PHOTOLYSIS OF CRYSTALLINE TRISOXALATOCOBALTATE (III) IN A DILUENT CRYSTAL

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
ANNE FENERTY
1969

ABSTRACT

PHOTOLYSIS OF CRYSTALLINE TRISOXALATOCOBALTATE(III) IN A DILUENT CRYSTAL

By

Anne Fenerty

Trisoxalatocobaltate(III) was incorporated into the $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ lattice by isomorphous[1] replacement of $Al(C_2O_4)_3^{3-}$ to permit spectrophotometric analysis of the dark green compound.[2]

Trisoxalatocobaltate(III) undergoes the following photolytic reactions:

1. Intramolecular oxidation and reduction.
2. Substitution.
3. Racemization.

It was generally believed[3] that substitution takes place when ligand field bands are irradiated and redox reactions take place in the charge transfer region. Some evidence of redox reaction at higher wave lengths has been found, however, and it was suggested[4] that the tail end of the charge transfer band extends into the ligand field region.

To determine the type and mechanism of the reaction at differing wavelengths we set out to measure quantum yields on irradiation, by following the decrease in absorbance of the ligand field bands. This proved to be impossible as

the decomposition products of the reaction absorb at these wavelengths.

The crystal study method has been adopted for the following reasons:

(1) Dilution.

(2) Identification of the reaction products trapped in the crystal which slows down radical recombination.

(3) Observation of polarizations due to the D_3 symmetry of the crystal, and of the lower symmetries of the products.

(4) Elimination of solvent effects.

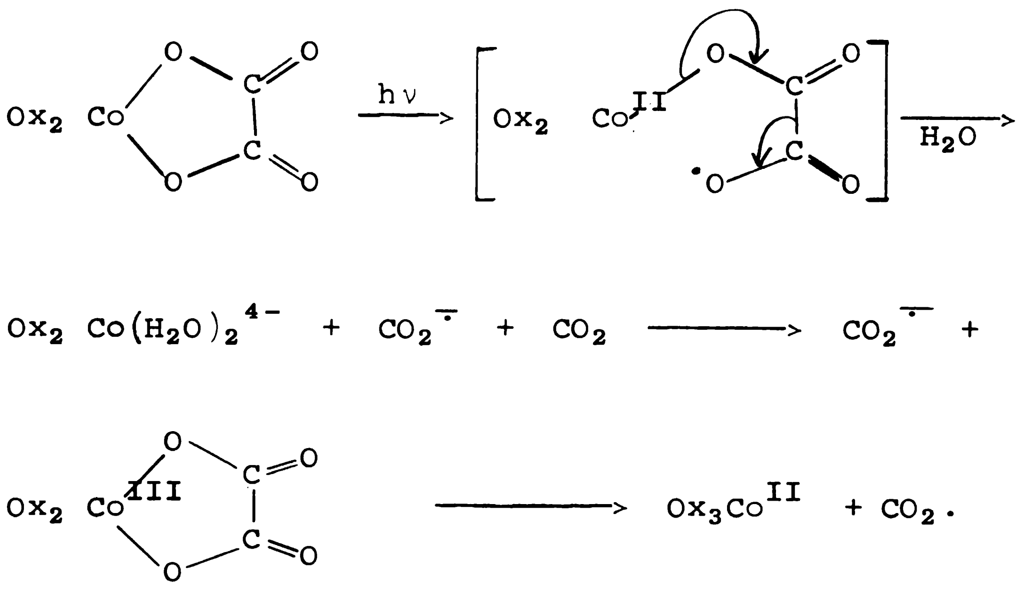
The following results were obtained:

(1) We found the reaction to be identical in both of the ligand field bands.

(2) On irradiation a band of high molar extinction develops at 320-350 mμ. It is polarized, and attributed to[5] the $4a_1 \longrightarrow 2b_1$ transition in $CO_2^{\overline{\cdot}}$, which has C_{2v} symmetry.

(3) $Co(C_2O_4)_3^{4-}$ has been identified as the main reduction product, through the polarization of the ligand field transitions, which show D_3 symmetry.

The suggested mechanism is:



(4) An approximate first order rate constant was calculated. The half life on irradiation is between 2.3-7.4 minutes. This is using the lowest optical density value as D_∞, which is quite possibly incorrect as any further decrease is obscured by the very intense band growing in at 320 mμ.

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By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1969

ACKNOWLEDGMENT

I wish to thank Dr. S. T. Spees for his guidance, encouragement and constant availability for discussions and suggestions involving the problems in this project. In addition I acknowledge the help Dr. Carl Brubaker gave me in understanding the theoretical aspects underlying this work. Finally, I thank my husband, Michael for his patience and support.

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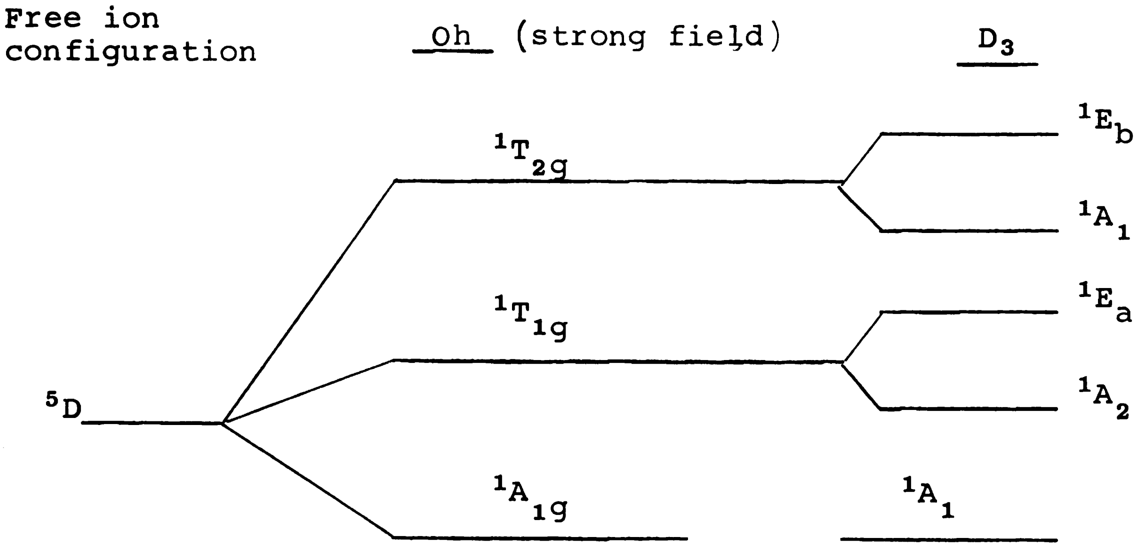
INTRODUCTION

Trisoxalatocobaltate(III) is a hard acid-hard base complex. With 24Dq crystal field stabilization energy and three bidentate chelate rings, the complex is kinetically inert. It has been the subject of much work including both thermal, and conventional photochemical activation[6], flash photolysis[7], and of e.s.r. studies, on the radicals produced on irradiating a frozen aqueous solution[8].

Work involving a diluent crystal has been originated by Piper and Carlin[2] to study the visible polarized spectra of trisoxalatometallates.

