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The Absorption Spectrum of
Praseodymium Iodide*

Presented to

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and

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of the requirements for graduation with
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DEDICATION

To my loving wife, Donna, who has made our first Holiday Season together the best one I have ever experienced.

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INTRODUCTION

Spectral and fluorescence studies of the lanthanides have taken place since 1907. The bands that are seen at room temperature in the absorption spectra can be resolved at lower temperatures. The resolved peaks at lower temperatures are actually the crystal field splitting components of the energy levels. Since these peaks are usually grouped in regions of not more than $200 - 300 \text{ cm}^{-1}$, of which each group is usually separated by more than this amount, these groups of peaks can be associated with the energy levels of the system. By averaging the energies of the groups of peaks, the center of gravity of each group of crystal field splitting components can be determined. Henceforth in this paper each group of crystal field splitting components will be referred to as a J level. One phenomenon that has been noticed, but not necessarily particular to the lanthanides, is that as a particular ion forms bonds of differing covalent nature, the centers of gravity of the J levels shift. Specifically, as the covalent nature of the bond increases, a shift of the center of gravity of the J levels toward the red increases. This chemical shift known as the nephelauxetic effect, has been discussed in general¹, and in particular for praseodymium.²

Further work has been done for praseodymium to show that this is indeed the case. Specifically, the shifts for praseodymium doped lanthanum fluoride, lanthanum ethyl sulfate and yttrium aluminum garnet have been shown.³ They also were able to show an increased shift in average energy of the J levels as the nearest neighbor to the praseodymium ion increased with covalent nature, as defined by Pauling.⁴

The spectra for praseodymium doped lanthanum fluoride⁵, lanthanum chloride⁶, and lanthanum bromide⁷ have been studied and are well known.

The praseodymium iodide crystal exhibits a space symmetry of D_{2h}^{17} and the praseodymium ion has a site symmetry of C_{2v} .⁸

Although previous studies of praseodymium iodide have been made, a detailed analysis of the absorption spectrum of the crystal has not been made prior to this.

RESULTS

The synthesis of anhydrous praseodymium iodide, PrI_3 , by techniques analogous to those developed by Fried⁹ to prepare other anhydrous iodides has been accomplished.

Utilizing these techniques a thin film of the anhydrous iodide was obtained along the walls of a small piece of quartz tubing. From this the absorption spectrum of praseodymium iodide was obtained in transmission at room temperature, 298°K ; boiling liquid nitrogen temperature, $\sim 77^\circ\text{K}$; and boiling liquid helium temperature, $\sim 4^\circ\text{K}$. The region studied was from $4000 - 22,500 \text{ cm}^{-1}$.

A basic analysis of the spectrum has identified ten of the thirteen possible levels in praseodymium with some indication of the structure of the ground state.

DISCUSSION

The use of low temperature techniques for observing the spectra of ions has been discussed at length.¹⁰ By reducing the temperature the upper levels of the ground state are progressively depopulated and therefore the spectra are simplified greatly. The spectrum of praseodymium iodide is shown in Figures I through VII, with Figure III showing the simplifying nature quite clearly. The numbers on each side of the spectra are slit widths. It can now be assumed that the observed absorptions are the crystal field splitting components. From liquid helium temperature spectra the actual J level multiplets can be identified and the center of gravity of each J level can be calculated. By slight warming of the sample just after obtaining the liquid helium spectrum, peaks can be seen "growing in" from absorptions due to newly populated levels of the ground state. While measurement of fluorescence levels in single crystals is the primary source of reliable data on the ground state splitting the use of the "growing in" or hot band technique makes it possible to obtain some information about the ground state structure.

An analysis of the liquid helium spectrum after slight warming has shown that there is an abundance of peaks that grow in at energies around 19 cm^{-1} and 27 cm^{-1} lower than the adjacent peaks. Although most of the hot

band energies in this paper are relative to the adjacent peaks, the formation of a hot band could be due to any of the electronic components of the level. During the analysis of the spectra, energies of the hot bands relative to all components of the level were noted. Those of the above mentioned energies were the ones seen most frequently. From this it is predicted that two excited levels of the ground state have these energies. Table I contains a tabulation of the liquid helium peaks along with the calculated center of gravity for each J level.

An elementary analysis of the f^2 configuration shows that there are thirteen energy levels possible, the ground state being 3H_4 . In the case of f-electron spectra, the f-electrons are shielded and the effect of the ligand field is small. It is therefore expected that the bands seen in praseodymium iodide would have nearly the same energy as those in other praseodymium crystals. Although we do not observe it, we expect to see absorptions due to the 3H_5 group in the region of 2100 cm^{-1} .

Figure I shows the first group that we do see, 3H_6 . As marked in the figure, there are two definite hot bands. With slight warming a peak at 4283 cm^{-1} grows in and the peak at 4301 cm^{-1} shrinks. The same thing happens with the peaks at 4598 cm^{-1} and 4619 cm^{-1} . As

