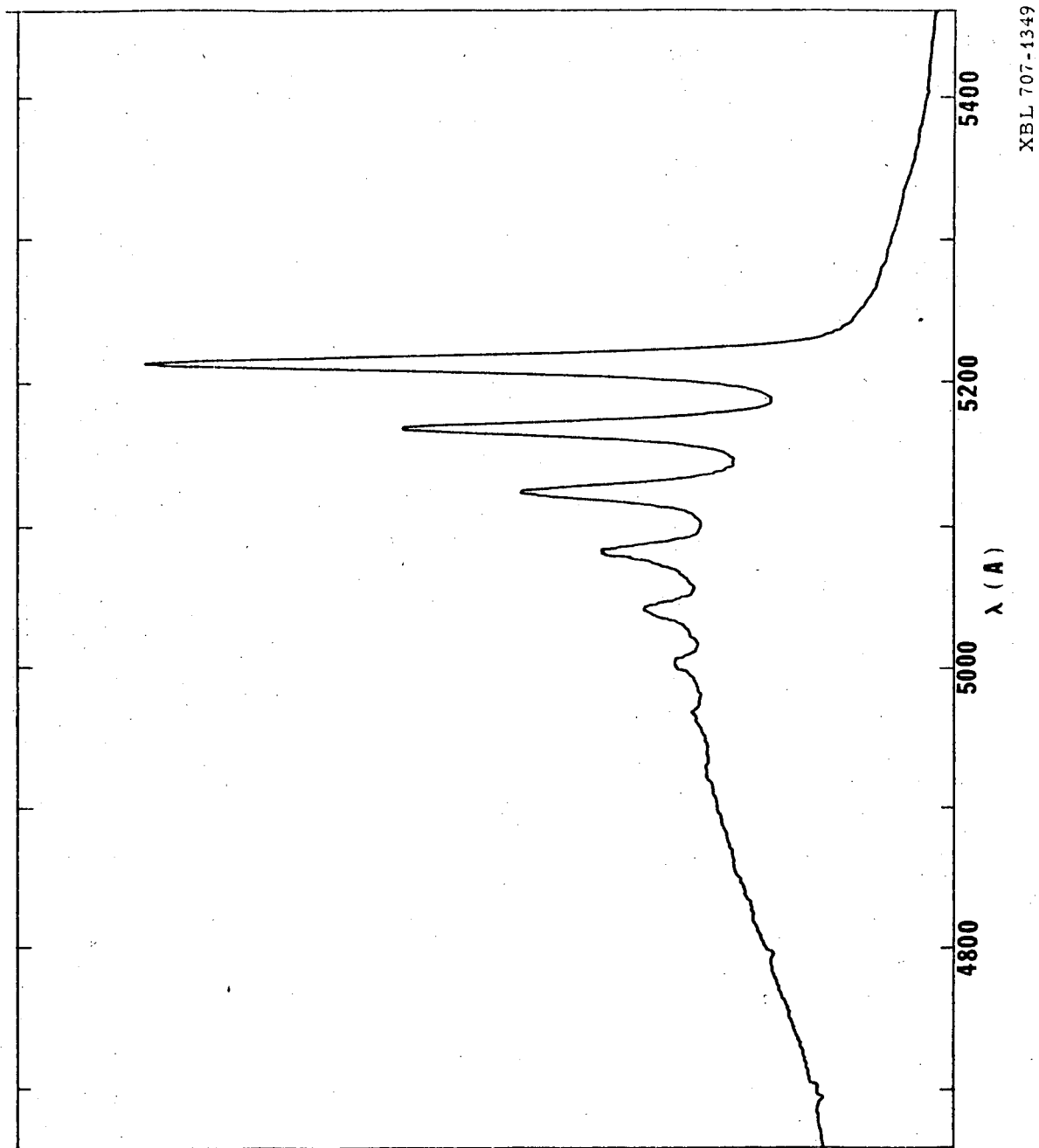
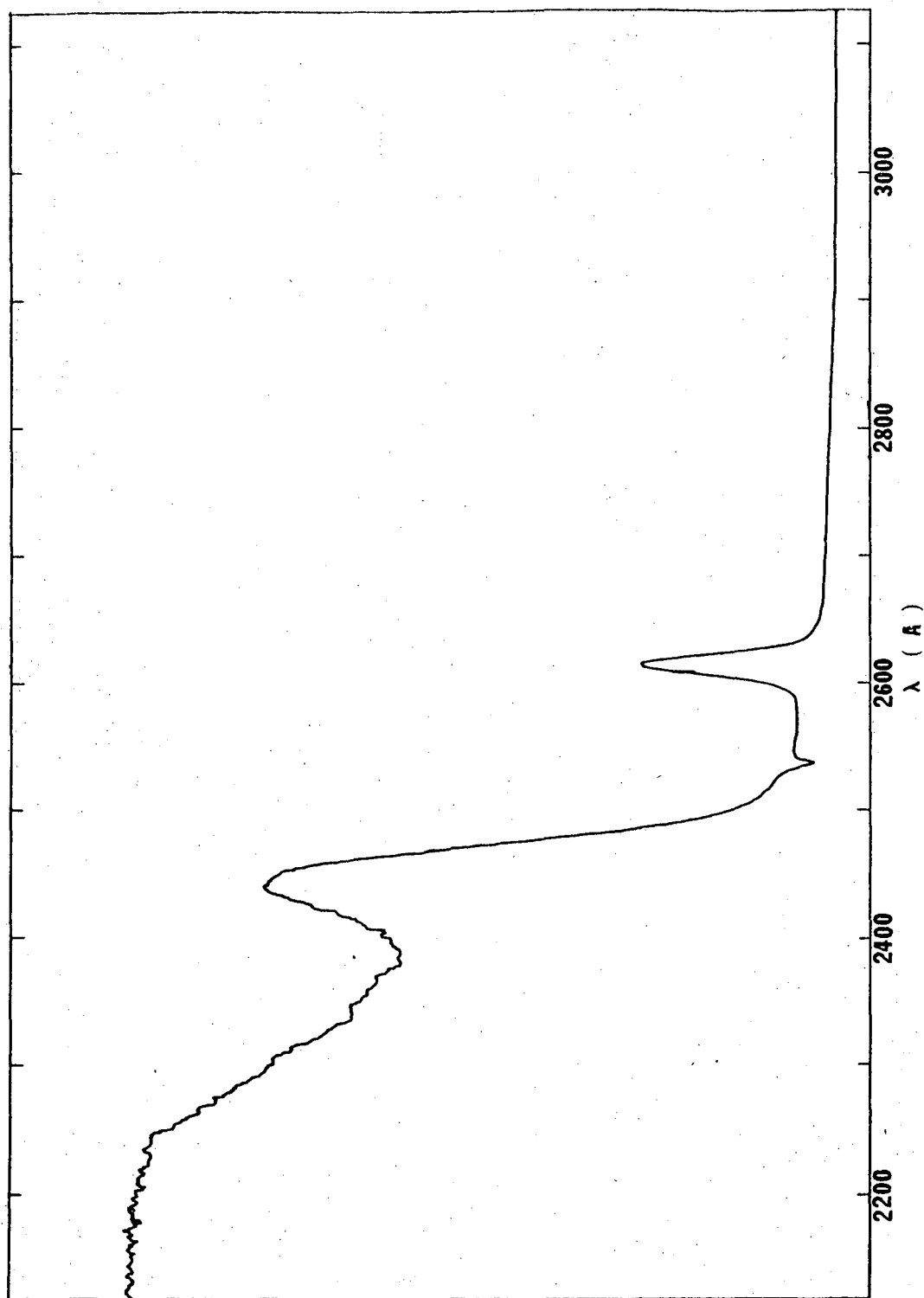