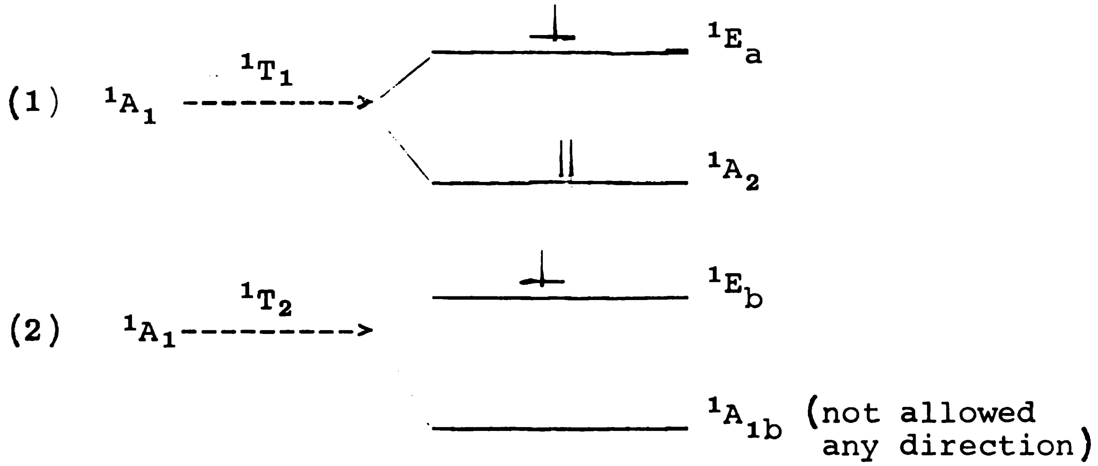
Trisoxalatocobaltate(III) has pseudo octahedral symmetry if only the oxygen atoms directly coordinated are considered. The symmetry is lowered to D_3 due to the chelating rings. As a result of this the Laporte forbidden d-d transitions become allowed electronically. Carlin and Piper measured the splitting of the octahedral excited states and determined the trigonal field strength parameter.

The low spin d^6 Co^{III} ion has t_{2g}^6 configuration. Ground state is ${}^1A_{1g}$. In the visible region the two spin allowed excited states $t_{2g}^5e_g$ in an octahedral field are: ${}^1T_{1g}$ and ${}^1T_{2g}$. These are split as follows:



Due to the low symmetry, transitions are only allowed for certain orientations of the electric vector of the incident light. The crystal is definitely dichroic and looks green when viewed in light parallel to the C_3 axis. It is blue in light incident normal to the axis.

By taking the triple direct product for each transition in each of the orientations and finding out if it contains the totally symmetric, irreducible representation the polarization of the spectrum can be calculated. It is as follows;



The $^1A_1 \longrightarrow {}^1T_1$ transition is found at 608 mμ in the solution and is split into 610 mμ for $^1A_1 \longrightarrow {}^1A_2$ and 602 mμ for $^1A_1 \longrightarrow {}^1E_a$. The $^1A_1 \longrightarrow {}^1T_2$ transition is at 427 mμ.

The method used by Piper and Carlin was to cut sections from the crystal both perpendicular to and parallel to the C_3 axis. The former they called axial and the latter orthoaxial sections. When the spectrum of an orthoaxial section was examined in polarized light the selection rules were confirmed.

The spectrum obtained with light polarized parallel and perpendicular to the C_3 axis was called the π and σ spectrum, respectively. The σ spectrum was identical to the axial spectrum.

We adapted this method to study the effects of irradiation on a single crystal.

HISTORICAL

Photolysis of trisoxalatocobaltate(III) has centered on the compound in solution. Only a limited number of crystal studies were made.[9,10]

Due to the fact that it belongs to the D_3 group, the compound is dissymmetric. Both its photoracemization[11] and partial photoresolution[12], using circularly polarized light, were studied.

Due to the thermal instability of $Co(C_2O_4)^{3-}$, isotope studies of ligand exchange reactions are difficult to perform. The $C_2O_4{}^{2-}$ exchange was followed, however, by precipitation and radioassay of the free oxalate as $CaC_2O_4 \cdot H_2O$[13]. It was found that oxalate exchange has a half life of > 130 hr. at 50^0, compared to a thermal decomposition half life of 6.5 hrs at 50^0. This proves that the thermal decomposition proceeds by a mechanism not involving reversible equilibration of $C_2O_4{}^0$ or $C_2O_4{}^-$.

We believe that the mechanism of thermal decomposition is one of intramolecular oxidation-reduction, identical to the photochemical reaction. The work done on thermal reactions in the solid during this study, is not enough, however, to draw definite conclusions.

The most characteristic reaction of $Co(C_2O_4)_3^{3-}$ is the redox reaction. The ligand $C_2O_4^{2-}$ is easily oxidizable, and the process involves homolytic bond breaking by transfer of a σ bonding electron primarily located on the ligand, into an empty e_g orbital, located on the metal.

Trisoxalatocobaltate(III) has a charge transfer band in the near uv at 242 mμ with a molar absorbance of 20,000[2]. Irradiation in this region produces reduction of $Co^{III} \longrightarrow Co^{II}$ with the primary quantum yield half the reduced Co^{III}.

In an aqueous solution spectrum the $^1A_1 \longrightarrow {}^1T_1$ transition is at 608 mμ and the $^1A_1 \longrightarrow {}^1T_2$ at 427 mμ. There is no splitting of the excited states in solution and the molar extinction is 152 for the $^1A_1 \longrightarrow {}^1T_1$, and 200 for the $^1A_1 \longrightarrow {}^1T_2$ band[14].

While redox reactions are usual in the charge transfer region their existence in the long wavelength ligand field bands has been questioned[4].

Several theories have been advanced to explain the phenomenon:

(1) Promotion of a d electron from a t_{2g} orbital to an e_g orbital creates electron-ligand repulsion, followed by possible bond breakage[6].

(2) Due to the wide band widths the pure electronic energy differes from the band maxima. If the charge transfer band would have the lower electronic energy it could

extend below the ligand field transition band. In this case the oxidation-reduction reaction could be caused by energy absorbed in the ligand field band, through radiationless conversion to the charge transfer band.

EXPERIMENTAL

Preparation of Compounds

$K_3[Co(C_2O_4)_3]$. Prepared according to Palmer[15] from oxalic acid, potassium oxalate and cobalt(II) acetate. The latter was substituted for cobalt(II) carbonate. The complex cobalt(II) oxalate was oxidized by PbO_2 in the dark, to prevent photochemical reduction. After recrystallization the salt was dried over $CaCl_2$ for a week.

While the usual formula is $K_3[Co(C_2O_4)_3]\cdot 3\ 1/2\ H_2O$, $C_2O_4^{\,2-}$ analysis and measurement of ϵ at 427 and 608 yielded the anhydrous formula. The value of ϵ_{427} determined from an average of three samples yielded:

$$\epsilon_{427} = \begin{matrix}202\\198\\200\end{matrix} = 200 \quad \text{and} \quad \epsilon_{608} = \begin{matrix}155\\151\\150\end{matrix} = 152.$$

This agrees well with that of Karipides[16]: $\epsilon_{419} = 208$, $\epsilon_{600} = 160$.

