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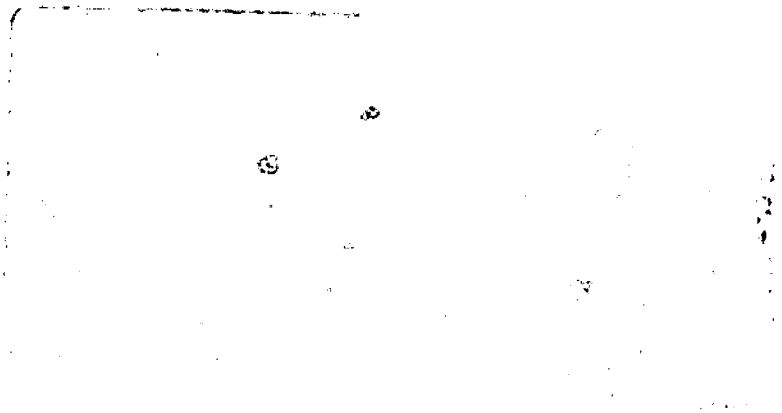

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Contract No. W-7405-eng-48

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John B. Gruber and John G. Conway

February 4, 1961

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ABSTRACT

The polarized absorption spectrum of Am^{+3} in $LaCl_3$ has been studied from 2000A to 16.0μ. In almost every instance the peaks or lines observed are sharp, completely polarized, and appear in definite groupings. Transitions have been observed from the ground level, $^7F_0$, to excited levels of the ground term, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, and $^7F_6$. For the particular point symmetry, C_{3h}, which is consistent with experiment, magnetic-dipole transitions are observed from $^7F_0$ to excited J=1 levels, and forced electric-dipole transitions are observed from $^7F_0$ to the excited crystal-field-split sublevels μ=±2 and 3 of J levels greater than one. A J-level assignment has been made for various groupings in the visible and ultraviolet.

THE POLARIZED ABSORPTION SPECTRUM OF Am^{+3} IN $LaCl_3$*

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INTRODUCTION

Although many investigators[1-3] have reported the solution spectra of Am^{+3}, relatively few papers have appeared in the literature on the solid state sharp line spectra of Am^{+3}. Stover and Conway in 1952 published part of the absorption spectrum of hydrated americium trichloride,[4] and Iakovlev, Gorkenko-Germanov, Zenkova, Razbitnoi, and Kazanskii have reported a study of the absorption spectra of Am^{+3} in the double sulfates of potassium, thallium, rubidium, and cesium.[5] In addition, Gruen, Conway, McLaughlin, and Cunningham have observed the fluorescence spectrum of Am^{+3} in $LaCl_3$.[6] However, although essentially all of the energy regions containing sharp line spectra have been observed either in absorption or fluorescence, and the theory of analysis has been discussed--notably by Hellwege[7] and Judd[8] for Eu^{+3}, the rare earth analog, there has been to date no serious analysis of the solid-state spectra of Am^{+3}.

A detailed analysis of the energy spectrum is very much needed since it would reveal the multipolarity of the transitions observed and yield information on the quantum nature of the states of the free ion. In addition, a knowledge of the symmetry character, and the relative position of the crystal quantum sublevels of a crystal-field split J level, would give us some indication of the degree to which the field-free levels of Am^{+3} are split by the crystal field.

PREPARATION OF SINGLE CRYSTALS

Single crystals of $AmCl_3$-$LaCl_3$, containing Am^{+3} in amounts from 0.1 to 10% by weight, were prepared in the following manner. A known volume of Am^{+3} (americium-241; half life: 458 yr) in 2.0 M HCl was added to a quartz sublimation tube. The ion-exchange-purified Am^{+3} was found to be spectroscopically pure, and an α assay of the solution gave a reliable value for the concentration of americium. The solution was slowly evaporated on a vacuum line and anhydrous $AmCl_3$ formed by heating the hydrate slowly in the presence of dry HCl. After the tube was flushed repeatedly with dry argon, a known quantity of spectroscopically pure anhydrous $LaCl_3$ was added. The mixture was then thoroughly degassed and melted to form a solution. The sublimation and single-crystal growing techniques employed were quite similar to those reported by Sayre, Sancier, and Freed,[9] and Gruen, Conway, and McLaughlin.[10] The intense radioactivity of americium-241, as well as the hygroscopic nature of anhydrous $LaCl_3$, requires that the crystal be mounted in a dry-nitrogen-atmosphere box suitably prepared for radioactive work.