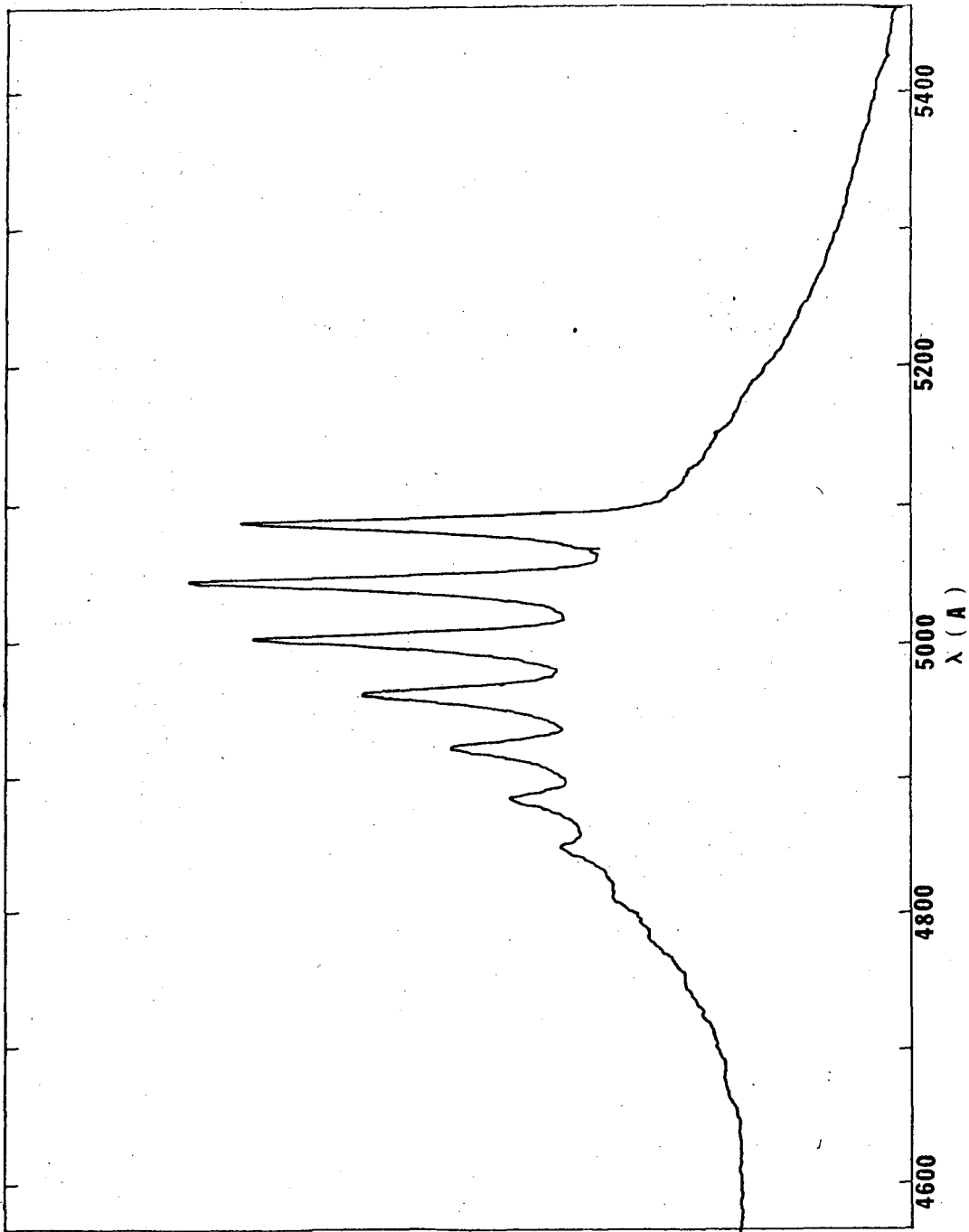