Furthermore, there was no loss in weight on drying the salt over P_2O_5 for a week.

$C_2O_4^{\,2-}$ Analysis: Following Palmer's[15] method for the di-μ-hydroxotetraoxalatodicobaltate(III) ion, the salt was decomposed and Co^{III} was precipitated as cobalt(III) oxide, by using excess sodium hydroxide. After filtration the decantate was acidified, heated to boiling, and titrated with a 0.105N $KMnO_4$ solution.

C_2O_4 = in $K_3[Co(C_2O_4)_3]$ Calculated: 60.0%
Found: (1) 59.0
(2) 59.2.

From these results we conclude that water is absent.

Co^{2+} Analysis. The amount of Co^{2+} in $K_3[Co(C_2O_4)]$ was determined by simultaneous spectrophotometric analysis. Analytical wavelengths are: 602, 625 mμ.

To an aqueous solution of the salt, acetone and a thiocyanate solution was added in 4:5:1 proportion[17].

The blue $Co(SCN)_4^{2-}$ has an absorption band at 625 mμ for which we determined $\epsilon_{625} = 2180 \pm 5\%$ and $\epsilon_{602} = 1725 \pm 5\%$.

For $Co(C_2O_4)_3^{3-}$ $\epsilon_{602} = 152$ and $\epsilon_{625} = 130$.

The amount of Co^2 in $K_3[Co(C_2O_4)_3]$ is:

(1) 0.95%
(2) 1.27%
= 1%

Calculations were doublechecked by the known concentrations of $Co(C_2O_4)_3^{3-}$.

$NaMg[Al(C_2O_4)_3]\cdot 9H_2O$. Prepared according to Palmer[15] and checked against the known molar extinction: $\epsilon_{258} = 141$.

Preparation of Cobalt(II) Oxalate. As complex oxalates of Co^{2+} are products of $Co(C_2O_4)_3^{3-}$ photolysis, an attempt was made to determine their spectrum and composition.

Job's method of continuous variation was used in an attempt to distinguish between $Co(C_2O_4)_2(H_2O)_2^{2-}$ and $Co(C_2O_4)_3^{4-}$. By using a 3:1 ligand-metal ratio a purple complex salt was prepared along with the insoluble pink simple salt. A 4:1 ratio gave a similar but more concentrated spectrum. See Figure 1.

$$\begin{tikzcd}
Co(H_2O)_6^{2+} + C_2O_4^{2-} \arrow[r, shift left] & CoC_2O_4 \arrow[l, shift left, "K_1"] \arrow[d, shift left, "C_2O_4^{2-}"] \\
Co(C_2O_4)_3^{4-} \arrow[r, shift left, "K_3"] & Co(C_2O_4)_2(H_2O)_2^{2-} \arrow[u, shift left, "K_2"] \arrow[l, shift left]
\end{tikzcd}$$

The concentration of $Co(C_2O_4)_3^{4-}$ is expected to be low as $K_1 = 3.72$, and $K_2 = 2.31$, as determined by ion exchange.[18]

The visible spectrum of the $Co(H_2O)_6^{2+}$ ion has been determined by us and the results agree well with those of Roberts and Field[29]. The visible absorption maximum was found at 510 mμ, while their value was 512 mμ. Our value of $\epsilon_{510} \approx 5$, agrees with their $\epsilon_{512} = 5$.

A 3:1 oxalate-ligand ratio results in the shift of the absorption maximum to 535 mμ, with a shoulder at 510 mμ and at 490 mμ. See Figure 1. This agrees with their value of 535 mμ.

No uv peak was found, till 185 mμ. A wide, weak ir peak was found at 1215 mμ. Cotton and Wilkinson[19] show

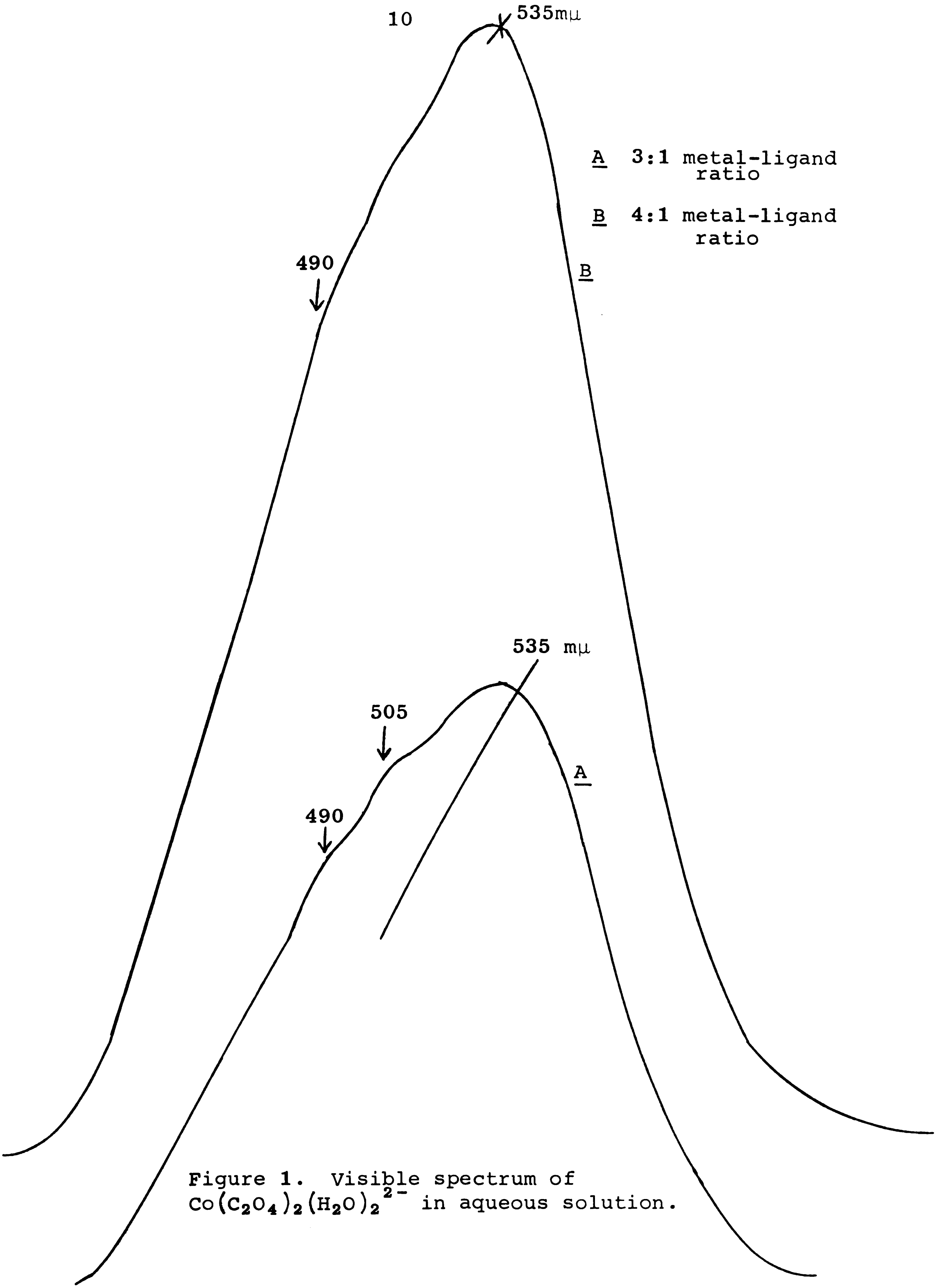


Figure 1. Visible spectrum of $Co(C_2O_4)_2(H_2O)_2^{2-}$ in aqueous solution.

this peak at 1210 mμ for $Co(H_2O)_6^{2+}$.