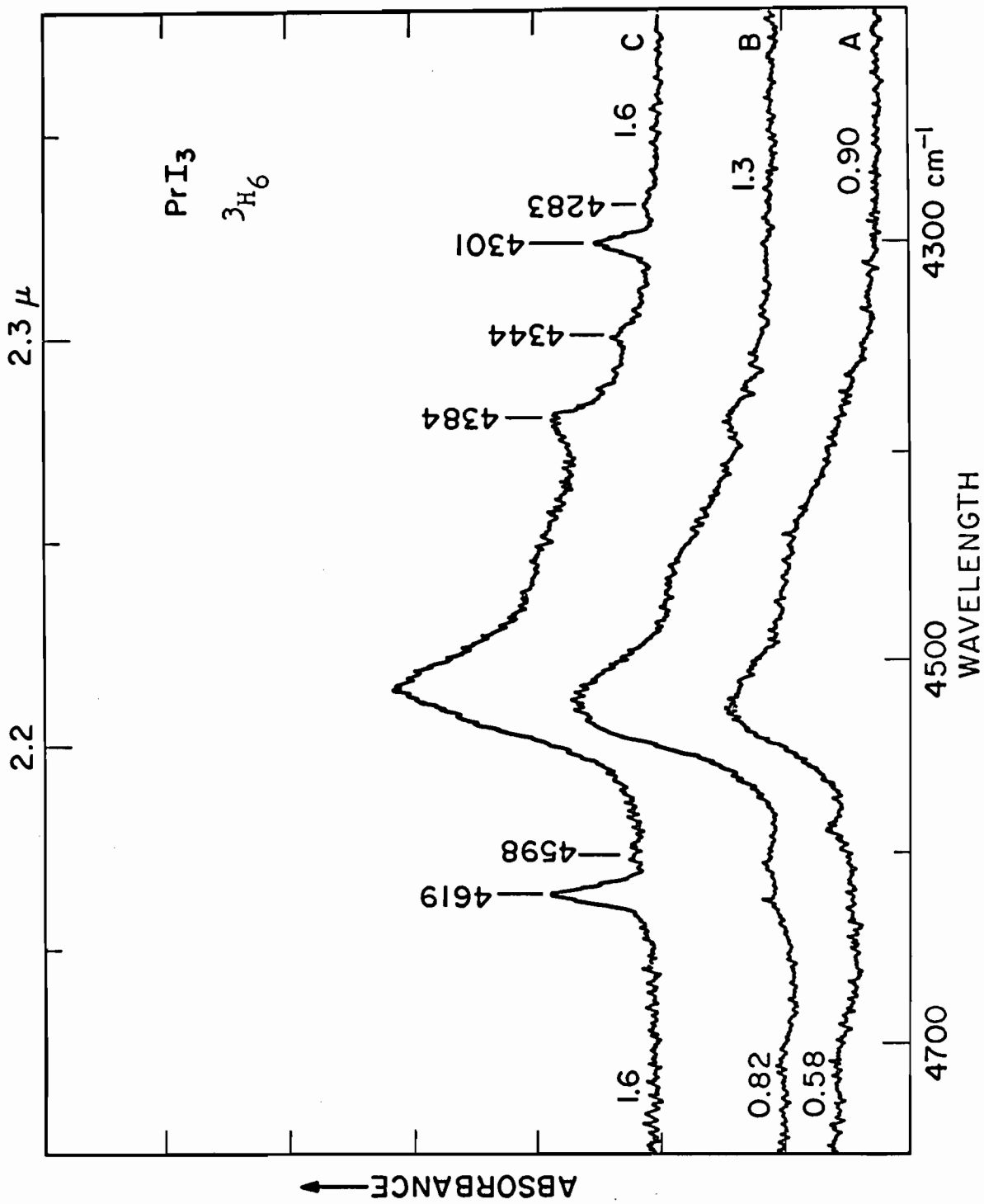


FIGURE I. Absorption spectrum of PrI_3 at (A) 298 $^\circ\text{K}$, (B) $\sim 77^\circ\text{K}$, and (C) $\sim 4^\circ\text{K}$ in the region from 4300 cm^{-1} to 4700 cm^{-1} .

can be seen, the difference in energy between these peaks is 18 cm^{-1} and 21 cm^{-1} respectively.

Figure II shows the next J level, 3F_2 . The hot band shown in the liquid helium spectrum, 30 cm^{-1} from its nearest peak, is very evident in the liquid nitrogen spectrum and it also shows a further growing band adjacent to it, 48 cm^{-1} of lower energy than the original helium peak.

Figure III shows the next two groups. The first group, 3F_3 , which shows itself near the 6300 cm^{-1} energy, exhibits hot bands at 6236 cm^{-1} and 6205 cm^{-1} . These bands are 20 cm^{-1} and 51 cm^{-1} of lower energy from the 6256 cm^{-1} peak. As can be seen in the liquid nitrogen and room temperature spectra there are many strong peaks. These peaks could very well be satellite peaks of the lowest level ground state transition. Further analysis may well show the missing peaks in the helium spectrum that may be due to forbidden transitions.

The next group, 3F_4 , has the same aspects. There are many peaks evident in the room temperature spectrum that may well be used to determine the missing cold temperature forbidden transitions, and also help determine the ground state splitting.

Although no strong absorption was observed in the predicted energy range, there is another J level, 1G_4 ,

