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Photophysics of Aqueous $Pt(CN)_4^{2-}$

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Abstract

A detailed study of the non-Beer's law behavior of the absorption features of the u.v. spectrum of aqueous $K_2Pt(CN)_4$ and $BaPt(CN)_4$ allows a more definitive set of excited state assignments than previously possible for the monomer. Concentration dependence, quenching, and lifetime studies of the several room temperature emission features allow a distinction between fluorescences and phosphorescences, and a probable assignment as to the oligomers responsible. Two excited state absorptions are found, and a long lived chemical transient.

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Introduction

The tetracyanoplatinites, known for well over a hundred years, have been variously studied by quite a number of investigators. Our interest, however, was stimulated by recent work of Gliemann, Yersin, and co-workers[1-9] who studied the low temperature emission from various salts of $Pt(CN)_4^{2-}$. They concluded that the stacking which occurs in the crystal leads to a splitting of the platinum z-axis orbitals, the emission properties being sharply dependent on the Pt-Pt distance, R. Our interest was in whether stacking association might occur in solutions and, if so, in the consequent photophysical and photochemical behavior.

Emission from aqueous solutions of the Ba, Mg, and K salts is well known,[10-15] the most recent work being that of Rossiello and Furlani[16] and Webb and Rossiello.[17] The matter of possible oligomer formation in solution has not been directly studied, however, nor have there been any clear assignments of the emission features. Day[18,19] did conclude that since the tetracyanoplatinites form insulating crystals in which the molecular units are clearly distinguishable, it seems a priori probable that the lowest crystal excited states are neutral Frenkel excitons formed from   simple molecular transitions coupled by an intermolecular interaction potential. The simplest approximate treatment is by Davydov theory.[20] One predicts a shift to lower energy of the transition which is polarized along the Pt-Pt axis, or the z-direction, proportional to R^{-3} (as observed).

The absorption spectrum of $Pt(CN)_4^{2-}$ has been analyzed theoretically by various authors,[21-33] but only one paper has specifically attempted a treatment of the dilute aqueous solution spectrum.[29] The spectrum is

complex; there are four distinct but non-symmetric features which may be deconvoluted into six gaussian components.

Experimental

Materials. - The tetracyanoplatinite salts were prepared by a modification of a literature method.[34] To platinum(II) chloride (Alpha Inorganics) was added a 20% excess of potassium cyanide dissolved in a minimum of water. The resulting solution was filtered and the filtrate evaporated at 60 to 80 °C to about half the volume (12 cm^3 for 5 g PtCl$_2$) and allowed to cool. The resulting crystals could be recrystallized from dilute aqueous potassium cyanide. Ba[Pt(CN)$_4$].4H$_2$O was prepared by adding a slight excess of barium chloride to a warm concentrated solution of the potassium salt of the complex, filtering off any Ba(OH)$_2$ that formed. Crystals separated on cooling, and were recrystallized from dilute aqueous barium chloride. Other chemicals used were of reagent grade.

Absorption spectra. - Routine spectroscopic measurements were made by means either of a Cary model 14R or a Beckman Acta MVI recording spectrophotometer. In order to examine the concentration dependence of the more intense absorption bands, however, it was necessary to use a micrometer, variable path-length cell (Beckman-Research and Industrial Instruments Co., Ltd., England, model BC-14). Pathlength settings would be read to 0.0005 cm directly and to 5x10^{-5} cm with the vernier. The scale was calibrated by means of measurements on standard potassium chromate solutions. The cell could be thermostatted to ± 1 °C.

Emission spectra. - Most of the measurements were made with the use of an Aminco model 4-8400 excitation grating monochromater and model 4-8401 emission grating monochromator. Excitation was by a 200 W Xe-Hg

lamp and the detector was a Hamamatsu R446 photomultiplier tube (PMT).

Excitation spectra were run on a Perkin-Elmer model MPF-3 spectro-
fluorimeter (R446 PMT)[35] or a Perkin-Elmer model 650-10S instrument equipped
with either a R454 or a R928 PMT.   All emission spectra are uncorrected.

Time-resolved measurements. - Emission lifetimes and time-resolved
emission spectra were obtained by means of a Korad pulsed Nd-glass
laser system previously described.[36,37] Typically, a 20 nsec pulse of
353.3 nm wavelength was used for excitation, and a 14 stage RCA 7265 PMT
as detector. Suitable filters were used to screen out scattered light.
Two sets of emission spectra were obtained with the use of an optical
multichannel analyzer (OMA) detector (courtesy of EG and G PARC) which
included a model 1205A OMA, model 1211 high frequency pulse generator,
and model 1205B silicon intensified vidicon (SIT). Transient absorption
spectra were determined with the use of a monitoring beam at right
angles to the excitation pulse, again as previously described.[37,38]
A standard polaroid film was used to verify the polarization of the
emissions. The transmission of crossed polaroid films varied with wavelength,
but was a maximum of 0.4%.

Results

Absorption spectra. - The results of a series of measurements using
the micrometer cell are shown in Fig. 1. The features of interest are
the lack of concentration dependence of the peak at 280 nm and the
strongly non-Beer's law behavior of the long wavelength tail, which
grows to a strong shoulder in 0.635 M $K_2Pt(CN)_4$. The extinction coefficients
in the figure are apparent ones, based on the Pt(II) formality, C. If
the long wavelength feature is due to a single oligomer formed according

to the equilbrium

$$n \ Pt(CN)_4{}^{2-} \quad \underset{=}{K} \quad [Pt(CN)_4{}^{2-}]_n \quad , \quad\quad\quad (1)$$
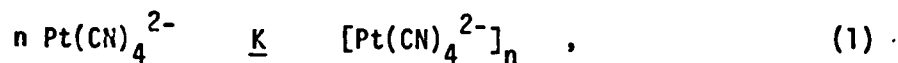
then if most of the complex is monomer, the apparent extinction coefficient
of the long wavelength region should be given by $\varepsilon_{app} = \varepsilon_n K C^{n-1}$ where
ε_n is the extinction coefficient of the oligomer. As shown in Fig. 2,
a satisfactory fit was obtained with $(n-1) = 2$ or $n = 3$, so that trimer
formation is indicated.