The 3:1 ligand-metal spectrum is attributed to $Co(C_2O_4)_2(H_2O)_2^{2-}$.

It is expected that the cis-$Co(C_2O_4)_2(H_2O)_2^{2-}$ isomer is present, as it is the likely product, formed on removal of an oxalate ligand. Rapid isomerization is, however, expected as Co^{2+} complexes are labile.

$Co(C_2O_4)_3^{4-}$ has D_3 symmetry. This serves as an important distinction between these two compounds in the solid phase, as shown by the polarized spectrum.

Actinometry

The original purpose of this investigation was to measure quantum yields for the photodecomposition of trisoxalatocobaltate(III), at different wavelengths.

Due to the relative inaccuracy of radiometers, an attempt was made to utilize a chemical actinometer, $K[Cr(NH_3)_2(SCN)_4]$ (Reinecke salt), according to Adamson's[20] method. A 3×10^{-2} M solution of the salt was prepared. The reaction involves aquation of one ligand.

$$Cr(NH_3)_2(SCN)_4^- + H_2O \xrightarrow{h\nu} Cr(NH_3)_2(SCN)_3(H_2O) + SCN^-$$

The quantum yields for the photoaquation at different wavelengths are known, and from the measured concentration and volume of the solution, the light intensity can be calculated:

$$-\frac{dc}{dt} = \frac{\Phi I_a}{V}$$

I_a = intensity of absorbed light

c = concentration of the solution

V = volume of the solution

Φ = quantum yield.

Ideally $I_a = I_0$ which required the concentration of solution to be high enough to absorb all the light. According to Adamson, reflected light is negligible; we found, however, that it was 9%, from a glass cell, at normal incidence, and corrected for it.

The solution was photolyzed using a neon laser, λ = 6328 Å, and a 30 ml volume, 10 cm long glass cell. After adding the solution the cell was stoppered and stirred magnetically.

The concentration of the photoreleased thiocyanate was determined as the iron thiocyanate complex:

$$\epsilon_{max} = 4.3 \times 10^3, \text{ at } 450 \text{ m}\mu.$$

In order to prevent aquation of more than one ligand the percent photolysis must be kept low: 0.61% at 600 mμ, and generally between 0.6-10%.

The intensity of the neon laser was about the same as that of our Hg-Xe lamp, i.e. 10^{-6} einsteins/sec. This is several magnitudes higher than Adamson's (10^{-9} einsteins/sec).

Thus, to avoid excessive photoreaction, one can either dilute the solution or shorten the irradiation time. Neither of these alternatives is satisfactory; in the case of a dilute solution correction has to be made for light transmitted through the solution, and for light reflected from the back window. Short irradiation does not allow for variations of light intensity and may also introduce timing errors.

We found also that the prepared Reinecke salt[12] contained free thiocyanate, and so did its ammonium salt, from which it is prepared.

Further work on actinometry was abandoned when it became clear that the optical density of our crystal on irradiation is a function of more than one species, and quantum yields cannot be measured exactly.

Preparation of $NaMg[Co(C_2O_4)_3]$ Crystals

Solutions containing ten, five, and one percent by weight, of $K_3[Co(C_2O_4)_3]$ in saturated $NaMg(Al(C_2O_4)_3] \cdot 9H_2O$ were prepared. The solutions were evaporated slowly while standing in a dark place. A precipitate, believed to be CoC_2O_4 from the thermal decomposition, formed, and had to be filtered off.

$Al(C_2O_4)_3^{3-}$ is isomorphously[1] replaced by $Co(C_2O_4)_3^{3-}$, and when the solution became saturated the dilute crystals precipitated. A seed crystal was taken and hung from a thread into the solution, and as it grew the solution was frequently filtered to remove the decomposition product.

The crystals belong to the hexagonal system and grow quite readily from solution. The 1% trisoxalatocobaltate(III) crystals were not transparent throughout, showing some cobalt(II) oxalate inclusion. This was quite likely present in the opaque five and ten percent crystals too. Growing crystals at a lower temperature might be necessary to prevent decomposition.

The crystals were cleaved with a razor blade. Axial sections were those split normal to the C_3 axis of the D_3 ion. This is also the C_6 axis of the hexagonal system. These sections were relatively easier to cut, while the orthoaxial sections, cut parallel to the main axis broke and had to be sandpapered, and then rinsed with distilled water to prevent reflection from the surface.

Irradiation

The crystal sections were mounted in a metal spool which was placed into a holder to which a Nicol prism polarizer was attached. This equipment has been described previously[10].

The light source was a high pressure, 1000 volt Hanovia xenon-mercury arc lamp, supplied with a Hanovia compact arc lamp power system, which contained the current regulator and rectifier. The lamp operates at 15 amps, 60 volts dc., and is air cooled by a fan in a Schoeffel lamp housing. The lamp is vented through the top of the housing into the fumehood to exhaust any ozone formed by the arc.

Output is mainly in the visible and ir, with lesser amounts of uv light. The energy distribution (Table I) for a similar system is taken from a Schoeffel manual.

Table I. Energy distribution of a 2500w Xe-Hg arc lamp

Wavelength Range(Å)	Energy (w)	Percent of Total
2000-4000	2.95	18.9
4000-7000	6.34	40.5
7000-14,000	6.35	40.6

Monochromator filters could be inserted into the lamp sleeve. Due to the high power output they had to be water-cooled. We found that the focal length of the converging lens in the lamp housing was too short, and a convex lens had to be added to focus the light on the crystal. The mount was placed directly into the focal point of the lens, with the polarizer in back (attached photo). Only two runs were made with polarized light.

Various wavelength regions were selected by employing appropriate interference and glass blocking filters. Their spectral characteristics were determined spectrophotometrically. All but one of the filters used had the secondary ir windows blocked out. The results from this one filter, T.p. = 365 mμ, were ambiguous, and are not shown in this work. Filter spectra were established in the 200 mμ-700mμ region.


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Table II. Monochromator filters.

Filter Designation	Spectral Slit Width (mμ)	Peak Transmittance		Remarks
		Wavelength (mμ)	Optical Density	
5850	300-490	360-390	.07	
365	316-458	365	.29	IR window at 675
417	397-447	417	.54	
427	416-458	427	.34	
553	532-576	553	.42	
572	552-602	577	.43	
460-90-2	450-IR	470-IR	.10	Short wavelength cutoff
2424	600-IR	578-IR	.07	Short wavelength cutoff

After irradiation the mount was immediately placed into the sample compartment of a Cary 14 spectrophotometer. Spectra were obtained using polarized light.

Before analysis, the position of the light beam from the slit was centered on the crystal. After this adjustment at the beginning of each run, care was taken not to move the spool in the mount as this introduces a large error due to the high optical density and local nonhomogeneity of the crystal.