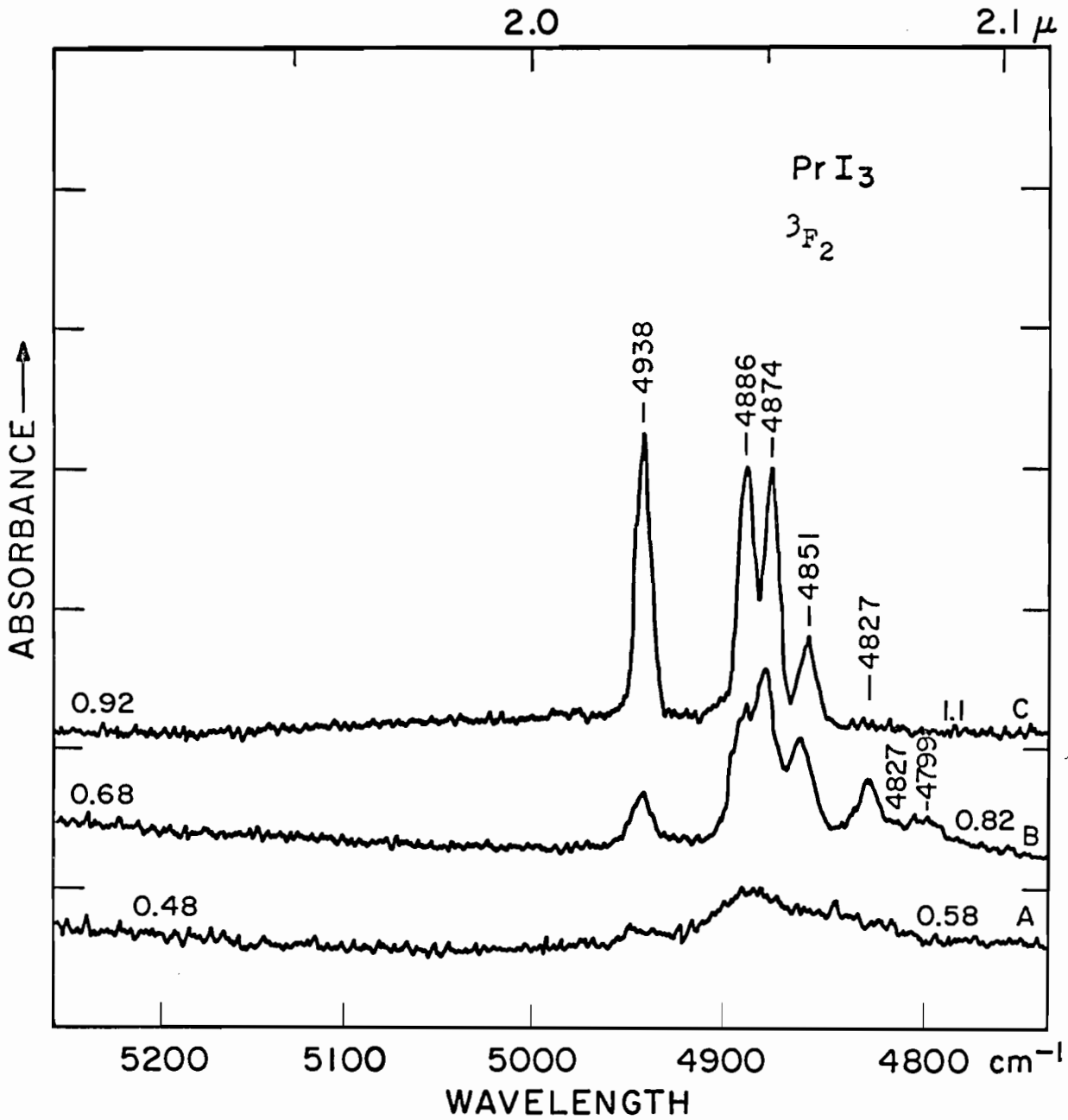


FIGURE II. Absorption spectrum of PrI₃ at (A) 298°K, (B) ~77°K, and (C) ~4°K. in the region from 4800 cm⁻¹ to 5200 cm⁻¹.