In order to determine whether the $AmCl_3$-$LaCl_3$ mixed crystal system preserved C_{3h} symmetry about the cation sites, anhydrous $PrCl_3$ was added to the mixture before the single crystals were grown. When the absorption spectrum of the single crystal was taken, the Pr^{+3} lines were found to have the same polarization and energy positions as reported by Sayre, Sancier, and Freed.[9] We conclude, therefore, that the symmetry about the Pr^{+3} ion is similar to that reported by Sayre, Sancier, and Freed, who had no Am^{+3} in their crystals, and that the symmetry about the americium ions very probably is C_{3h}. Also, the observed polarization spectrum of $AmCl_3$-$LaCl_3$ is consistent with the selection rules for C_{3h}.

SPECTROGRAPHIC EQUIPMENT

The absorption spectrum of the single crystals was taken with a Jarrell-Ash Wadsworth-mount 3.4-m spectrograph. Two gratings were used in this instrument--one with 7,500 lines per inch and another with 15,000 lines per inch. In the first order, the reciprocal linear dispersion was 10.1 A/mm and 5.3 A/mm respectively. Crystals were maintained at selected temperatures of 77°K (liquid nitrogen) and 4°K (liquid helium) in quartz and pyrex dewars.

Light sources included an air-cooled high-pressure mercury lamp (BH6), a water-cooled, high-pressure mercury lamp (AH6), a 100-watt tungsten lamp, and a commercially available Kistiakowsky-type hydrogen-discharge lamp. Three types of polarizers were employed: a Nicol, an Ahrein with ultraviolet-transmitting cement, and a Wollaston. Iron and mercury lines served as wavelength references, and the photographic plates were measured on a precision screw-type comparator.

The solution spectrum of Am^{+3} in 0.2 M DCl-D_2O was taken on a Cary Model 14 spectrophotometer which was calibrated at the factory with an AH4 mercury arc. Infrared spectra were taken on a Beckman IR-5 infrared spectrophotometer and a Perkin-Elmer Model 112-U spectrometer.

THE POLARIZED ABSORPTION SPECTRUM

The polarized absorption spectrum of Am^{+3} in $LaCl_3$ was studied from 2000A to 16.0μ. In almost every instance, spectral lines observed are sharp and completely polarized. Definite groupings of lines appear in every portion of the spectrum (see Fig. 1), and an analysis of the crystal-field splitting, which will appear shortly, indicates these groupings can be assigned to a given J manifold.

For the particular point symmetry, C_{3h}, which is consistent with experiment, the polarized transverse and the axial spectra indicate forced electric-dipole as well as magnetic-dipole transitions. Magnetic-dipole transitions are observed from $^7F_0$ (the ground level) to excited J=1 levels, and forced electric-dipole transitions are observed from $^7F_0$ to the excited crystal-field-split components $\mu=\pm 2$ and 3 of J levels greater than one. The quantum numbers, μ, have been defined by K. H. Hellwege,[7] and the selection rules have been worked out by K. H. Hellwege,[7] and Sayre, Sancier, and Freed.[9]

Many of the sharp lines in the visible and near-ultraviolet spectra split into two components in a Zeeman field. Thus, from the g values and the total number of allowed transitions to a given J manifold, we can establish a value for the field-free J level. The sublevels split in a magnetic field are indicated in Table I, as is a possible J-level assignment for the various groupings. Such polarized data, consistent with Am^{+3} in a C_{3h} point-symmetry site, identify the J levels of 1, 2, and 3 uniquely, and larger J values only indicatively. Complications in the analysis of the Am^{+3} spectrum result from the intermediate coupling effects and the intermixing of crystal-field components of a given J level with those of J levels having nearly the same energy.