After analysis the crystal was immediately returned for further photolysis. During this time the instrument was zeroed again and the indicator was returned to starting position. Thus, there was very little delay between photolysis and the scanning of the spectrum. This was done to minimize the chances of radical decay.

Light intensity was measured using a YSI Kettering Model 65 Radiometer. The sensing probe was a dual thermistor bolometer. Accuracy was ± 5% full scale in use. For the Hg-Xe light source the readings were off scale and a 0.9 Bausch and Lomb neutral density filter was used to get them on to the highest (2.5×10^6 ergs/cm^2 sec) scale.

Tests were made to ascertain that all the light intensity incident on the crystal was absorbed. Light was centered on the crystal and the intensity of the incident and transmitted light measured. Light measurements behind the crystal were identical to the background light in the room.

No light could be lost by reflection from the mount, as the light was focused down to the size of the crystal section.

The optical density of both sides of an irradiated and visibly partially decomposed crystal are the same. We conclude from these tests that $I_a = I_0$, and there is no scattering due to the decomposition product.

Bausch and Lomb 0.6 and 0.9 neutral density filters were also used for spectral measurements to compensate for the high optical density of the crystal. The filters were calibrated in the 400-700 mμ region. A box to hold the filters was made up for the reference compartment of the Cary 14. Thin sections of dilute (1%) crystals could be run without filters.

The mount and the spool holding the crystal section, as well as the polarizer, were calibrated in this region.

To study the uv spectrum, the crystal was inserted into a ring, cut from a doublefaced foamed adhesive. The ring was then stuck on a uv silica cuvette. The polarizer was an Abbe prism, which allowed more of the light to pass through the crystal than the Nicol prism.

Quantum yield calculations were made for an aqueous solution of trisoxalatocobaltate(III). This solution was irradiated with the 6328 Å light from a helium-neon laser. The energy output of this laser is at the same order as that of our Hg-Xe arc lamp ($I = 10^6$ ergs/sec), but the plane polarization and monochromaticity could have increased effects on the crystal.

Quantum yields were determined by laser irradiation of the solution in a liquid cell, stirred by a magnetic stirrer. A reference solution was kept at the same temperature in the room. The effect of irradiation was determined by differential spectrophotometry to compensate for any decomposition due to thermal effects and to uv irradiation from the room light.

It was found that transmitted light was negligible, when compared to the background radiation. Therefore $I_0 = I_a$ where I_0 = incident light and I_a = absorbed light. This neglects the small amount of light, which is reflected from the front window at a normal angle of incidence.

The effect of thermal decomposition on the optical density of a crystal was determined by the following method: A crystal section was fitted into the metal spool of the mount. The mount was then placed into a test tube which was wrapped with black electrical tape to prevent any photochemical reaction. It was then placed into a larger test tube, which loosely sealed on top with cotton wool, and immersed into a stirred water bath at 70^0.

RESULTS AND DISCUSSION

The visible spectrum of potassium trisoxalatocobaltate(III), Figure 2, shows two well defined peaks in this region. We could therefore chose to irradiate either band. Polarizations of ligand field transitions of the reaction products were investigated using σ and π spectra of orthoaxial sections. The σ section spectrum and that of an axial section are identical.

We found that the optical density of the crystal on irradiation was not a direct function of time. At the start, the optical density decreased, and on prolonged irradiation it increased. This was not consistent, however, but varied from crystal to crystal. The optical density of the host crystal itself also increased upon irradiation, which might be due to thermal effects.

The discernible change in the spectrum on irradiation is found in the shape of the absorption bands. Both bands broaden and then flatten out completely. This is also seen with $K_3[Co(C_2O_4)_3]$ alone, Figure 3. The higher frequency ligand field band disappears first. The optical density increases greatly in the area of the band, a phenomenon also found in the π spectrum, where this 427 mμ band is forbidden.

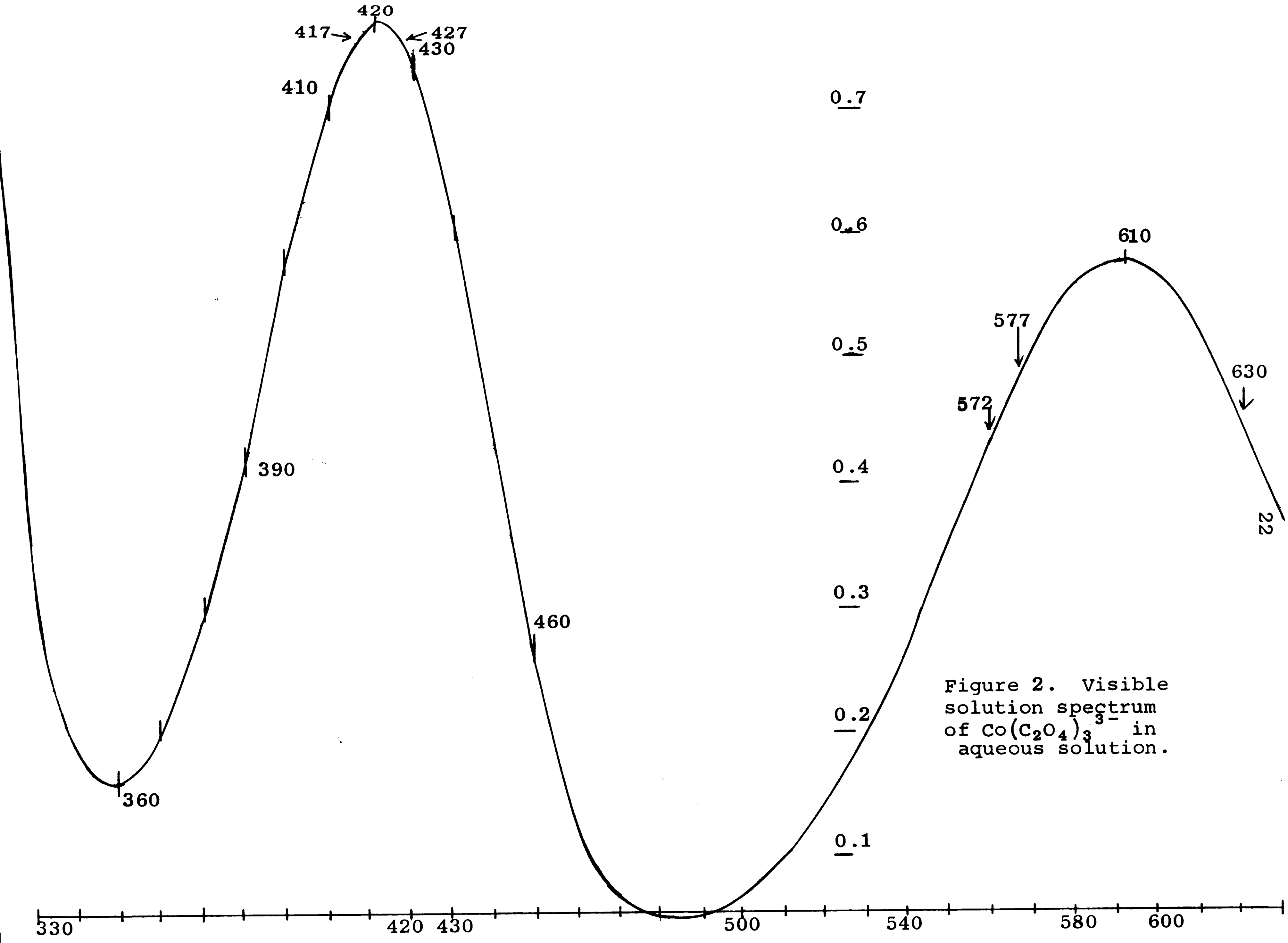


Figure 2. Visible solution spectrum of $Co(C_2O_4)_3^{3-}$ in aqueous solution.