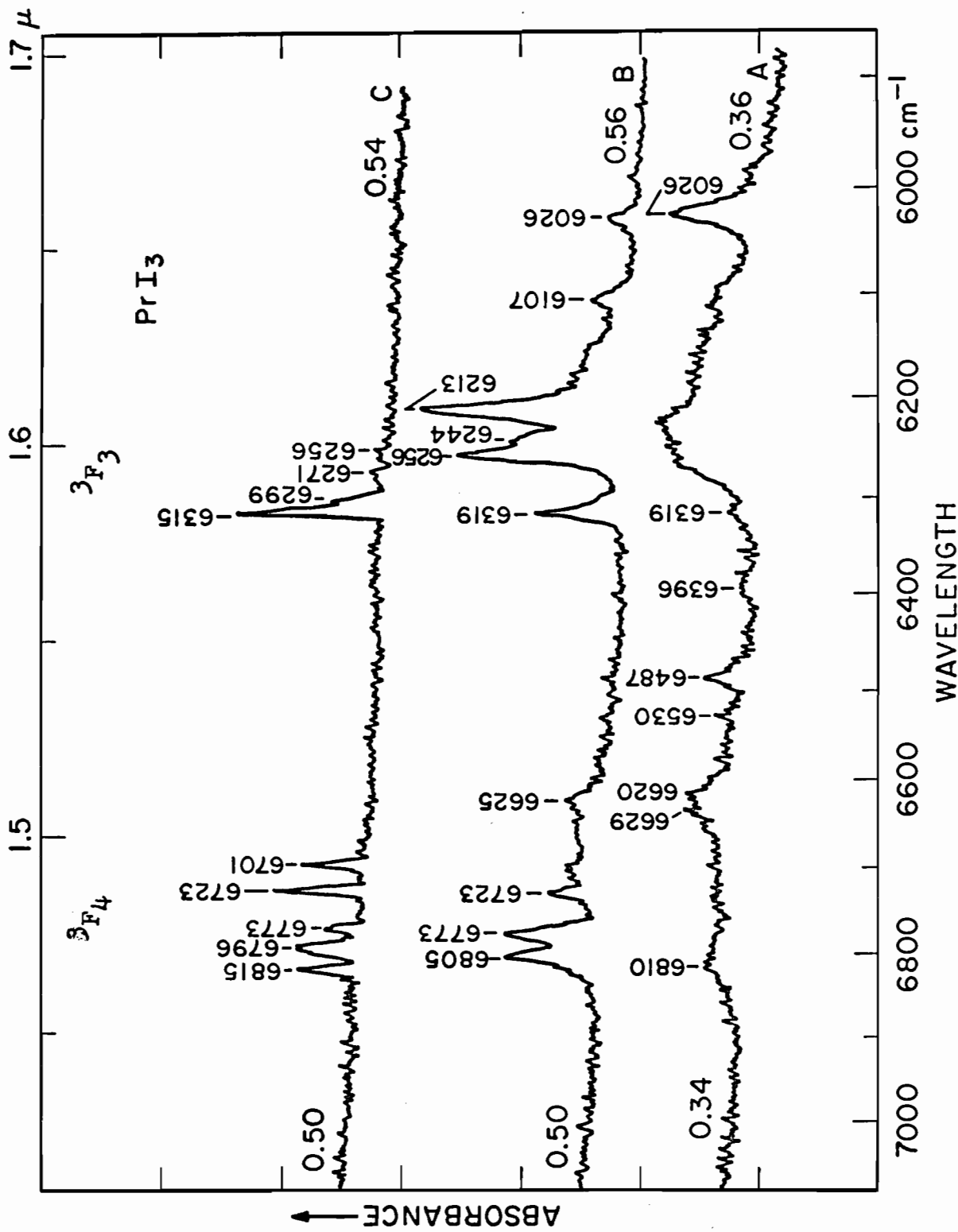


FIGURE III. Absorption spectrum of PrI_3 at (A) 298°K , (B) 77°K , and (C) 4°K in the region from 6000 cm^{-1} to 7000 cm^{-1} .

that is expected to be seen in the $10,000 \text{ cm}^{-1}$ region. The only evidence of the absorption is a very weak set of peaks almost indistinguishable from the noise. This therefore implies that there are strong selection rules governing this transition. It should be remembered that although the levels are assigned specific L'S states they are not pure states and there are spin-orbit interactions. The selection rules state that there will not be transitions between states of different multiplicity. There are singlet states that show absorptions in this spectrum. This is due to the spin-orbit interactions, and therefore the singlet states do have a certain amount of triplet character. The differences in triplet character between each group would be evidenced by the relative intensities of the absorptions.

Figure IV shows the next group, 1D_2 . One hot band is evident and it coincides with the liquid nitrogen peak at $16,396 \text{ cm}^{-1}$. This is 19 cm^{-1} of lower energy than the liquid helium peak at $16,415 \text{ cm}^{-1}$.

Figure V shows the next level, 3P_0 , with one hot band 24 cm^{-1} of lower energy. Since there is only one level in this state, the absorption that is observed is solely from one level in the ground state. This simplifies the interpretation even more because there is only this one level.

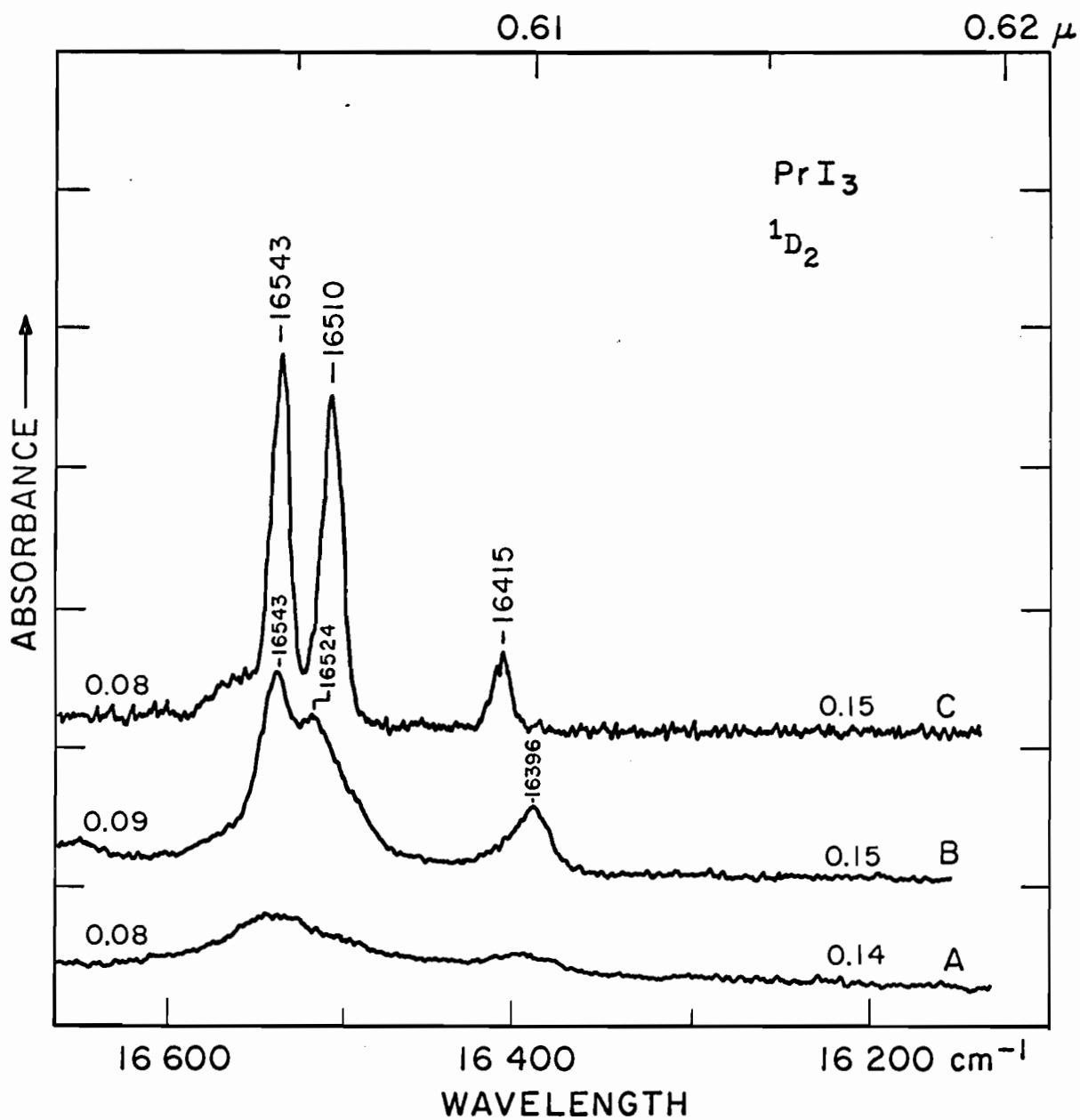


FIGURE IV. Absorption spectrum of PrI₃ at (A) 298°K, (B) ~77°K, and (C) ~4°K in the region from 16200 cm⁻¹ to 16600 cm⁻¹.