The apparent extinction coefficients at 366 nm for a 0.236 formal
solution obey a linear Arrhenius plot, with a slope corresponding to
a ΔH for reaction (1) of - 7.2 kcal mole^{-1}. Although not studied in
detail, increasing ionic strength led to increasing ε_{app}, interpreted
as increasing association, as might be expected.

It was of interest to look for non-Beers law behavior in the rest
of the absorption spectrum. The results are shown in Fig. 3. $Ba[Pt(CN)_4]$
was used because qualitative indications were that K for association was
larger with Ba^{2+} as the counter ion that with K^+. It was thus possible
to work with lower concentrations, a necessity to avoid reaching the
limit of the micrometer cell. That is, the intensity of the 216 peak is
so large that a Beers law study would have been inaccurate if the potassium
salt had been used. As may be seen in the figure, the intensity of both
the 216 nm and the 255 nm peaks is reduced at higher concentrations,
while that of the 230 nm peak is unaffected. The fractional reductions
in the former peaks are not the same, indicating that oligomer absorption
does not go to zero or that more than one component is present, only one
of which is concentration sensitive. The latter is the more likely
possibility; Mason and Miller[10] do conclude that both features should
be split into pairs of Gaussian components. The actual data are as

follows. For the dilute solution ϵ_{app} is 2.30×10^4 at 216 nm and 1.19×10^4 at 255 nm, in $M^{-1}cm^{-1}$ units, while for the concentrated solution the values are 19,650 and 10,190, respectively. The dashed curve in the figure indicates what the absorption spectrum might be for an oligomer-only solution.

Emission spectra. - The emission shown by aqueous $Pt(CN)_4^{2-}$ is quite complex in its behavior. As illustrated in Fig. 4, the spectrum is concentration dependent. The feature around 455-460 nm, labelled II, is barely evident with a 0.56 M solution, strengthens with 0.70 M solution, and becomes an actual maximum if the ionic strength is raised.[39] The emission is evidently associated with some oligomer. Feature IV, at 350 nm, is observed with 313 nm excitation; its concentration dependence was not studied because of absorption problems. Note that at 313 nm excitation feature III, at 410 nm is unchanged from 366 nm excitation, while feature II is essentially absent, presumably because of the low concentration used. Feature I is shifted to shorter wavelengths relative to its position with 366 nm excitation. Finally, there is an indication of a shoulder on the long wavelength side of feature I, roughly in the 550 nm region.

Some of the above observations have been reported previously. Khvostikov[10] saw an emission at 525 nm with a resolved shoulder at 555 nm, and Rossiello and Furlani[16] found emissions at 410 and 552 nm. The two sets of authors thus cover our features Ia, I, and III. Features II and IV appear to be newly observed in this work.

In a more quantitative investigation of concentration dependence, we find that feature III at 410 nm (with 366 nm excitation) varies linearly with c^4, with zero intercept, over the range 0.392 to 0.560 M. This behavior contrasts with the conclusion of Rossiello and Furlani

that the 410 emission is due to dimer formation. These authors, however, do not give their basis for this conclusion.[40] The peak maximum in the 480-530 nm region shifts with concentration, note Fig. 13 of Ref. 38, unlike the case with the 410 nm peak. The peak intensity showed no simple power dependence of formal concentration, however; log-log plots were curved, of slope around five.

As in the case of feature I of the absorption spectrum, the emission intensities were temperature dependent, decreasing with increasing temperature, as would be expected if they were due to one or another oligomer. The 410 nm emission (366 excitation) gave a slightly curved Arrhenius plot for data over the range of 2 - 25 °C (about 0.24 M solutions), of average slope corresponding to a heat of oligomer formation of - 9.0 kcal $mole^{-1}$. The data for emission in the 500-530 nm region were also temperature dependent, again gave a slightly curved Arrhenius plot, of slope corresponding to a heat of oligomer formation of about -14 kcal $mole^{-1}$, or significantly larger.

Excitation spectra were also obtained. First, as evident in Fig. 4, the emission spectra are excitation wavelength dependent. Figure 5 illustrates this effect in more detail.[41] Clearly, several components are present. There is one at 445 nm, strongest with 300 nm excitation, another at about 465 nm, strongest with 320-330 nm excitation, and another in the region of 485-490 nm, strongest with 340 nm excitation. A weak feature is seen at around 525 nm.

Figure 6 shows a direct excitation spectrum taken under special conditions. The longer wavelength emissions have a relatively long lifetime (see further below) and, as to be detailed in another paper, are quenchable by dissolved oxygen and by NO_2^- ion. These emissions will be labelled as phosphorescences; the remaining ones will be called

fluorescences. Figure 6 shows the excitation spectrum of the 410 nm feature
(closer to 408 now) under complete phosphorescence quenching conditions.
The excitation centers at 335 nm. The solid line in the figure shows
the unquenched portion of the emission; we regard the shoulder around
460 nm as real, that is, we consider it to be a fluorescence component
and not due to incompletely quenched phosphorescence.

Emission lifetimes and time-resolved spectra. - Table I summarizes the
average measured phosphorescence lifetimes for a series of concentrations
and for both the potassium and the barium salts. Note that in each case
a single lifetime, τ, is observed. There is a clear concentration effect,
the lifetime increasing with increasing concentration. There is no sig-
nificant variation in τ with emission wavelength, however. Thus for
the 0.26 M solution of the potassium salt, τ was 548 nsec at 560 nm and
555 nsec at 575 nm (353 nm excitation). This lack of wavelength
dependence contrasts with the data of Tkachuk and Tolstoi[13] which showed
τ values in 77 K frozen solutions which ranged from 30 nsec at 470 nm
to 1.2 μsec at 520 nm. However, our emissions labelled II and III in
Fig. 4 were prompt at room temperature (< 9 nsec). One or another of
our observed emissions may correspond to their 30 nsec emission at
77 K.

Time resolved emission spectra are shown in Fig. 14 of Ref. 38. One
spectrum, collected during the first approximately 30 nsec following the
353 nm excitation pulse with 0.15 M $K_2Pt(CN)_2$) shows two peaks, corresponding
to features II and III in Figs. 4 and 6. A second spectrum, taken
with a 200 nsec delay, clearly shows only feature I as a broad emission
centered at 520 nm with a possible short wavelength shoulder.