Table I. Visible and ultraviolet absorption spectra, polarization, and intensities of Am^{+3} in $LaCl_3$

Wave length(A) (in air) 77°K	Wave numbers (in vacuum) 77°K	P	I	Comments
5119.1	19,529	σ	7[a, b]	Intense, broad-line complex group. Could be a single state or several states of approximately the same energy.
5093.0	19,630	σ	10[c]	
5089.6	19,642	σ	4[d]	
5083.2	19,667	π	8[d]	
5075.0	19,699	π	10[c]	
4623.1	21,624	σ	5[b, e]	Broad; has unresolved structure.
4561.5	21,916	σ	8[a, f]	J=2
4432.4	22,555	π	6[a, g]	A possible J=3
4305.0	23,222	σ	6[a, b]	
4298.7	23,256	π	4[a, g]	
4262.5	23,454	π	3[d]	A complex structure. Could be a J=4, 5, 6, or 7
4260.0	23,468	π	3[h]	
4257.3	23,482	π	3[e]	
4245.2	23,549	π	7[h]	
4242.5	23,564	π	7[h]	
4239.9	23,579	π	7[h]	
4232.2	23,622	σ	7[d]	
4216.0	23,713	σ	6[i]	
4163.5	24,012	σ	4[a, f]	J=2
4041.9	24,734	π	5[g, j]	J=4, 5, 6, or 7
4038.8	24,753	σ	6[f, j]	
3968.2	25,193	σ	4[g, j]	
3963.8	25,221	π	4[f, j]	

Wave length(A) (in air) 77°K	Wave numbers (in vacuum) 77°K	P	I	Comments
3795.3	26,344	σ	9[b, d]	Intense, sharp line complex group. Probably due to two or three J levels of approximately the same energy.
3775.4	26,480	π	10[i]	
3773.0	26,497	π	4[d]	
3771.8	26,505	π	4[d]	
3765.0	26,553	σ	8[b, h]	
3759.5	26,592	σ	3[b, h]	
3754.3	26,629	σ	5[a, f]	
3745.7	26,690	π	3[d]	
3740.5	26,727	π	3[h]	
3732.6	26,783	σ	4[b, i]	
3658.2	27,328	σ	8[a, f]	A possible J=2 and J=4, 5, 6, or 7
3632.7	27,520	σ	5[a, f]	
3629.8	27,542	π	7[a]	
3627.9	27,556	σ	6[a, f]	
3574.6	27,967	π	2[i]	
3418.5	29,244	π	4[e]	J=8
3410.3	29,315	σ	4[e]	
3388.2	29,506	σ	4[e]	
3380.9	29,569	σ	4[e]	
3377.3	29,601	π	6[e]	
3155.0	31,687	σ	6[j]	J=1
3153.2	31,705	π	6[j]	
3077.8	32,481	π	4[d]	J=3
3067.7	32,588	σ	4[a]	
3060.1	32,669	π	4[d]	

Wave length(A) (in air) 77°K	Wave numbers (in vacuum) 77°K	P	I	Comments
2994.4	33,386	π	3[j]	
2993.6	33,395	σ	3[a]	
2986.4	33,475	σ	3[j]	
2939.2	34,013	σ	6[a]	A possible J=4, 5, 6, or 7
2934.0	34,073	π	10[d]	
2916.4	34,279	σ	7[a]	
2914.0	34,307	π	7[a]	

[a] Line width: 0.3 to 0.5A.

[b] Line broadened in magnetic field.

[c] Unresolved band structure.

[d] Line width: 0.5 to 1.0A.

[e] Line width: 2.0 to 5.0A; possible unresolved doublet.

[f] Absorption line split into two observable components in applied magnetic field.

[g] Line not broadened in magnetic field.

[h] Line width: 1.0 to 1.5A.

[i] Line width: 1.5 to 2.0A.

[j] Line width: 0.1 to 0.3A.

THE ^7F LEVELS

No absorption peaks are observed between 16.0 μ and 4.82 μ. The $^7F_1$ grouping consists of transitions from the ground level $^7F_0$ ($\mu=0$) to the sublevels $\mu=0$ (4.82μ) and $\mu=\pm1$ (4.55μ) of the $^7F_1$. These two peaks in the infrared have the proper polarized transverse spectrum and axial spectrum which indicate magnetic-dipole transitions (see Fig. 2 and Table II). Since these transitions appear in the region where quartz absorbs, the sample was enclosed in a tube having AgCl windows. The spectral region between 3.5μ and 16.0μ was observed at room temperature.