Fig. 4



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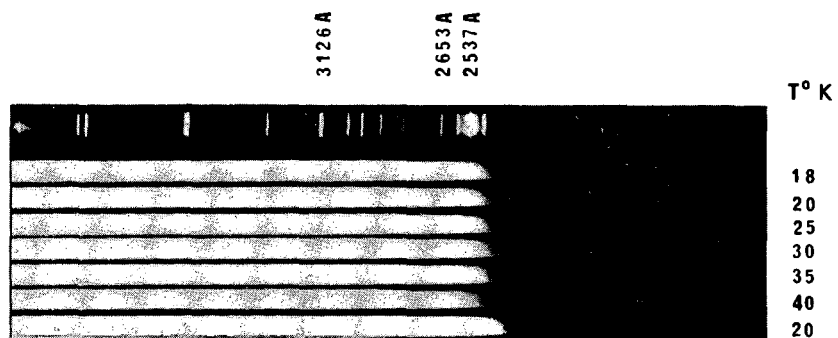
Fig. 5



XBL 707-1354

Fig. 6

-47-



XBB 707-3010A

Fig. 7

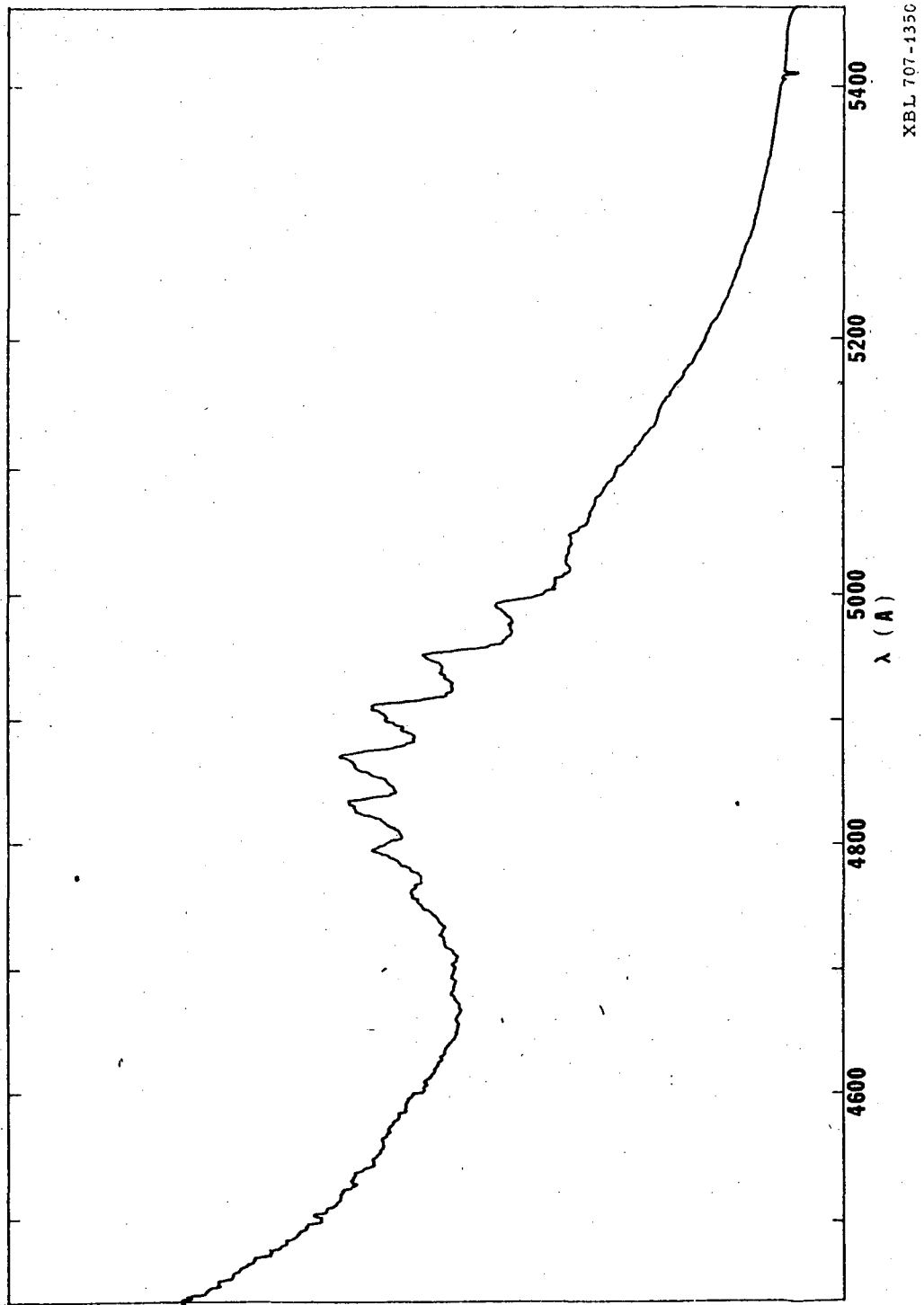