Polarization. - Some preliminary experiments were carried out to determine the polarization of the emissions, as given by

$$P = (I_z - I_{xy})/(I_z + I_{xy}) \qquad (2)$$

Here, z is the direction of polarization of the exciting pulse. The observed P for 0.0991 M Ba[Pt(CN)$_4$] was 0.54 for 410 nm emission, 0.49 for 440 nm emission, and 0.275 for phosphorescent emission at 512 nm. The general implication of the results (see Refs. 10,42) is that the fluorescence lifetime is shorter than the diffusional rotation time, while the phosphorescence τ is comparable to it, around 500-600 nsec.

Excited state absorption. - Several transient absorptions were observed. The first two have absorption maxima at 640 and 720 nm, as shown in Fig. 7 and disappeared with the phosphorescence lifetime. The spectra were taken by sequential measurements at successive wavelengths. A third feature has a band maximum around 825 nm, and a 2 μsec lifetime. This last was unaffected by dissolved oxygen sufficient to quench the phosphorescence. We suspect this absorption to be due to a chemical intermediate rather than to an excited state. If it is an intermediate, it is unstable and appears to return to starting complex since the PMT trace eventually returned to baseline. Thus any photochemistry in aqueous K$_2$[Pt(CN)$_4$] solutions is reversible on this time scale (in the absence of redox quencher).

Discussion

Our qualitative conclusions are summarized in the assignment table, Table II. The importance of the electronic structure of Pt(CN)$_4^{2-}$ monomer is attested by the existence of some twelve previous attempts at excited state assignments[22,23] (See Ref. 30 in particular). Our

contribution to the situation is in the information of Fig. 3 , which shows, for the first time, that the bands we label V and III do not obey Beers law, but partially disappear with increasing concentration. Referring to March and Miller,[30] our bands V and III deconvolute into two gaussian components each, and our observation is essentially that one of the components of each band disappears (or shifts to some hidden position) on oligomerization. Of the six low-lying spin-orbit allowed transitions, only two are of d_{z^2} parentage, $^1A_{1g} \rightarrow A_{2u}(^1A_{2u})$ and $^1A_{1g} \rightarrow E_u(^3A_{2u})$. These should be the concentration sensitive transitions. The reason is that oligomerization should strongly perturb orbitals of d_{z^2} parentage, through a Davydov shift to lower energy as Pt-Pt interaction occurs, while orbitals of other parentage should be relatively unaffected.

We can argue from the data of Yersin and Gliemann[3] that the $A_{2u}(^1A_{2u})$ state lies at 45.5 kK and the $E_u(^3A_{2u})$ one, at 39.4 kK above the ground state, in good correspondence with Fig. 3. These authors find, in studying crystalline salts of $Pt(CN)_4^{2-}$, that the z-polarized absorption fits the equation $E = 45.5 - 8\times10^5 R^{-3}$ (R in Å) which, in the monomer limit of $R \rightarrow \infty$, extrapolates to just 45.5 kK. Next, the fluorescence fits the equation $E = 42.9 - 8\times10^5 R^{-3}$, corresponding to a Stokes' shift of 2.6 kK. The phosphorescence then fitted the equation $E = 36.8 - 6.3\times10^5 R^{-3}$, and if we add the same Stokes' shift, the monomer limit gives 39.4 kK for the triplet absorption.

With the above assignments pinned, we can make the remaining ones for the monomer, as listed in Table III. These are consistent with the available data, including the CD,[33] MCD,[24,26] and polarization[32] results.

The assignments involving oligomers are necessarily qualitative as to state designation. First, we will take as acceptable that if a given feature depends on the $\underline{n}$th power of concentration, then the corresponding $\underline{n}$-mer is implicated. This stipulation neglects the possibly significant perturbation of ionic strength and ion-association effects at the relatively high concentrations involved. These effects, qualitatively, are in the direction of producing more association than corresponding to $\underline{n}$, that is, the apparent $\underline{n}$ value will be too large. However, comparison of curves $\underline{b}$ and $\underline{c}$ of Figure 4 suggests that while ionic strength has an effect, it is not so large as to change the nearest integral value of $\underline{n}$. This conclusion also applies to absorption feature I.

First, we see no absorption attributable to dimer. Judging from the findings with rhodium phosphine, arsine, carbonyl, or isocyanide complexes, dimer Davydov shifts are of the order of 6.5 kK.[43,44] If this were the case here, dimer absorption would be hidden under our bands III and II. The first oligomer we identify is the trimer, assigned from the concentration dependence of the intensity of band I. The dependence of ε_{app} on C^2 holds essentially over the whole band, so that the relative broadness of this band appears not to be due to absorption contributions by higher oligomers. Possibly the broadness reflects conformational looseness in the trimer. We assign the 353 nm fluorescence, curve II of Fig. 4, as trimer fluorescence, taking as reasonable the consequent Stokes' shift of 5.3 kK. It was not possible to verify the concentration dependence of the intensity of this emission because of self-absorption problems.

The 403 nm emission, unquenchable and hence also a fluorescence, has a concentration dependence of intensity indicating the source to

be a tetramer. Its excitation peak is around 330-340 nm (Fig. 5) and, applying the same Stokes' shift as found above, we place the tetramer absorption at 340 nm. The next fluorescence peak is around 460 nm, as seen in Fig. 6. We take this to be pentamer fluorescence and, again applying the same Stokes' shift, estimate the pentamer absorption to be at 370 nm. Yet another fluorescence is indicated in Fig. 6, at around 530 nm. At this point, the species is best designated as some n-mer.

Turning to the long-lived, quenchable emission, Fig. 5 indicates a component around 445 nm; the excitation is around 300 nm, suggesting that the emission is trimer phosphorescence. The 485 nm peak, Fig. 4(d) should be assigned as tetramer phosphorescence, but the concentration dependence of intensity in this wavelength region suggests a higher n-mer, and identification has at this point become uncertain.

While we can tentatively identify various phosphorescences, it should be recalled that they show a single exponential decay over the wavelength region involved. Very likely, excitation energy transfer processes couple the various oligomers. The observed lifetime is thus a complex function of the various concentrations and energy transfer rate constants.

The two excited state absorption features involve transition energies large enough that we are probably dealing with other than LUMO states. Actual assignment seems not possible.

A final consideration is the following. The literature gives a lower limit for the Davydov shift at the point of precipitation of d^8 square planar complexes as about 16 kK. The combination of Stokes' shift and singlet-triplet splitting in our case runs between 8.6 and

11.1 kK. There could thus be a total of some 27 kK between the monomer
singlet-singlet absorption and the phosphorescence at the oligomeriza-
tion or precipitation limit. The energy difference between the 560 nm
phosphorescence and the 216 nm absorption is 28.3 kK, in reasonable
agreement with the estimate.