The position of the $^7F_2$ level in the absorption spectrum is somewhat uncertain. In this rather high symmetry only one forced electric-dipole transition is allowed: $^7F_0(\mu=0)$ to $^7F_2(\mu=\pm2)$. A sharp peak at 2.75μ was observed to have the proper polarized transverse spectrum at 4°K and 77°K. However, this peak is close to an absorption peak of an impurity in the quartz dewar windows, and a water band at 2.9μ which has a very large molar-extinction coefficient. The Am^{+3} spectrum in this region was never obtained completely free of these peaks.

The polarized absorption spectrum of $^7F_3$, which appears in Fig. 3, was taken at 77°K and 4°K on a Perkin-Elmer instrument. This same multiplet was observed when several milligrams of anhydrous $AmCl_3$ were dissolved in D_2O-DCl, and the spectrum taken from 1.0 to 2.5μ on a Cary 14 spectrophotometer. When the blank was subtracted from the Am^{+3}-solution spectrum, a peak and a shoulder were observed near 1.85μ. Also single crystals of $LaCl_3$ containing Am^{+3} still in the original quartz growing tube were studied because the samples were completely free from water.

Table II. Infrared spectrum, polarization, and transitions of Am^{+3} in $LaCl_3$

Wave length(A) (in air) 77°K	Wave numbers (in vaccuum) 77°K	P	I	Trans. from $^7F_0(\mu=0)$ to:	Possible J-level assign-ment	Comments
48,200	2074	π, a	4	0		Magnetic-dipole transitions to this level from $^7F_0$.
45,500	2197	σ	5	±1	1	
27,500	3635	σ, a	3	±2	2	Electric-dipole transitions. Position of this level is some-what uncertain.
19,200	5208	π	3	3		Electric-dipole transitions
18,840	5307	σ, a	6	±2	3	
18,730	5340	π	3	3		
10,766	9282	σ, a	9[a]	±2		Electric-dipole transitions. This grouping was ob-served in the photo-graphic region of the infrared.
10,485	9535	π	10[a]	3	4	
10,474	9545	σ, a	8[a]	±2		
10,132	9867	π	5[b]	3		
8246	12,123	σ, a	3[a]	±2		Electric-dipole transitions. Several lines are rather broad; how-ever, complete polarization was observed.
8159	12,253	π	10[a]	3	5	
8144	12,275	π	8[c]	3	and	
8123	12,307	σ, a	10[c]	±2	6	
8060	12,404	σ, a	10[a]	±2		
8055	12,411	π	5[b]	3		
7956	12,566	π	5[a]	3		
7950	12,575	σ, a	4[a]	±2		

[a] Line width 3 to 8A.

[b] Line width 1 to 3A.

[c] Line width 8 to 15A: unresolved band structure.

The $^7F_4$, $^7F_5$, and $^7F_6$ multiplets may be studied in the photographic region of the infrared. Four clearly polarized lines (2σ and 2π) were observed at 1.05μ, and as few as eight lines were seen between 0.79 and 0.82μ (see Fig. 1). At 77°K and 4°K the spectrum is sharp, with only several broad lines. Since selection rules alone cannot distinguish between a J=4, 5, or 6, the designation given in Table II is based on the crystal-field-splitting calculations that will appear shortly.

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*This work was done under the auspices of the U. S. Atomic Energy Commission.

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FIGURE LEGENDS

Fig. 1. (A) The ultraviolet and visible polarized absorption spectra of Am^{+3} in $LaCl_3$ taken at 77°K and 4°K. Here the reciprocal linear dispersion is 5.25 A/mm. (B) The infrared polarized absorption spectrum of the 8000A groupings (the $^7F_5$ and $^7F_6$ multiplets) taken at 77°K. (C) The infrared polarized absorption spectrum of the 10,400A group (the $^7F_4$ multiplet) taken at 77°K. Here the reciprocal linear dispersion is 10.1 A/mm.

Fig. 2. The polarized absorption spectrum of the $^7F_1$ grouping of Am^{+3} in $LaCl_3$. The unpolarized spectrum is on the left, and the σ and π transverse spectra on the right.

Fig. 3. The polarized absorption spectrum of the $^7F_3$ grouping of Am^{+3} in $LaCl_3$. The σ transverse spectrum is given on the left and the π spectrum on the right. The spectra were taken at 77°K.