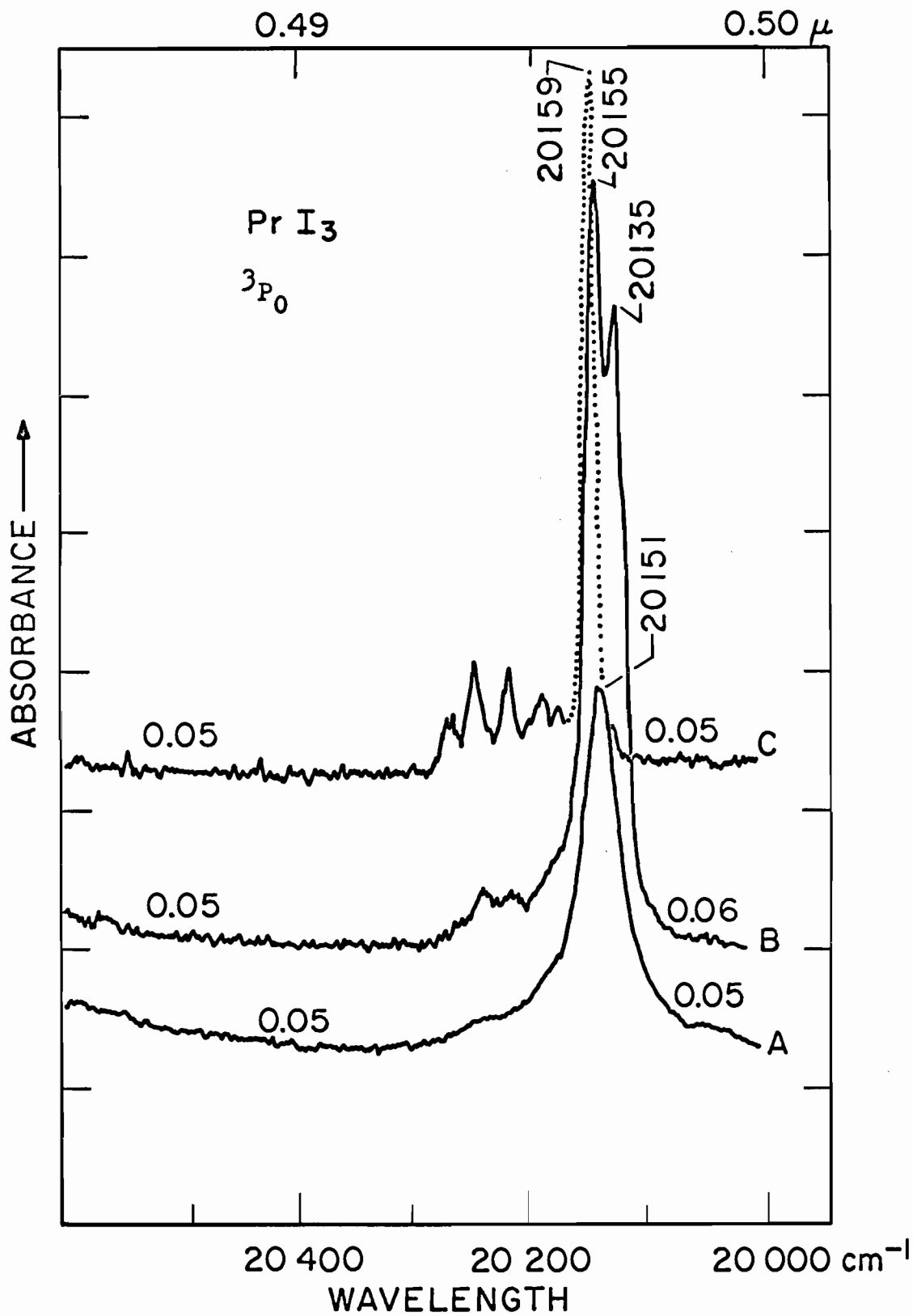


FIGURE V. Absorption spectrum of PrI₃ at (A) 298°K, (B) ~77°K, and (C) ~4°K in the region from 20000 cm⁻¹ to 20400 cm⁻¹.

The next two levels are shown in Figure VI. The first group, 3P_1 , has one hot band at 20719 cm^{-1} which is 26 cm^{-1} of lower energy than the one major peak seen for the group.

There are three hot bands seen in the 1I_6 level. There are two adjacent to the peak at 21047 cm^{-1} , one of 27 cm^{-1} and one of 53 cm^{-1} lower energy. Another hot band is 22 cm^{-1} of lower energy from the peak at 21135 cm^{-1} .

Figure VII shows the last level that can be seen, 3P_2 . There are no hot bands that could be seen in this group.

The one remaining level, 1S_0 , is not expected to be seen because of the absorption edge, analogous to that seen in the chloride⁶ and the bromide⁷, near $25,000\text{ cm}^{-1}$ with an absorbance greater than 2 and rapidly increasing.