Acknowledgement

Table I

Average lifetime (± 5%) at 510 nm of aqueous, argon deoxygenated
solutions of the barium and potassium tetracyanoplatiniates.

Salt	Conc.	Temp.	Lifetime
K^+	0.44 M	20-22°C	660 nsec
"	0.40	"	642
"	0.37	"	642
"	0.34	"	623
"	0.29	"	595
"	0.26	"	531
Ba^{+2}	0.109	18°C	724
"	0.099	20°C	539
"	0.091	RT (∼20°C)	447

Table II   Assignment of Absorption and Emission Features

Feature Absorption	Feature Emission	Wavelength, nm	Wave number, kK	Assignment	Comments
V		216	46.2	Monomer singlet-singlet abs.	Two components, one of d_z^2 parentage
	(VI)	(233)	(42.9)	Monomer fluorescence	Extrapolated from crystal data on R^{-3} dependence
IV		243	41.1	Monomer singlet-triplet abs.	
III		255	39.2	Monomer singlet-triplet abs.	Two components, one of d_z^2 parentage
	(V)	(271)	(36.8)	Monomer phosphorescence	Extrapolated from crystal data on R^{-3} dependence
II		280	35.8	Monomer singlet-triplet abs.	(Does not lead to emission)
i		295-300	33.7	Trimer abs.	From non-Beers' law behavior
Ia		335	29.8	Tetramer abs.	Excitation peak of 410 emission
	IV	352	28.4	Trimer fluorescence	5.3 kK Stokes' shift
Ib		370	27.0	Pentamer abs.	
	III	410	24.4	Tetramer fluorescence	5.4 kK Stokes' shift
	II	445	22.5	Trimer phosphorescence	Excitation around 300 nm
	II	460	21.7	Pentamer fluorescence	5.3 kK Stokes' shift
	I	485	20.6	Tetramer phosphorescence	Excited around 340 nm
	I,Ia	525-560		n-mer phosphorescence	
ESA		640	15.6	Excited state abs.	
ESA		720	13.9	Excited state abs.	

Table III

Spectroscopic Assignments of the Absorption-Bands

Band Fig. 3	Designation Ref. 30	Wave- length, nm	Wave number, kK	Transition $^1A_{1g}$ to	Polariza- tion	Parentage
V	6	213	46.8	$E_u(^1E_u)$	xy	$e_g(xz,yz)$
	5	216	46.2	$A_{2u}(^1A_{2u})$	z	$a_{1g}(z^2)$
IV	4	243	41.1	$E_u(^3B_{1u})$	both	$b_{2g}(xy)$
III	3	252	39.6	$E_u(^3A_{2u})$	xy	$a_{1g}(z^2)$
	2	258	38.7	$A_{2u}(^3E_u)$	z	$e_g(xz,yz)$
II	1	280	35.8	$E_u(^3E_u)$	xy	$e_g(xz,yz)$

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20. Authors dealing with solution association, particularly Gray[45]
    have discussed this phenomenon in terms of molecular orbital theory
    without giving the resultant red-shifted transition a particular

name, whereas the solid state physicists have called[1,19,21] the

observable, analogous solid state transitions, Davydov transitions.

We adopt this nomenclature, here and throughout the remainder

of the text, solely for the sake of an expediently short handle,

without specifically endorsing the mathematical applicability of

the theory to solution chemistry. See references 30-33 of our

reference 1 or reference 4 of reference 21 for reviews of Davydov

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39. It might be noted that literature reports have been that $Pt(CN)_4^{2-}$ solutions luminesce only at concentrations near saturation, with speculation that it was due to seed crystals at the onset of precipitation. We took great care that our solutions were not supersaturated, that is, that no microcrystalline material was present. As one approach, we confirmed that a 0.70 M solution should begin to show precipitate formation on cooling to 15 °C.[34] The solution was then warmed back to 26 °C, cooled to 15 °C and filtered through a 0.025 μm millipore filter before finally returning to 26 °C for the measurement.

40. The difference in implied concentration dependence could have arisen if these authors worked under conditions of low optical density and in the region of our trimer absorption, but without realizing that in making an absorption correction, they were taking out part of the power dependence of the emission on the total or formal concentration.

41. The considerable scatter evident in these data is due to the use of a 45° slant faced spectrofluorimeter cell. This greatly reduced the self-absorption problem, but led to increased scatter.

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Legends for the Figures

Figure 1.   Apparent molar extinction coefficients for various
             concentrations of $K_2Pt(CN)_4$. Concentrations: 1, 8.96×10^{-3} M;
             2, 0.152 M; 3, 0.218 M; 4, 0.311 M; 5, 0.445 M; 6, 0.635 M.
             Temperatures: 2, 3, and 5 are at 23 °C; 4 is at 25 °C;
             1 and 6 are at room temperature, ca. 26 °C.

Figure 2.   Relationship between apparent extinction coefficient
             (correction for a small estimated monomer contribution)
             and c^2, 25-27 °C. Wavelengths: 1, 295 nm.; 2, 297.5 nm;
             3, 300 nm.

Figure 3.   Disappearance of monomer charge transfer bands with
             increasing concentration and ionic strength. ———
             9.96×10^{-4} M $BaPt(CN)_4$; ..... 4.98×10^{-2} M $BaPt(CN)_4$ in
             0.376 M $BaCl_2$; ----- estimated dimer absorption spectrum.

Figure 4.   Emission spectra of aqueous $K_2Pt(CN)_4$ at 26 °C. (a) 0.56 M,
             366 nm excitation; (b) 0.793 M, 366 nm excitation; (c) 0.70 M
             in 0.783 M KCl, 366 nm excitation; (d) 0.0996 M, 313 nm
             excitation, Ba^{+2} salt.

Figure 5.   Excitation wavelength dependence of the phosphorescence
             band, 0.1 M $BaPt(CN)_4$. Excitation: ——— 300 nm;
             ..... 310 nm; ----- 320 nm; —·—·— 330 nm; ++++ 340 nm.