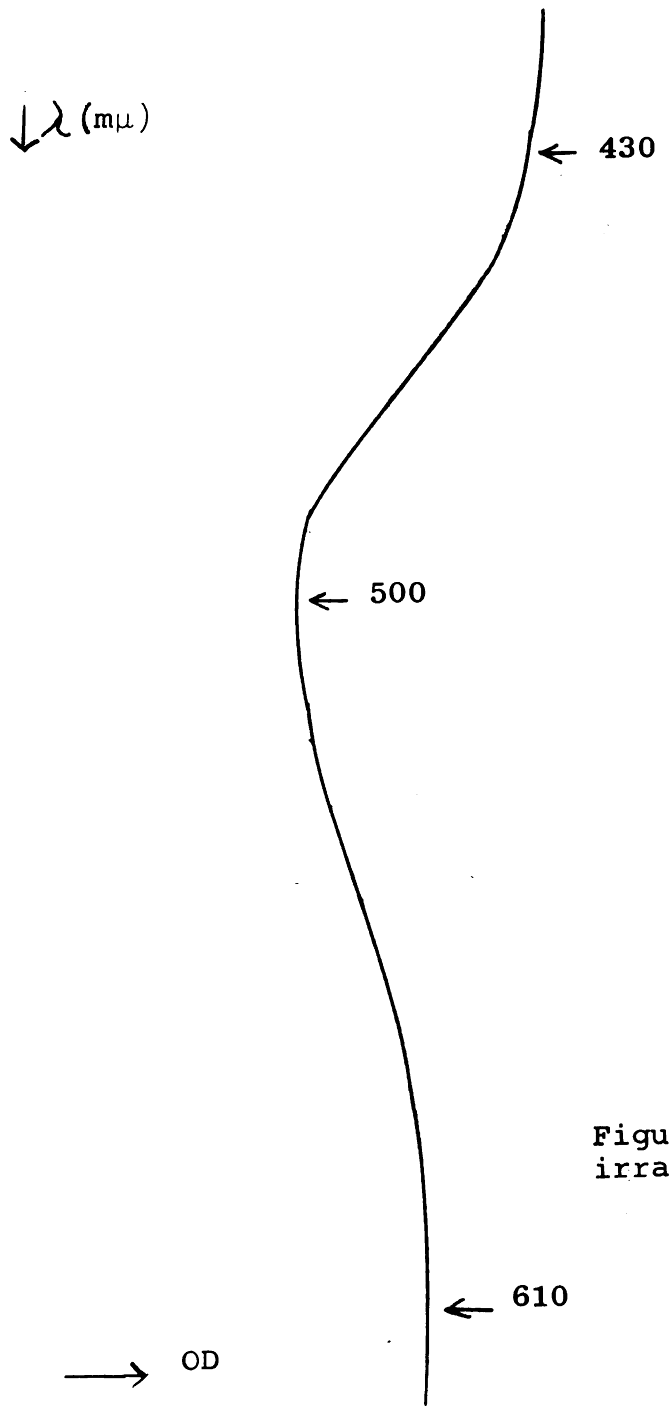


Figure 3. Visible spectrum of an irradiated $K_3[Co(C_2O_4)_3]$ mull.

These results suggest a strong absorption band developing in the near uv. It was located, as described before, at 320-350 mμ

Investigation of the Near Ultraviolet Absorption Band

The crystal spectrum of $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ was determined to find out if it could be a source of the band. It was found that the $\epsilon = 141$ band at 258 mμ was shifted toward the low energy region, 260-275 mμ in the crystal, but no band was found in the 320-350 region on irradiation.

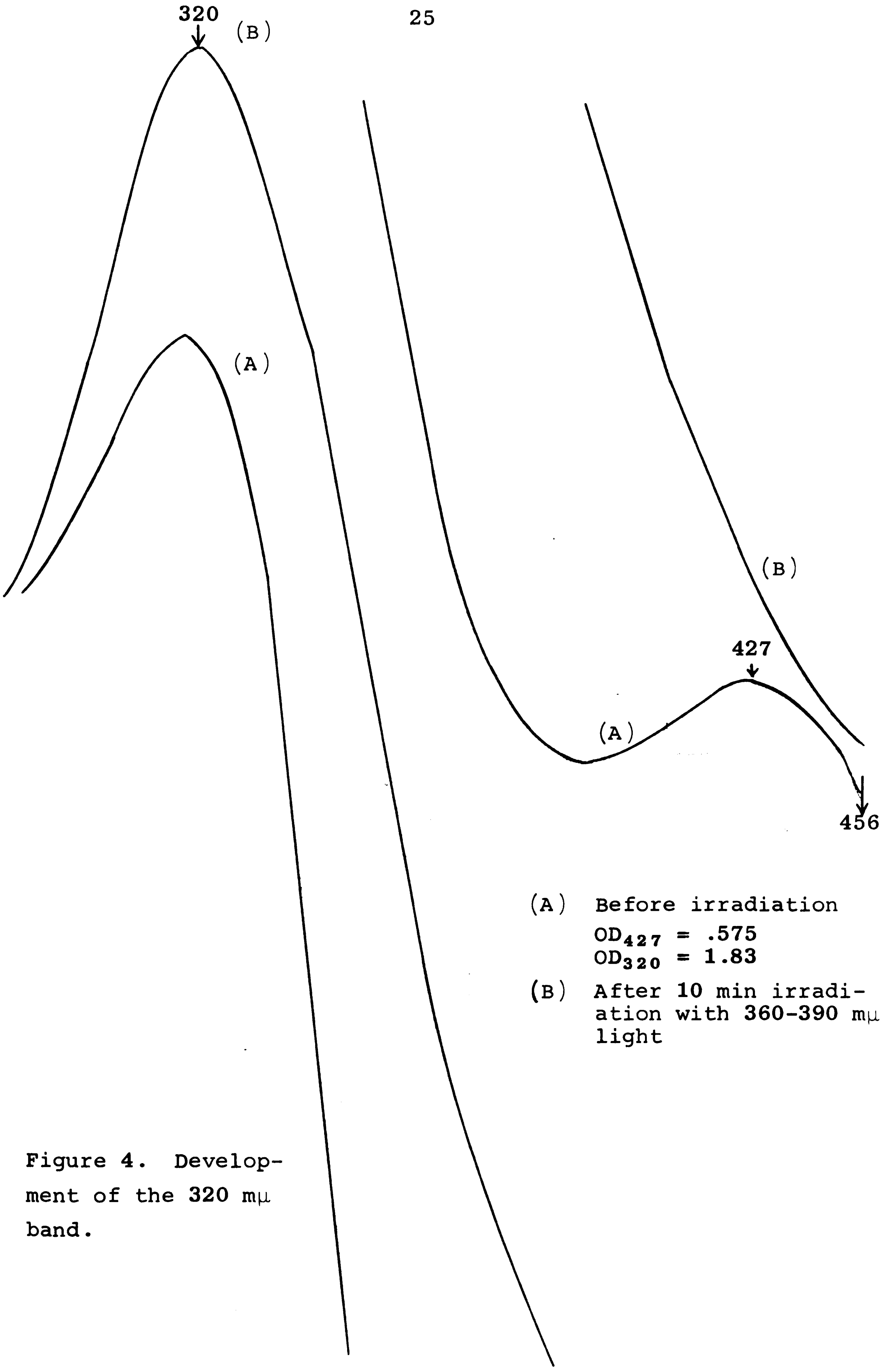
The charge transfer band, at 242 mμ, of trisoxalatocobaltate(III) is too far to cause this absorption.