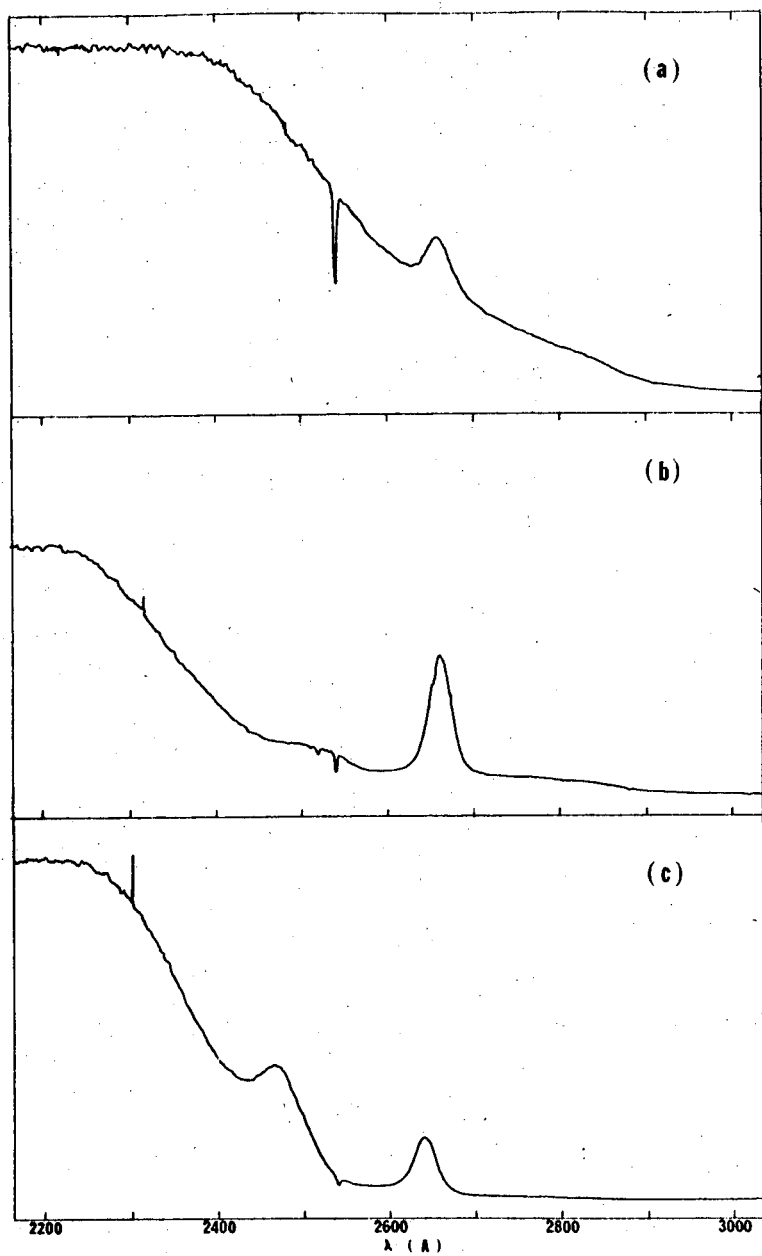
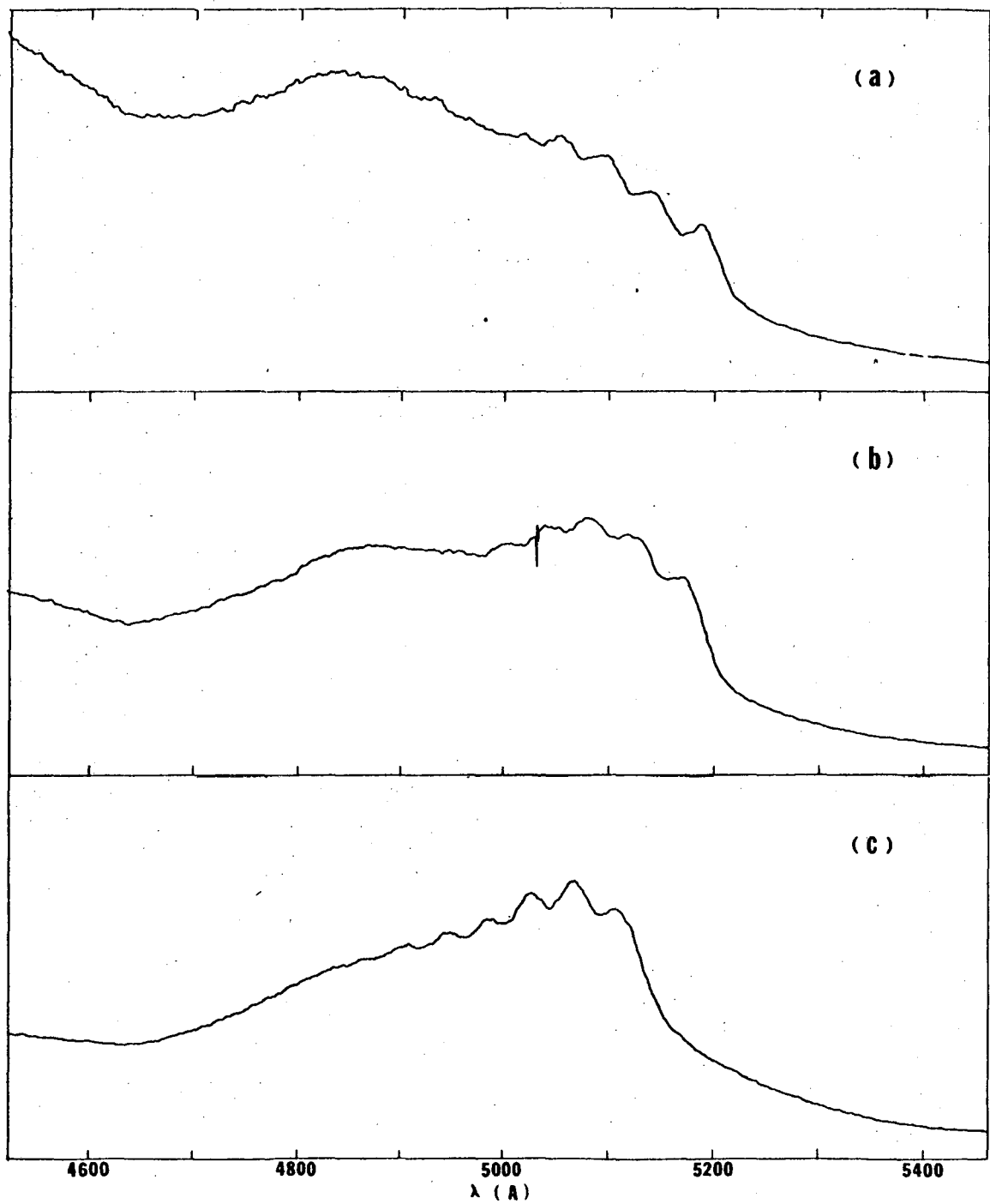