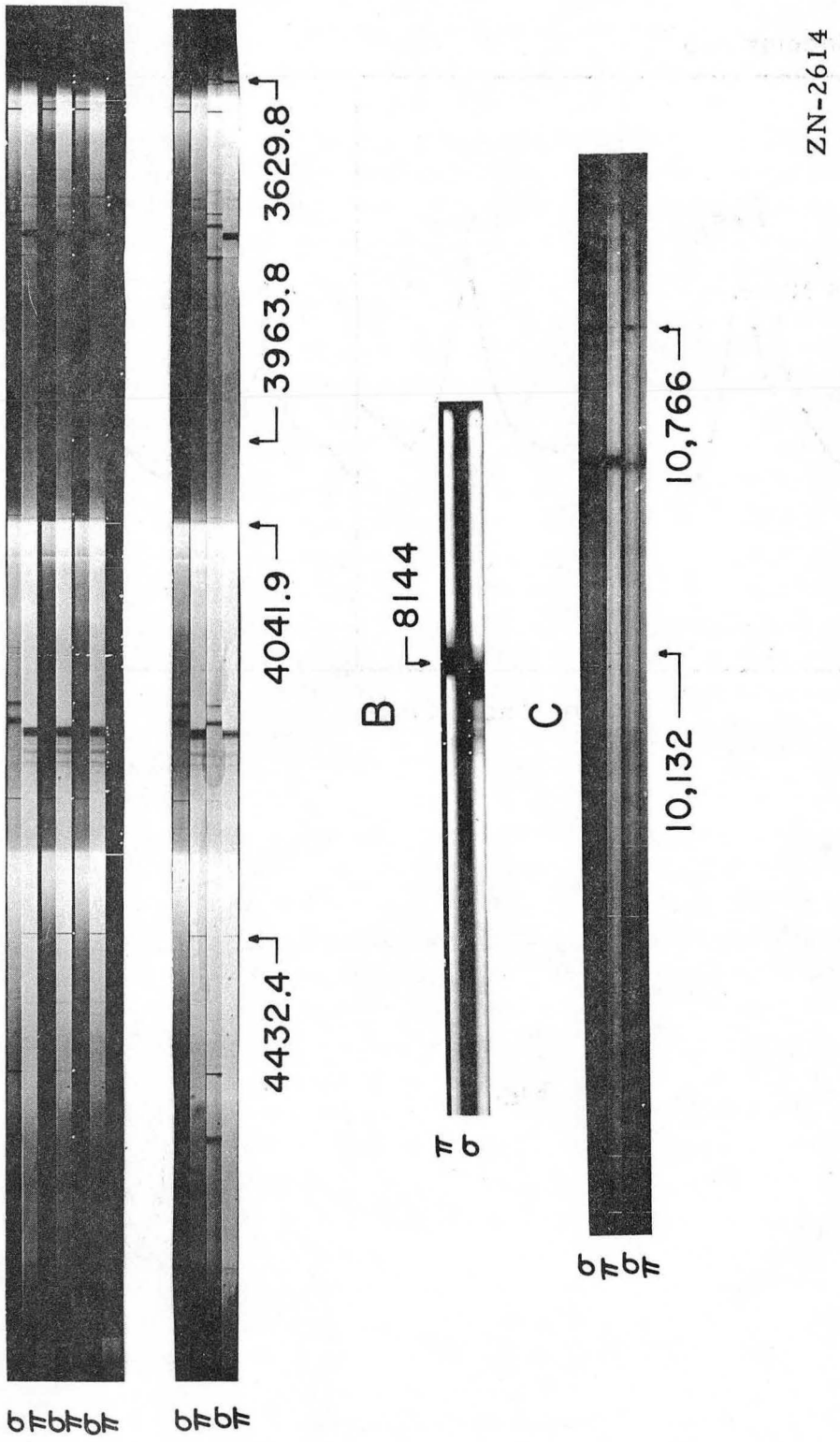
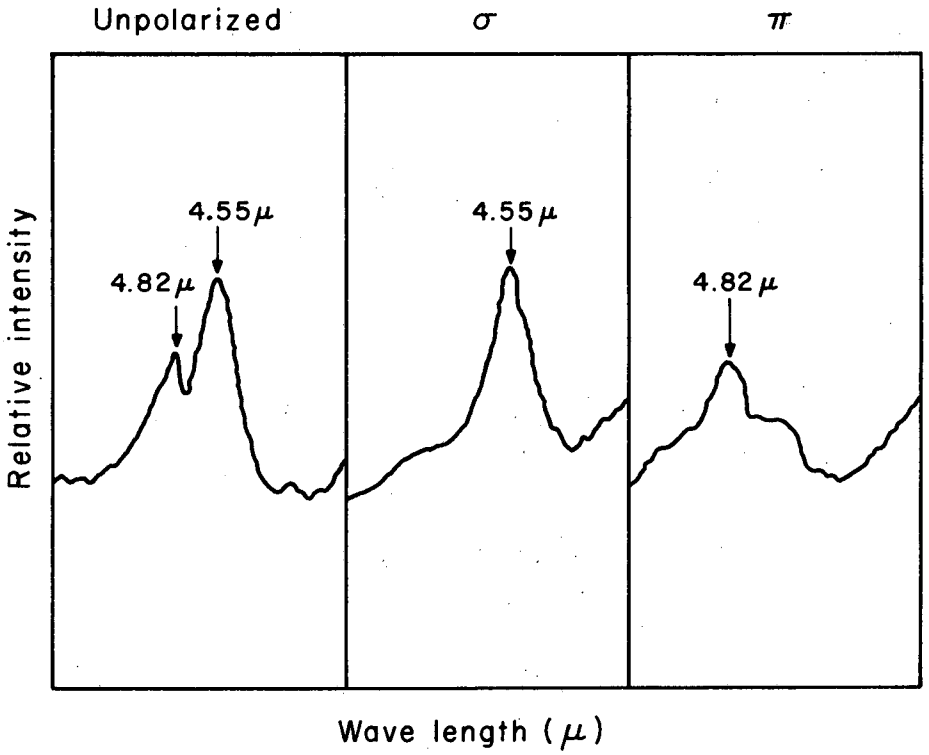