The solution spectrum of trisoxalatocobaltate(II) exhibits no uv band till 180 mμ.

The near ultraviolet absorption band, which is variously found between 320-350 mμ; has been attributed by us, to the carbon dioxide radical ion.

One of the reasons for this is that the optical density of the band, after short irradiation, seems independent of the trisoxalatocobaltate(III) concentration. This would be the case if the primary product of the photolysis is a radical with a high extinction coefficient. That this is the case is proven by the ease with which the band grows, on irradiation, to obscure the ligand field bands, Figures 4, 5.

The other reason supporting this theory is a report by Carrington and McLachlan[5], showing the carbon dioxide



(A) Before irradiation
$OD_{427} = .575$
$OD_{320} = 1.83$

(B) After 10 min irradiation with 360-390 mμ light

Figure 4. Development of the 320 mμ band.

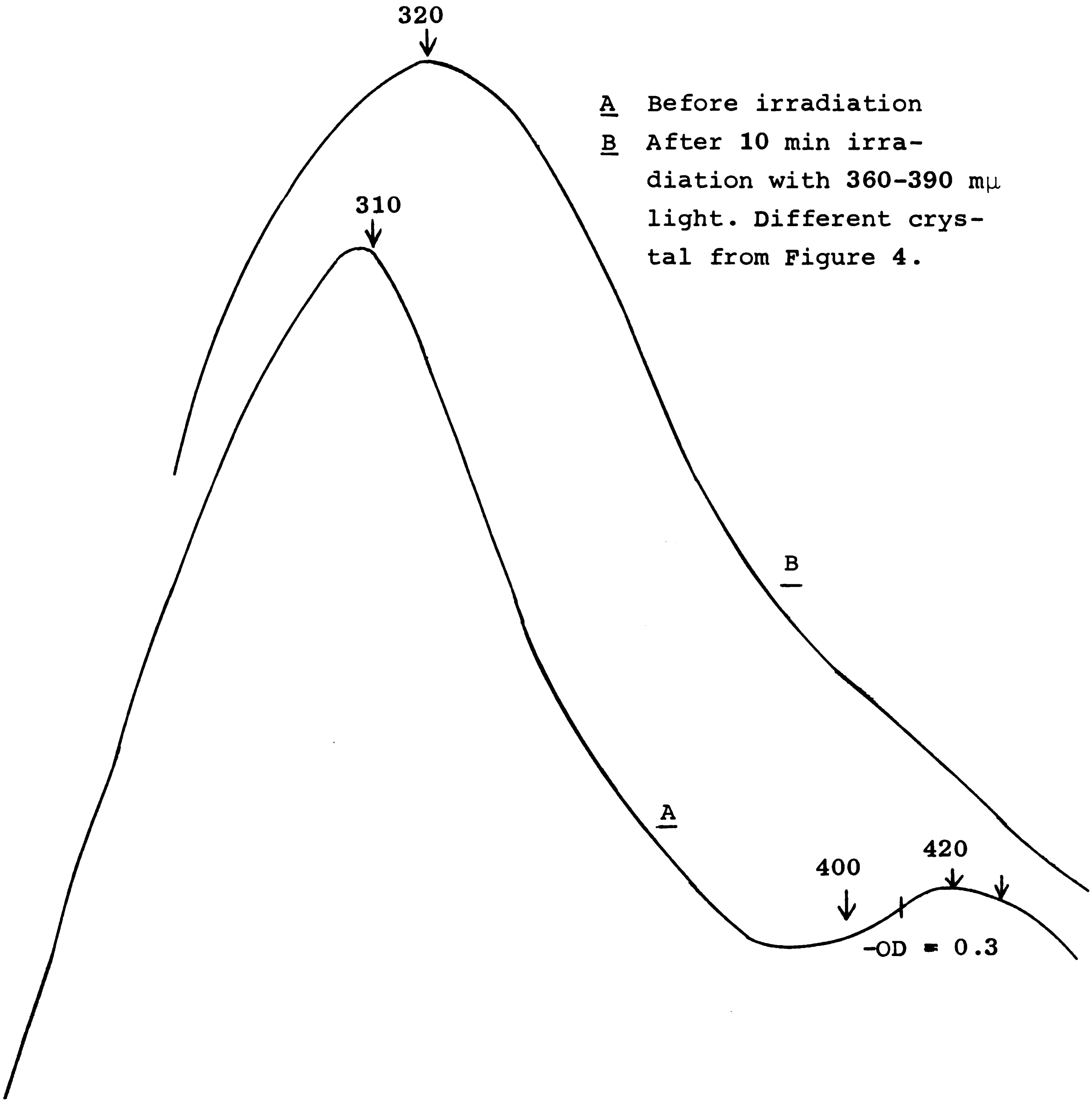


Figure 5. Development of 320 mμ band.

radical ion of C_{2v} symmetry, with the extra electron localized in a carbon sp^2 orbital. The transition giving rise to a reported band at 29,000 cm^{-1} (345 mμ) is from an antibonding a_1 to an antibonding b_1 orbital, i.e. $4a_1 \longrightarrow 2b_1$.

$4a_1 \longrightarrow 2b_1$ allowed only for the x direction

$z = A_1$
$x = B_1$
$y = B_2$

We measured the polarized spectrum of an orthoaxial section, which was irradiated for ten minutes, with light from 532-576 mμ. Absorption of light here is by the second, long wavelength ligand field band.

The spectrum before irradiation, exhibited the usual 260 mμ band, due to the host crystal. After fifteen minutes irradiation, a very intense band developed around 290 mμ, still showing a shoulder at 260 mμ. Since the absolute orientation of the crystal is not known, the direction is not known, but in one orientation of the polarizer the absorption was less intense and the original 260 mμ band was better resolved, Figure 6.

The 290-350 mμ band was found to be present in both dilute and more concentrated crystals. Its increase was found when irradiating with light of the following wavelengths: 360-390, 417 and 533 mμ.