Fig. 8



XBL 707-1353

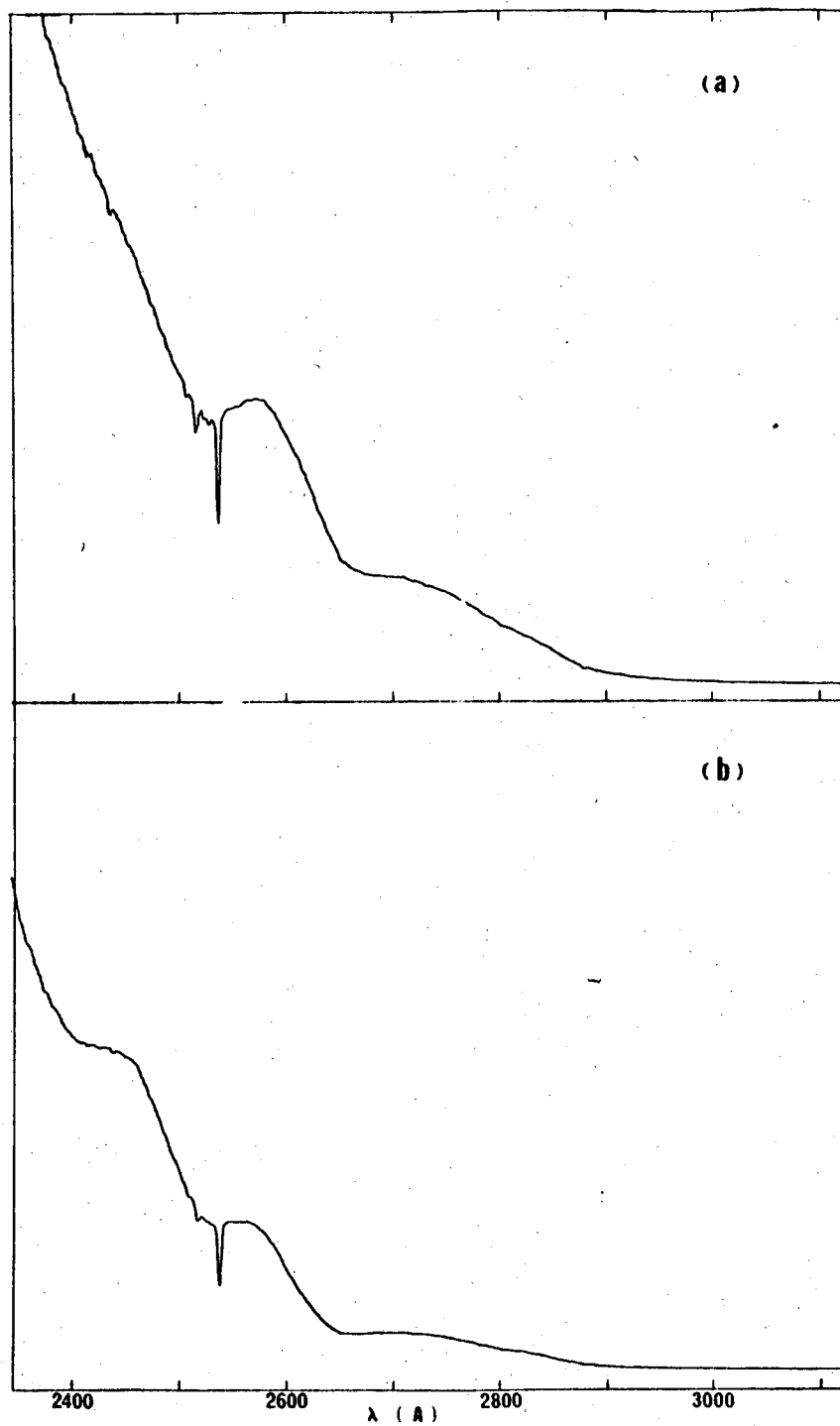
Fig. 9



XBL 707-1356

Fig. 10

-51-