From these hot bands a few of the ground state levels can be inferred. These are listed in Table I.

There is reported work on the fluorescence spectrum of the matrix isolated praseodymium iodide.¹¹ Although the results found in the literature should compare with those herein stated, they are shifted to the red more than expected. A graphical representation of the average energies of each J level is shown in Figure VIII. The constant shift to lower energies of each J level as bonds in the crystal become more covalent in nature is

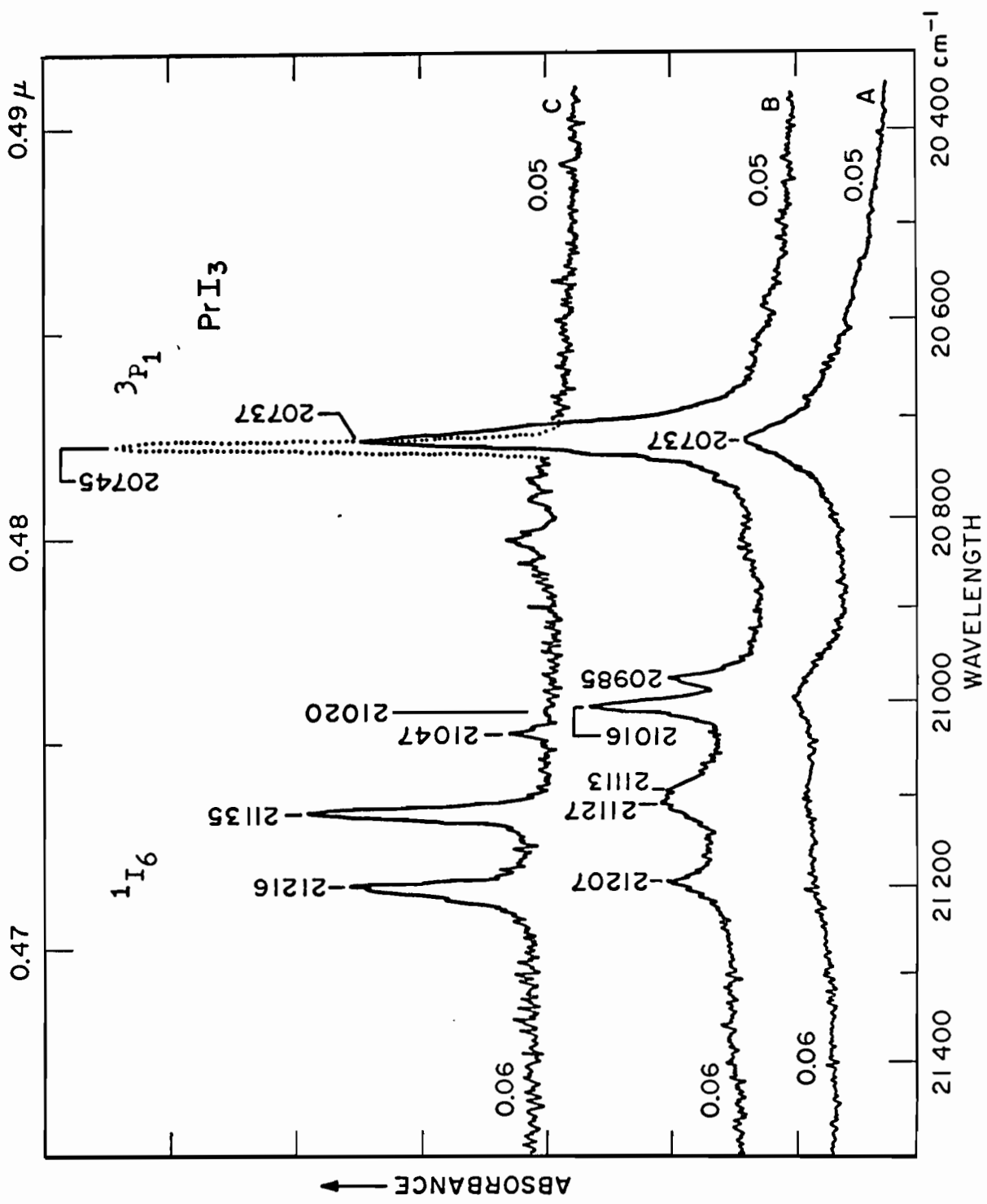


FIGURE VI. Absorption spectrum of PrI₃ at (A) 298°K, (B) ~77°K, and (C) ~4°K in the region from 20400 cm⁻¹ to 21400 cm⁻¹.