Figure 6.   Excitation and emission spectra for 0.40 M $K_2Pt(CN)_4$
             under conditions of complete phosphorescence quenching
             (0.01 M KNO_2). Dashed line: excitation spectrum; solid
             line: emission spectrum for 328 nm excitation.

Figure 7.   Excited state and chemical transient absorption spectra.
             Upper curve: 400 nsec after pulse; lower curve: 2.9 µsec
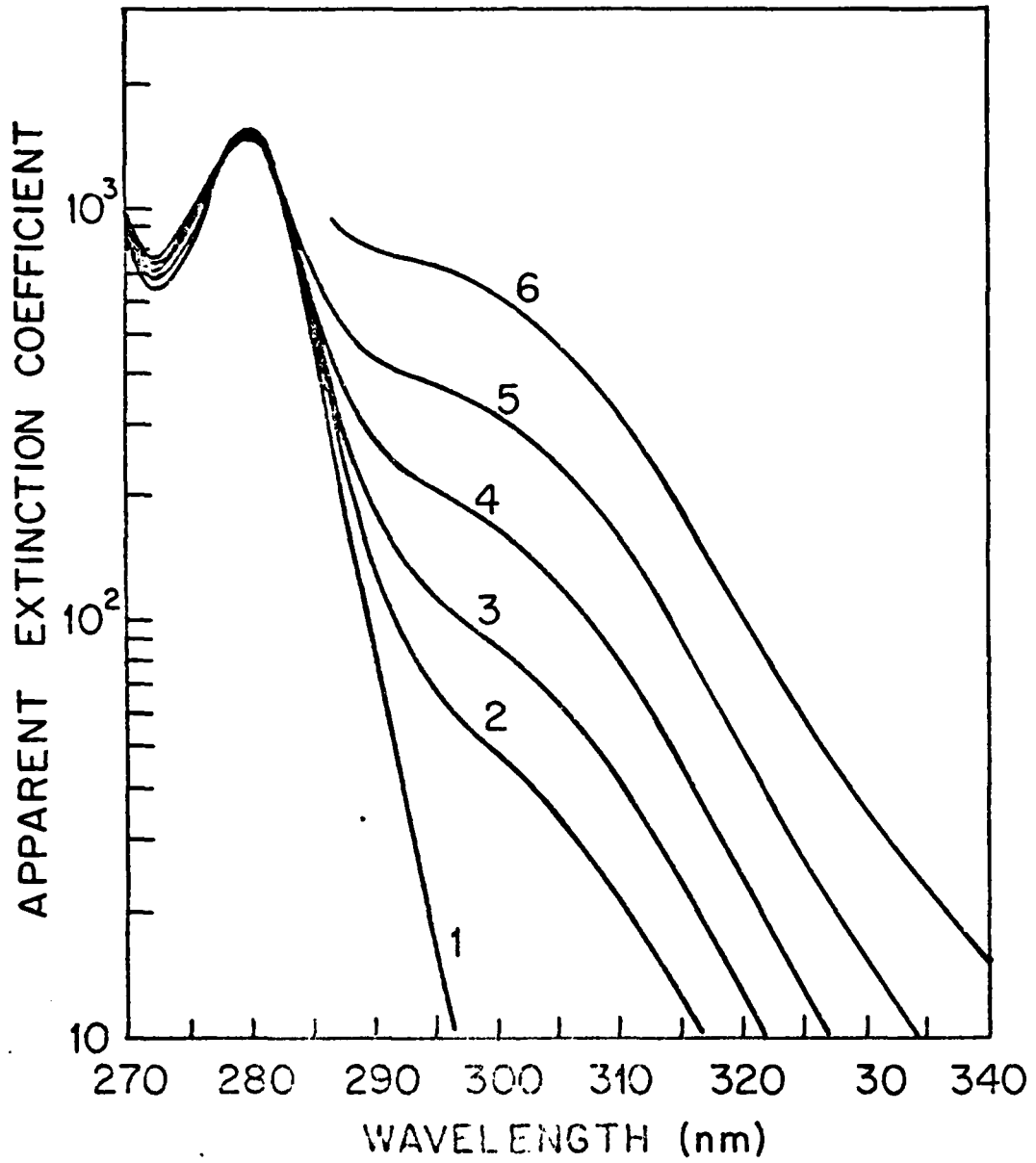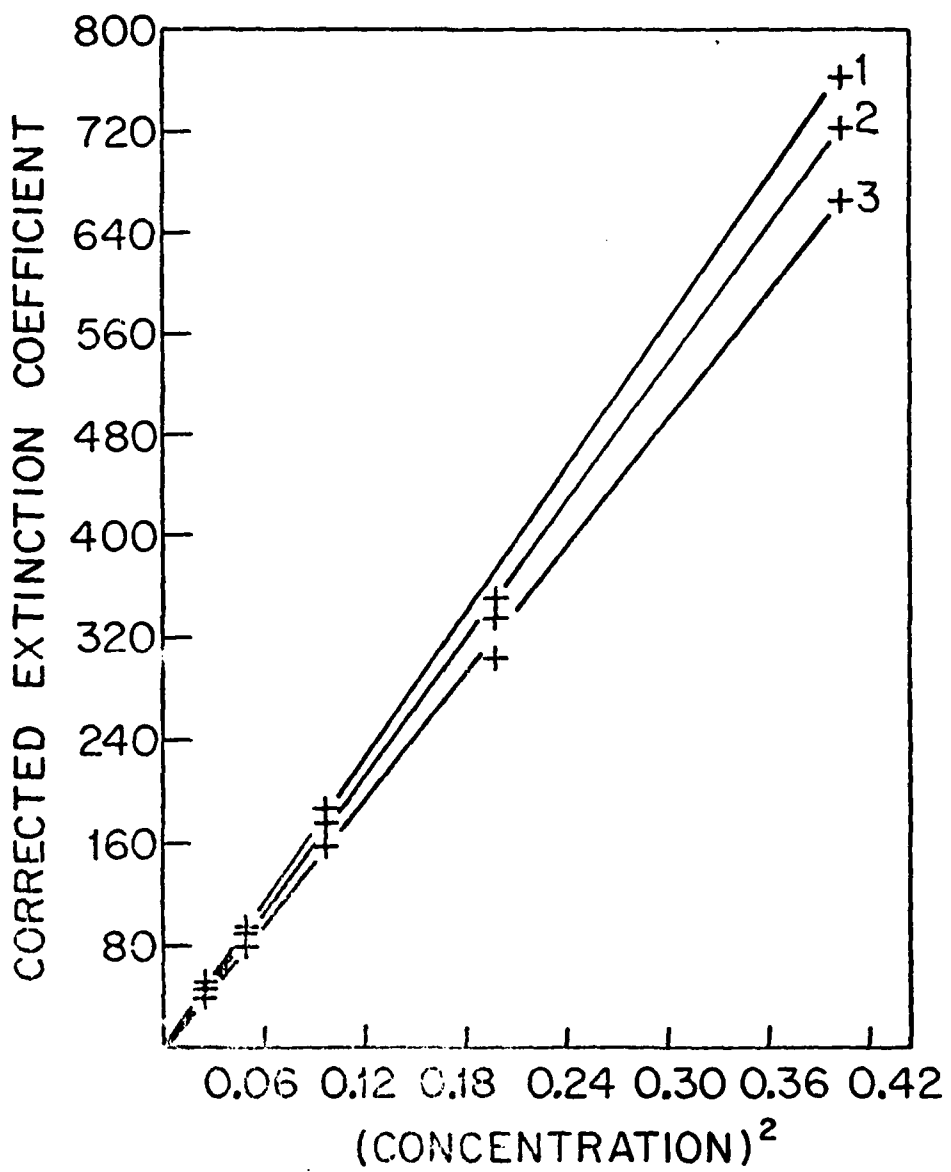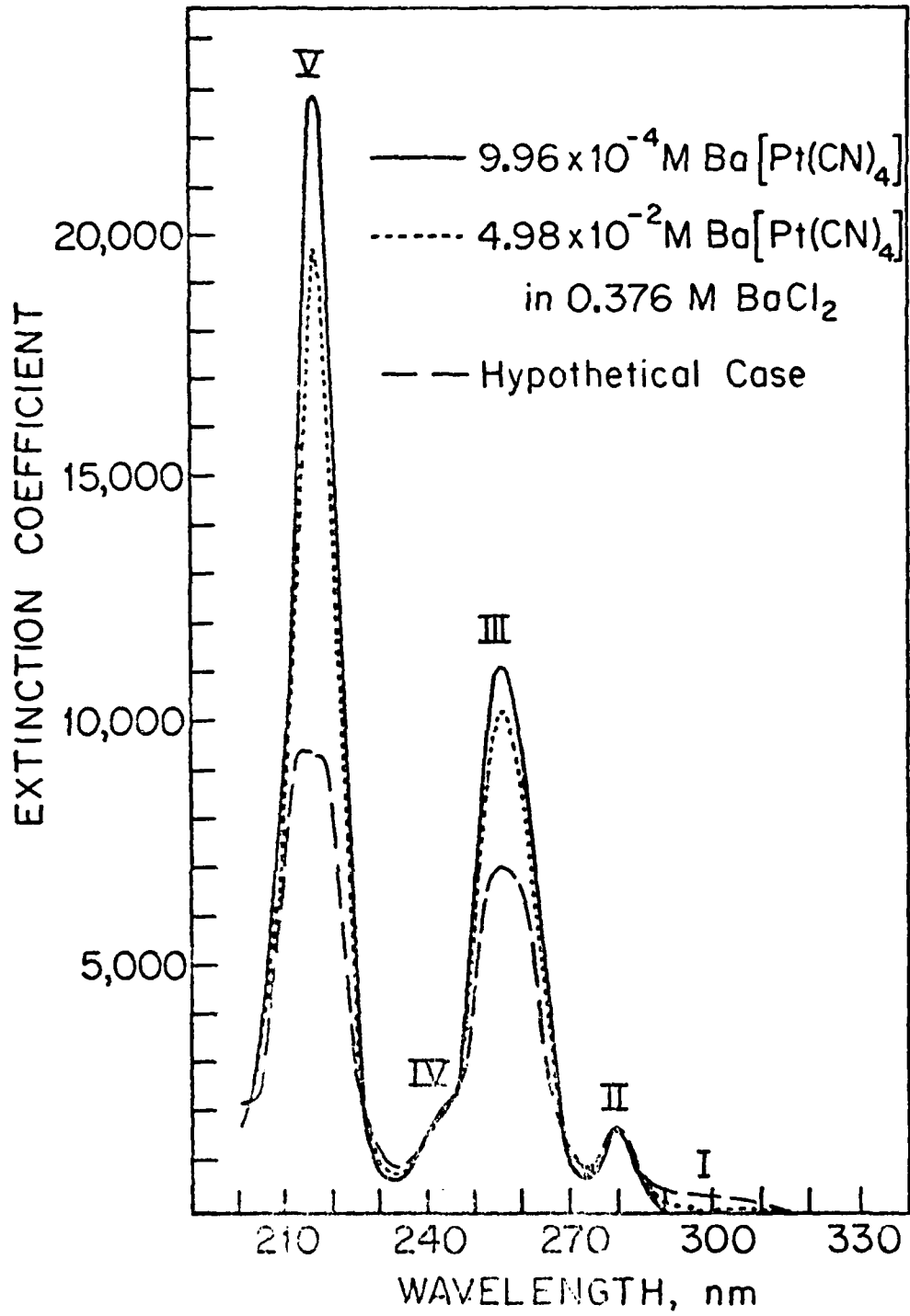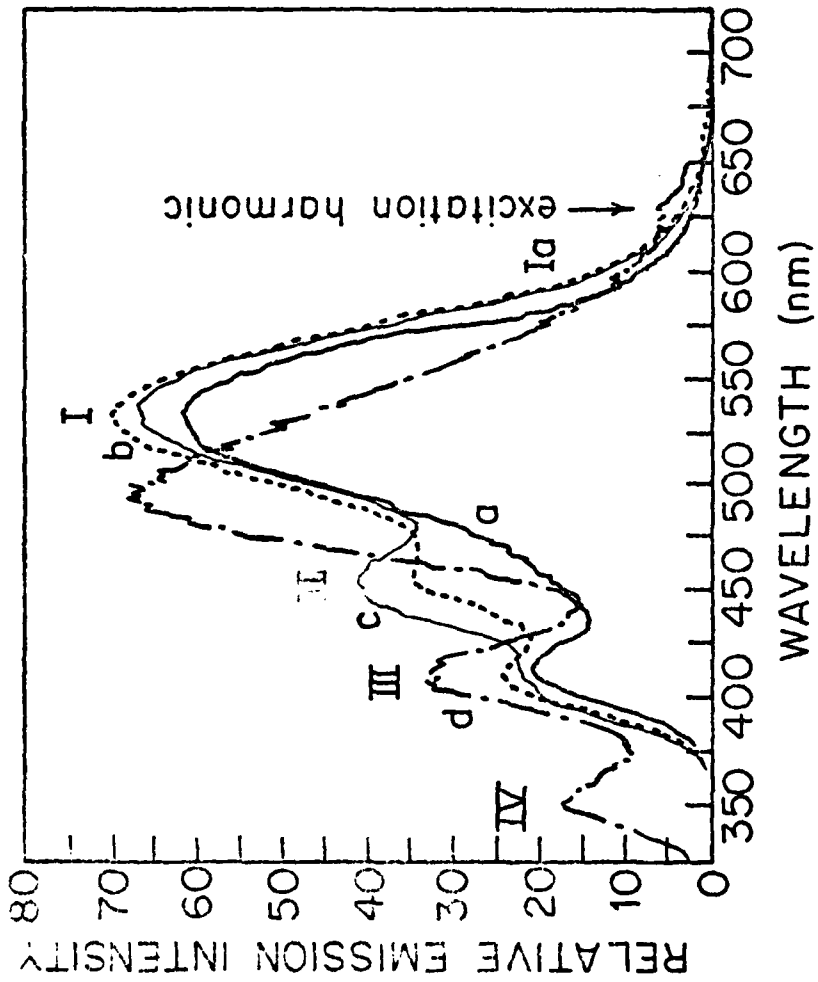   after pulse.