XBL 707-1355

Fig. 11

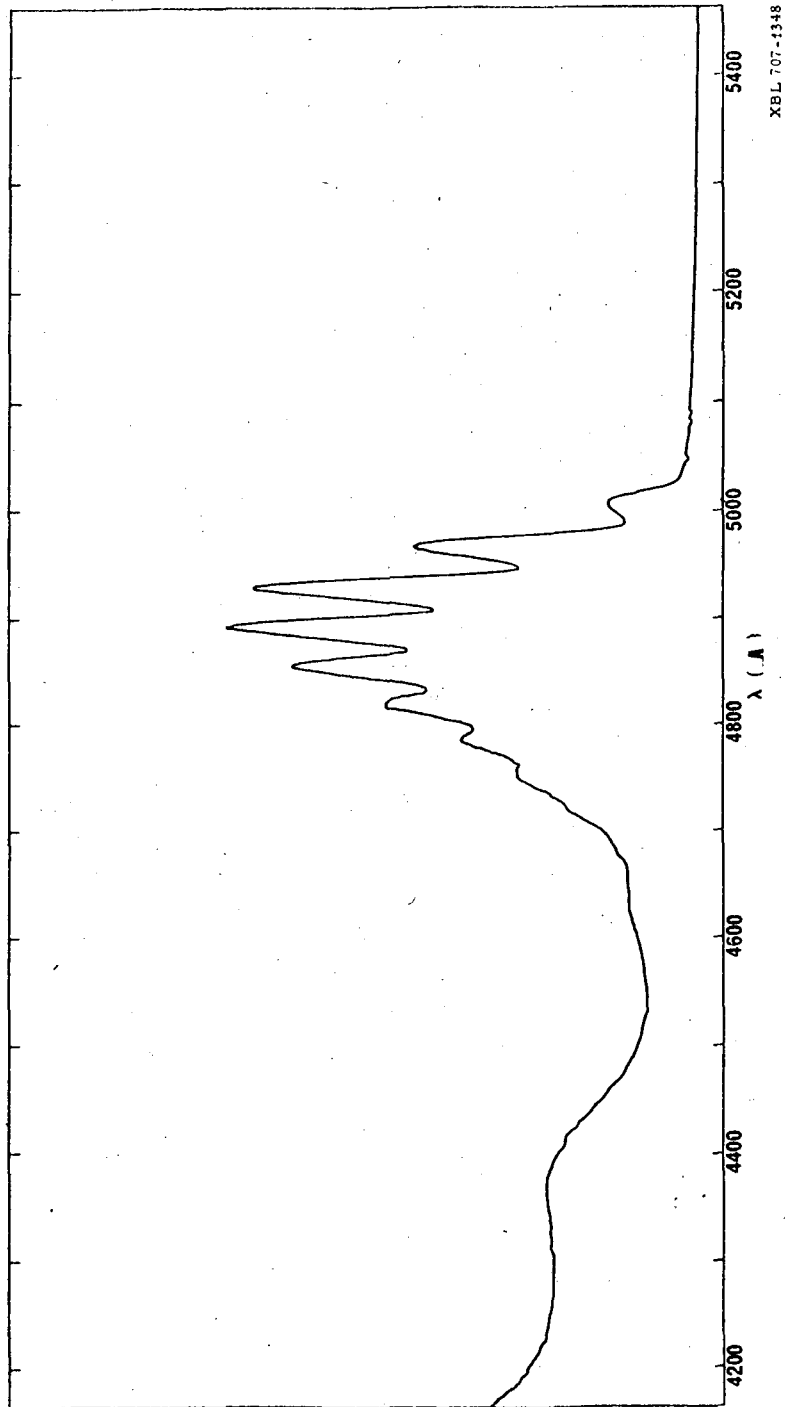
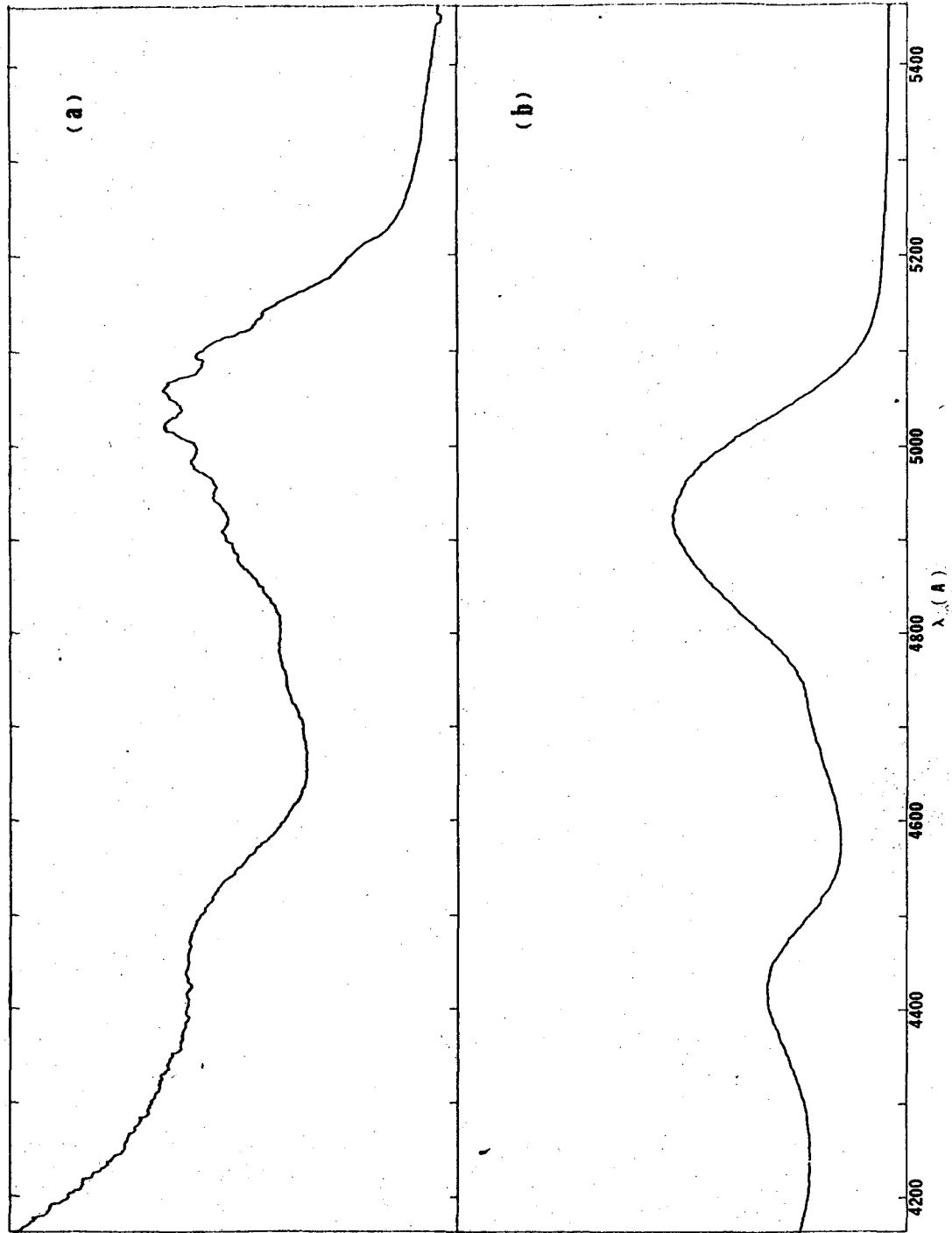