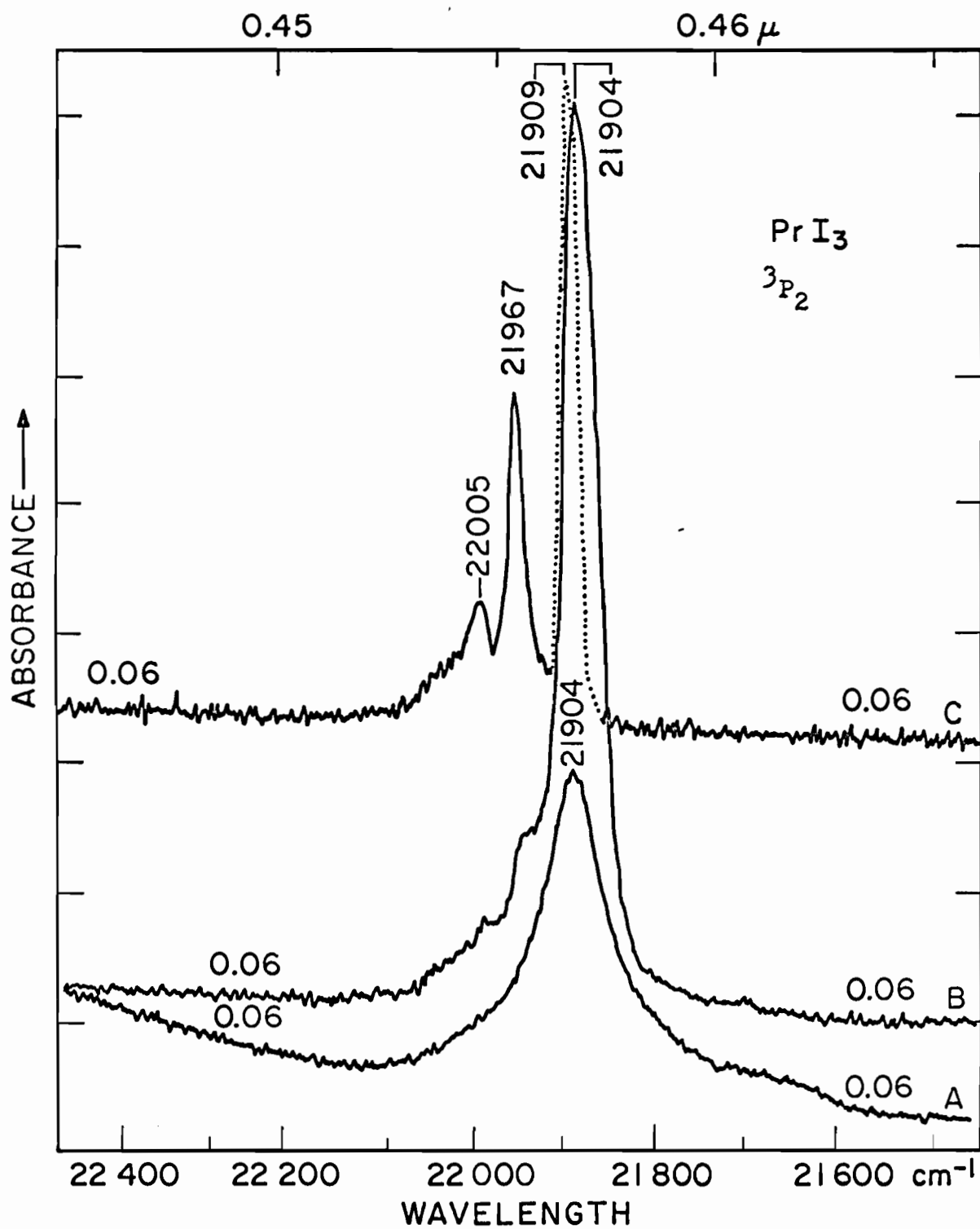


FIGURE VII. Absorption spectrum of PrI_3 at (A) 298°K , (B) $\sim 77^\circ\text{K}$, and (C) $\sim 4^\circ\text{K}$ in the region from 21600 cm^{-1} to 22400 cm^{-1} .

known as the nephelauxetic effect. As can be seen, the absorption spectrum herein reported shows a slight shift from the energies of praseodymium bromide, which are slightly shifted from those of praseodymium chloride. The larger shift reported from the matrix isolated technique is not expected and quite interesting.

The matrix isolated system should show a shift of lesser energy than the praseodymium iodide crystal, because it is essentially just the molecule, and it does not suffer the rigidity and constrictions of the crystal lattice. But this is not the case. In fact it seems as if there is more order in the matrix isolated system than in the crystal.

The absorption spectrum of gaseous praseodymium iodide¹² does show a shift of J levels toward the blue relative to those in the praseodymium iodide crystal, which is consistent with the above argument. Therefore the matrix isolated system is not as simple as first thought, and there is some effect of the matrix on the J level shiftings.