Fig. 1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π
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4.82μ
4.55μ
4.82μ
Wave length (μ)
MU-22035

Fig. 2

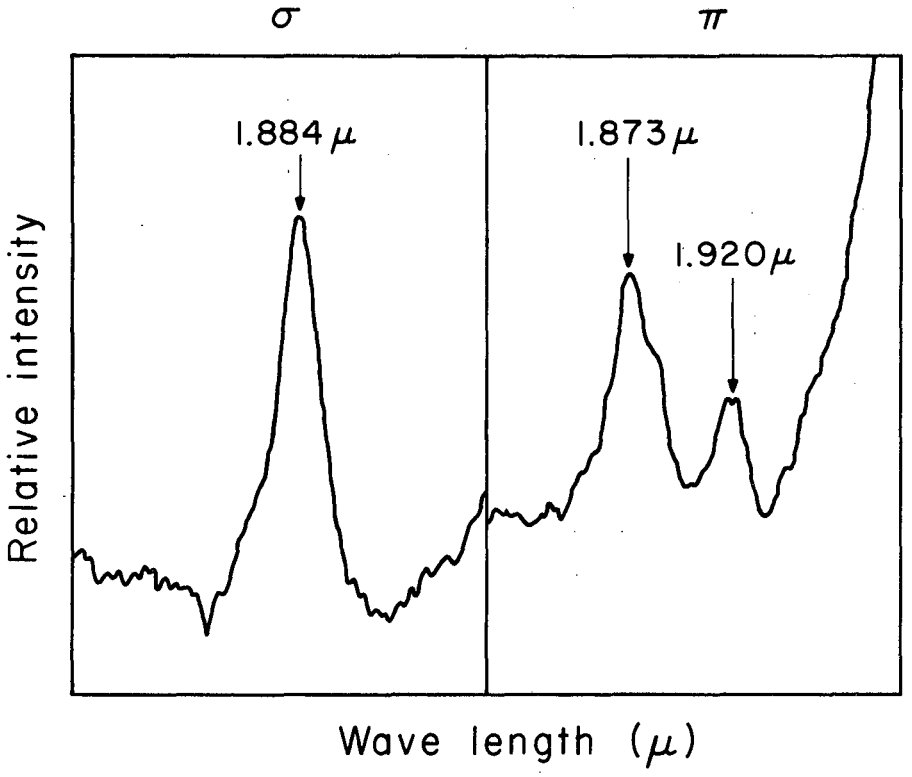
σ
π
1.884 μ
1.873 μ
1.920 μ
Relative intensity
Wave length (μ)
MU-22034

Fig. 3

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