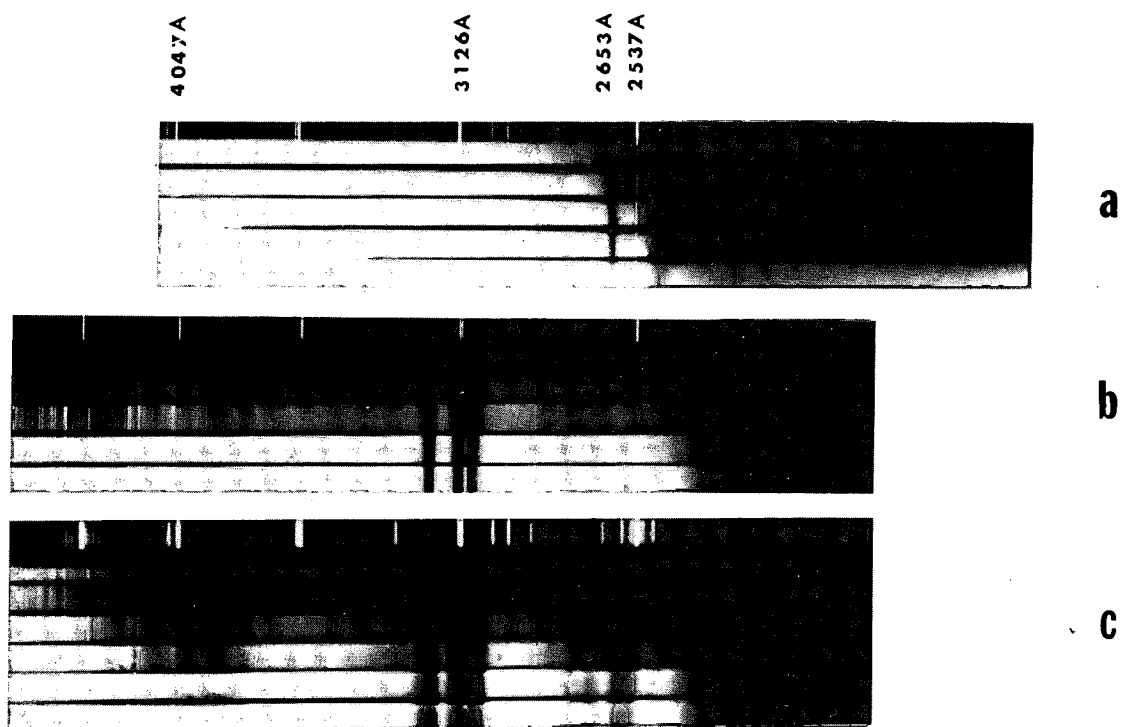
Fig. 12

4-19



XBL 707-1351

Fig. 13



XBB 707-3040

Fig. 14

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