Fig 1.

Fig. 2

Fig. 3

Fig. 11

EMISSIONS OF 0.1M Ba[Pt(CN)₄]

Excitation at:
——— 300 nm
········· 310 nm
– – – 320 nm
–·–·– 330 nm
–··–··– 340 nm

WAVELENGTH (nm)

RELATIVE INTENSITY

Fig. 5

Fig. 6

EXCITED STATE ABSORPTION

400 nsec after pulse

2.9 μsec after pulse

Wavelength, nm

$0.44 \text{ M } K_2[Pt(CN)_4]$
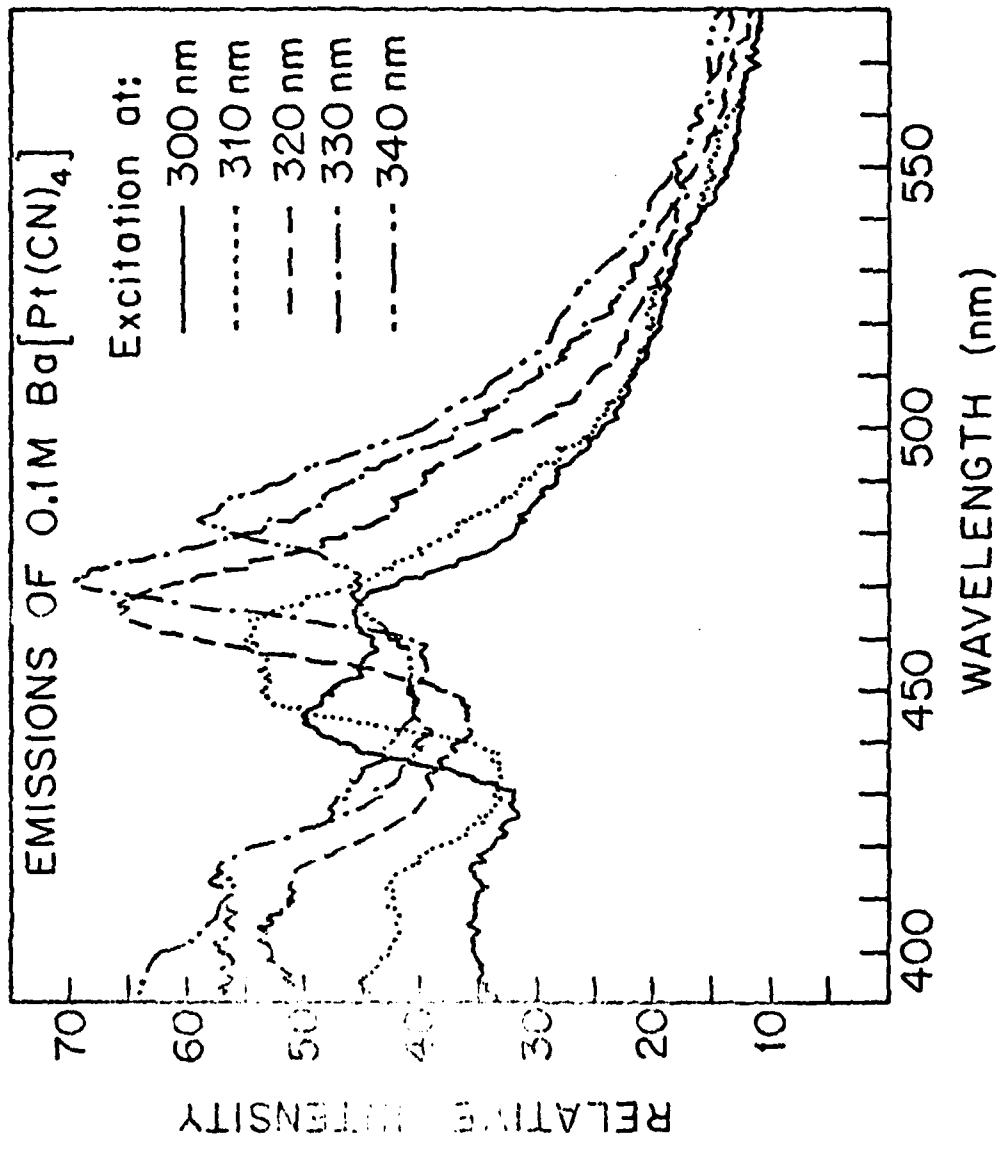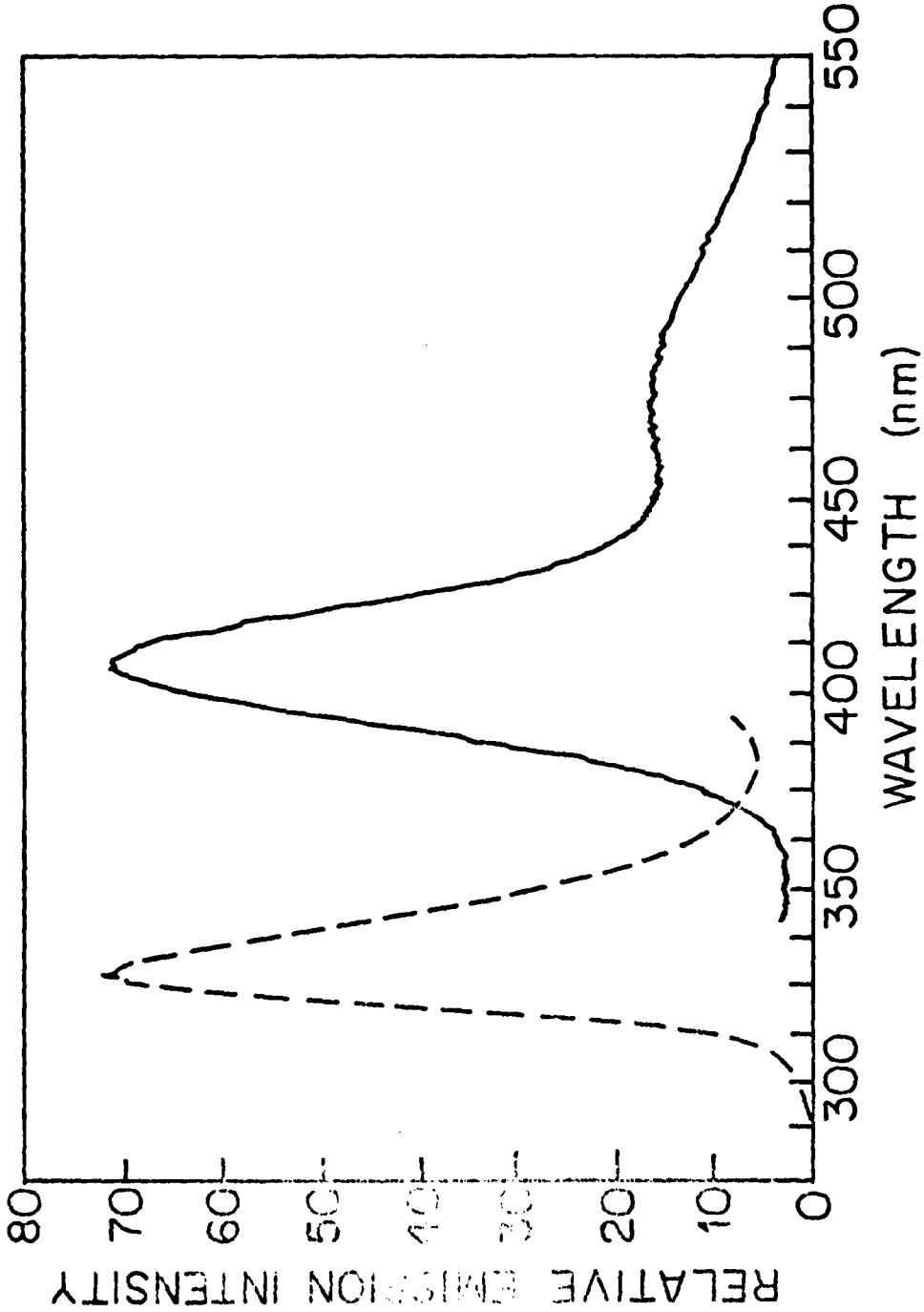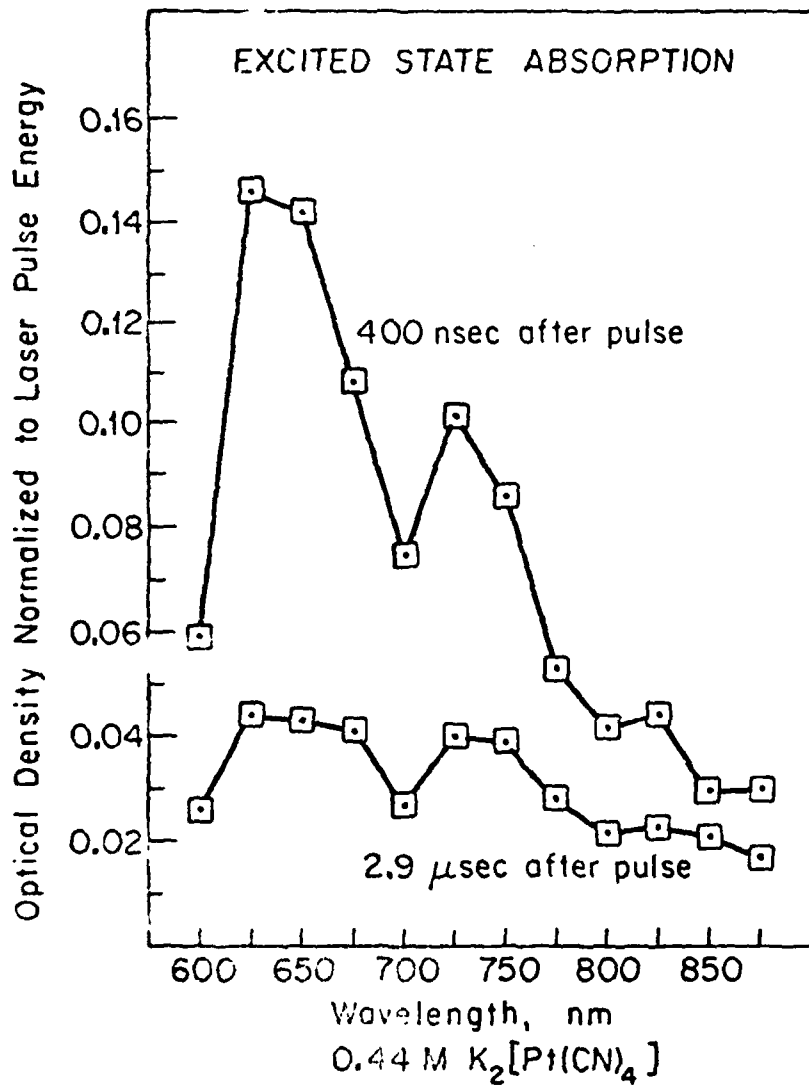
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