FREE-ION LEVELS in Pr IV

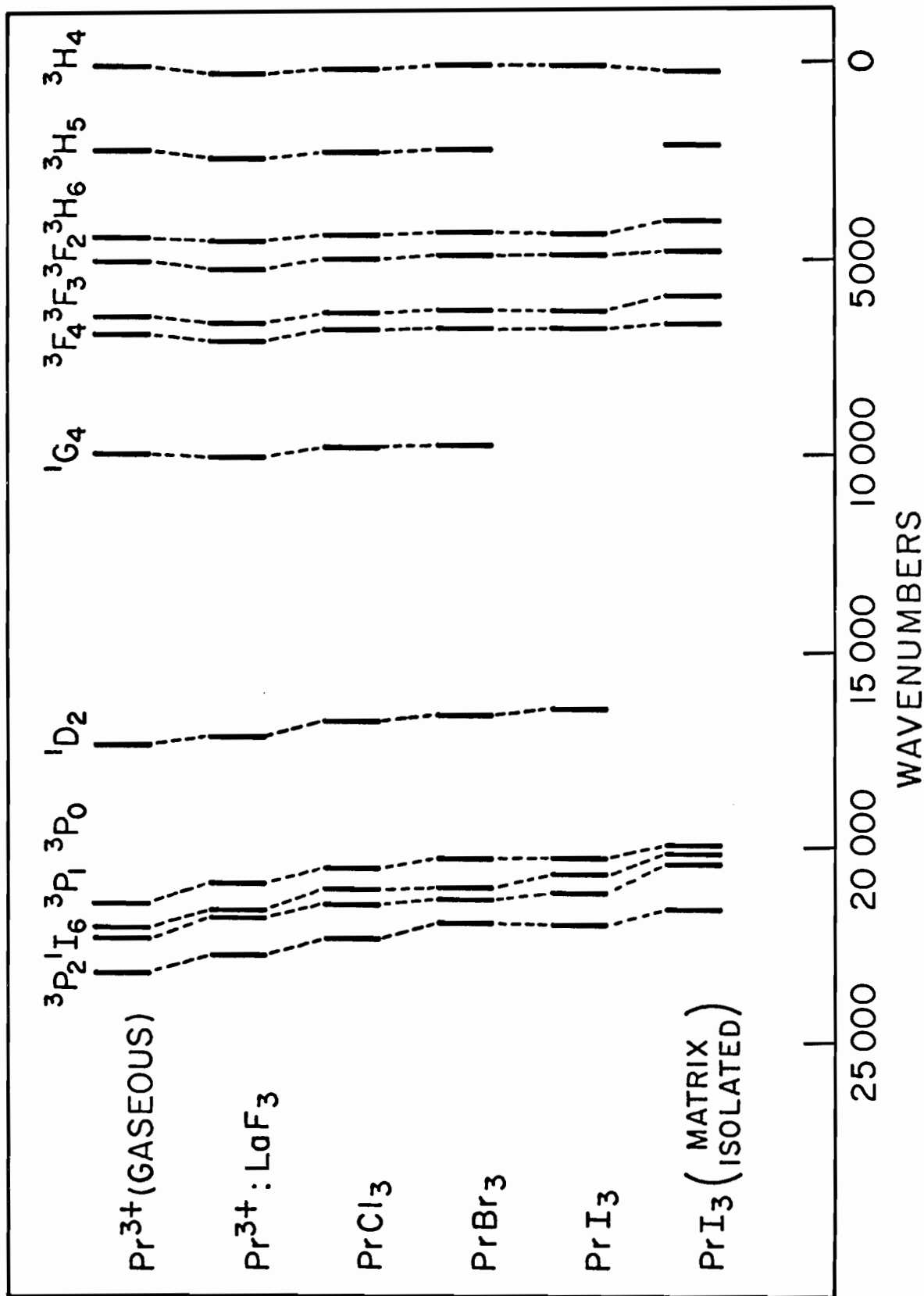


FIGURE VIII.

TABLE I. Energy levels of PrI_3 .

Multiplet levels ($2S+1$) L_J	(cm^{-1}) corr vac	Exptl. center of gravity (cm^{-1})
3H_4	0 (19) (27) (48)	
3H_5		
3H_6	4301 4344 4384 4619	4412
3F_2	4857 4874 4886 4938	4889
3F_3	6256 6271 6299 6315	6285
3F_4	6701 6723 6773 6796 6815	6762
1G_4		
1D_2	16415 16510 16543	16489
3P_0	20159	20159
3P_1	20745	20745

TABLE I. (cont.)

Multiplet levels (2S+1) _{L_J}	(cm ⁻¹) corr vac	Exptl. center of gravity (cm ⁻¹)
¹ I ₆	21047 21135 21216	21133
³ P ₂	21909 21967 22005	21960

FUTURE WORK

A detailed analysis of the absorption spectrum herein reported should be done, including the mathematical computation of the free-ion energy level parameters.

After the parameters have been determined an analysis should be considered to see whether any definite mathematical relationships can be made between, for example, the covalent nature of the bonds and the parameters. With the current amount of data existing for praseodymium this study is quite possible.

Further investigation should be made into the matrix isolated technique used for the fluorescence studies of praseodymium iodide. The current data show a larger shift of the average energies of the J levels than found herein.

EXPERIMENTAL

Synthesis of praseodymium iodide, PrI_3 . Into a piece of quartz tubing approximately 4 cm long and closed off at one end was placed 12 mg of commercially available 99.9% pure praseodymium oxide, Pr_6O_{11} . The oxide was dissolved in enough aqueous hydrogen iodide, HI to fill the tube $\frac{1}{4}$ full. The aqueous HI, of unknown concentration but fairly strong, was made by bubbling gaseous HI directly into deionized water. Commercially available aqueous HI was not used due to impurities that are introduced during manufacturing. The solution was then placed in boiling water for 30 minutes and then evaporated to dryness. A stream of nitrogen was blown over the sample to hasten the process. The tube, now containing hydrated praseodymium iodide, $\text{PrI}_3 \cdot x\text{H}_2\text{O}$, was placed into a piece of 6 mm OD quartz tubing, 25 to 35 cm long, also closed off at one end. This tube was then attached to a vacuum system and evacuated using a mercury diffusion pump. After closing off the system from the pump, 610 torr of HI was introduced into the system. Anywhere from 600 to 700 torr of HI is sufficient. NOTE: Care should be taken that the mercury in the pump never comes in contact with the HI in the system as mercury iodides will spontaneously be formed. The sample, under HI, was then slowly heated in a furnace to $\sim 300^\circ\text{C}$. The temperature was maintained for about 2 hours.

The original white hydrated iodide had now turned to a light green. The HI was frozen out of the system in a liquid nitrogen trap and the water and iodine that had come off of the sample was moved up the tube nearly to the top by moving the furnace along the tube. The furnace was returned to the end of the tube. After allowing the frozen HI to warm, the temperature was increased to $\sim 730^{\circ}\text{C}$. The HI was again frozen out after sustaining the temperature for about 30 minutes and the system was opened to the pump. Under vacuum, the yellow green iodide sublimed onto the sides of the tube and was carefully moved along the tube and concentrated in a region of 10 cm in length. The solid was spread out along this portion of tubing forming a thin film. This length of tubing was then sealed off and separated from the system, so that the solid stayed in an evacuated environment.

Obtaining the spectrum. All spectra were obtained on a Cary Model 14R spectrophotometer, which is capable of high resolution due to double monochromator construction. The iodide, in the quartz tube was affixed to a sample holder and placed into a Dewar flask made for liquid helium temperature measurements. The Dewar flask is a typical commercially available system. Within this Dewar flask, all three temperature range spectra were obtained, utilizing the same area of the sample.

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