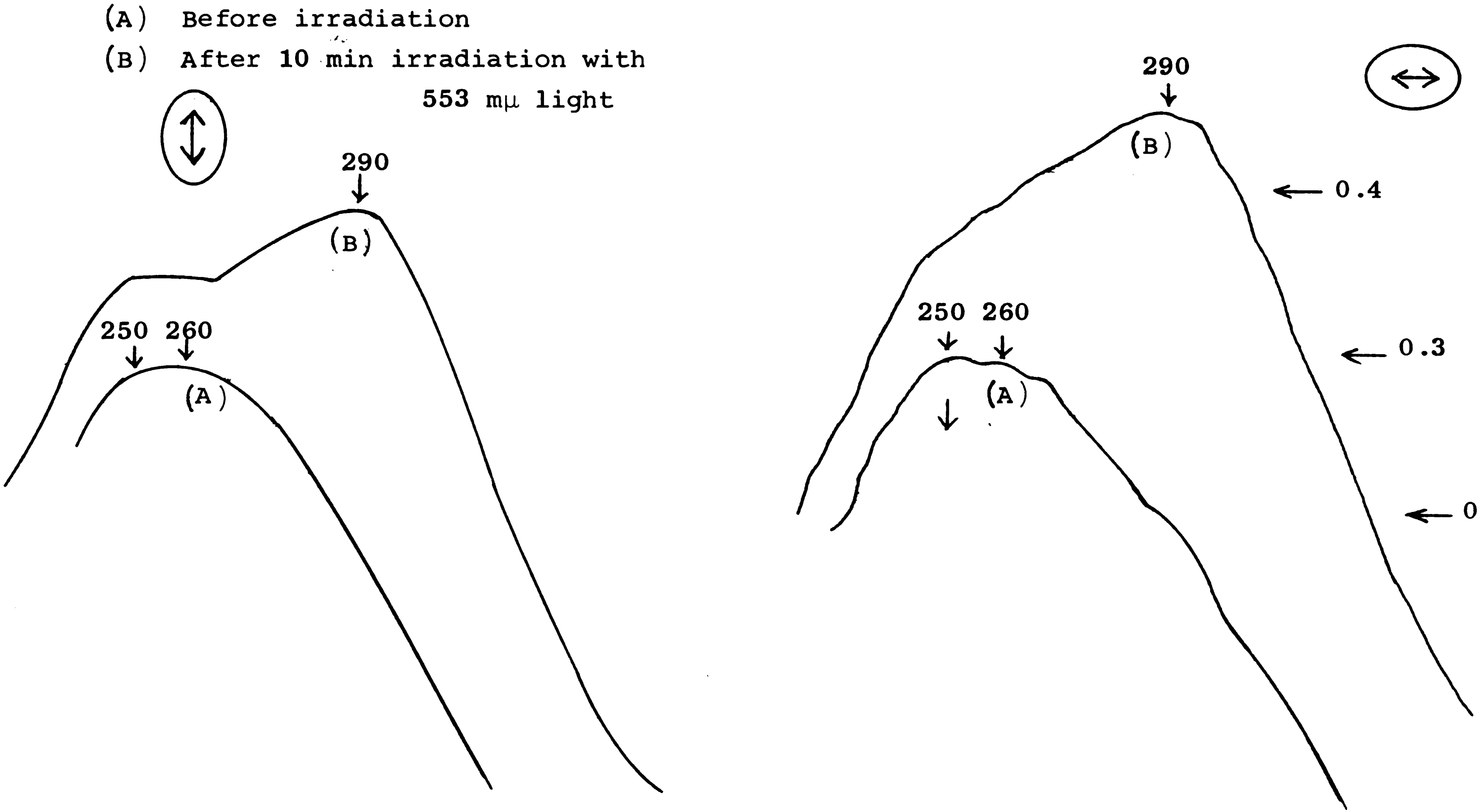


Figure 6. Polarization of the 320 uv peak in an orthoaxial dilute crystal.

Changes in the Two Visible Region Ligand Field Bands Upon Irradiation

As these bands represent different transitions, $^1A_1 \longrightarrow {}^1T_1$ and $^1A_1 \longrightarrow {}^1T_2$ respectively, the reactivities might be expected to differ. Sarma found the decay on irradiation, faster in the 610 mμ band. It is obvious that the effect of the high intensity uv band is to make exact calculations impossible. The reason for the higher quantum yield at the 610 mμ band might well be the fact that its decrease, due to decomposition, is less masked by the uv band than that of the 427 band.

Quantum yields for the trisoxalatocobaltate(III) ion in solution were made, using a neon laser (λ = 6328 Å). Assuming photodecomposition to be of first order the following formula was used:

(1) $$\frac{dc}{dt} = -\frac{\Phi I_a}{V}$$

Φ = quantum yield in moles per einstein

V = volume of solution in liters

c = concentration in moles/liter.

(2) $$\int -dc\ V = \int \Phi\ I_0\ dt$$

(3) Integration between limits: $(c_1 - c_2)V = \Phi I_0 (t_2 - t_1)$

(4) $$\Phi = \frac{(c_1 - c_2)V}{(t_2 - t_1)I_0}$$

from Beer's law $\log \frac{I_0}{I} = \epsilon\ c\ \ell$ = OD where: ℓ = cell path

ϵ = molar extinction coefficient

c = concentration in moles/liter

I = transmitted light

OD = optical density.

Substituting:

$$\Phi = \frac{(OD_1 - OD_2)V}{\epsilon\ \ell (t_2 - t_1) I_0} \qquad (5)$$

$(OD_1 - OD_2)$ = difference in optical density of irradiated and non-irradiated solutions.

OD_1-OD_2	$t_2 - t_1$ (sec)	V (ℓ)	I_0 (einsteins/sec)	ϵ_{610}	ℓ (cm)
.008	4.5×10^3	.026	2.82×10^{-6}	152	10

$\Phi = 1.09 \times 10^{-5}$ moles/einstein, for irradiation with 6328 Å light, monitored at the 610 band.

This result agrees with that of Kneten[12], who could not measure photodecomposition accurately enough by chemical analysis of Co(III), but estimated the limiting quantum yield from experimental accuracy to be not greater than 1.5×10^{-5}, at 610 mμ.

When crystal sections were irradiated we could not compensate for thermal effects. It was known that the thermal instability of the solution due to decomposition was considerably slowed down in the crystal. Some simple experiments were made to determine the change in optical density in the crystal on heating.

The thermal reaction was fitted to the first order rate equation:

$$-\frac{dc}{dt} = kc$$

Integrating $-\int_{c_1}^{c_2} \frac{dc}{c} = k \int_{t_1}^{t_2} dt \quad \therefore k = \frac{2.3}{t_2 - t_1} \log \frac{c_1}{c_2}$

From Beer's law

$$C = \frac{OD}{\epsilon \ell} \qquad \therefore \quad k = \frac{2.3}{t_2 - t_1} \log \frac{OD_1}{OD_2}$$

The change in optical density with prolonged heating time was not consistent. As was observed in the photochemical reactions the ligand field bands flattened but the overall optical density increased. At the start of the heating, both ligand field bands were raised by the same amount. The raising of the whole spectrum might be due to light scattering by the heated crystal. See Figures 7, 8.

Some irreproducibility was introduced by the removal of the spool from the mount, for heating, followed by replacement in the mount. The position could not be exactly reproduced.

The structure of the unit cell of the diluent crystal with chromium substituted for aluminum has been established by Frossard[21] by single crystal X-ray diffraction; there are two formulae units per unit cell. The compound is a nonahydrate. There are two hexaaquomagnesium ions and six non-coordinated water molecules per unit cell.

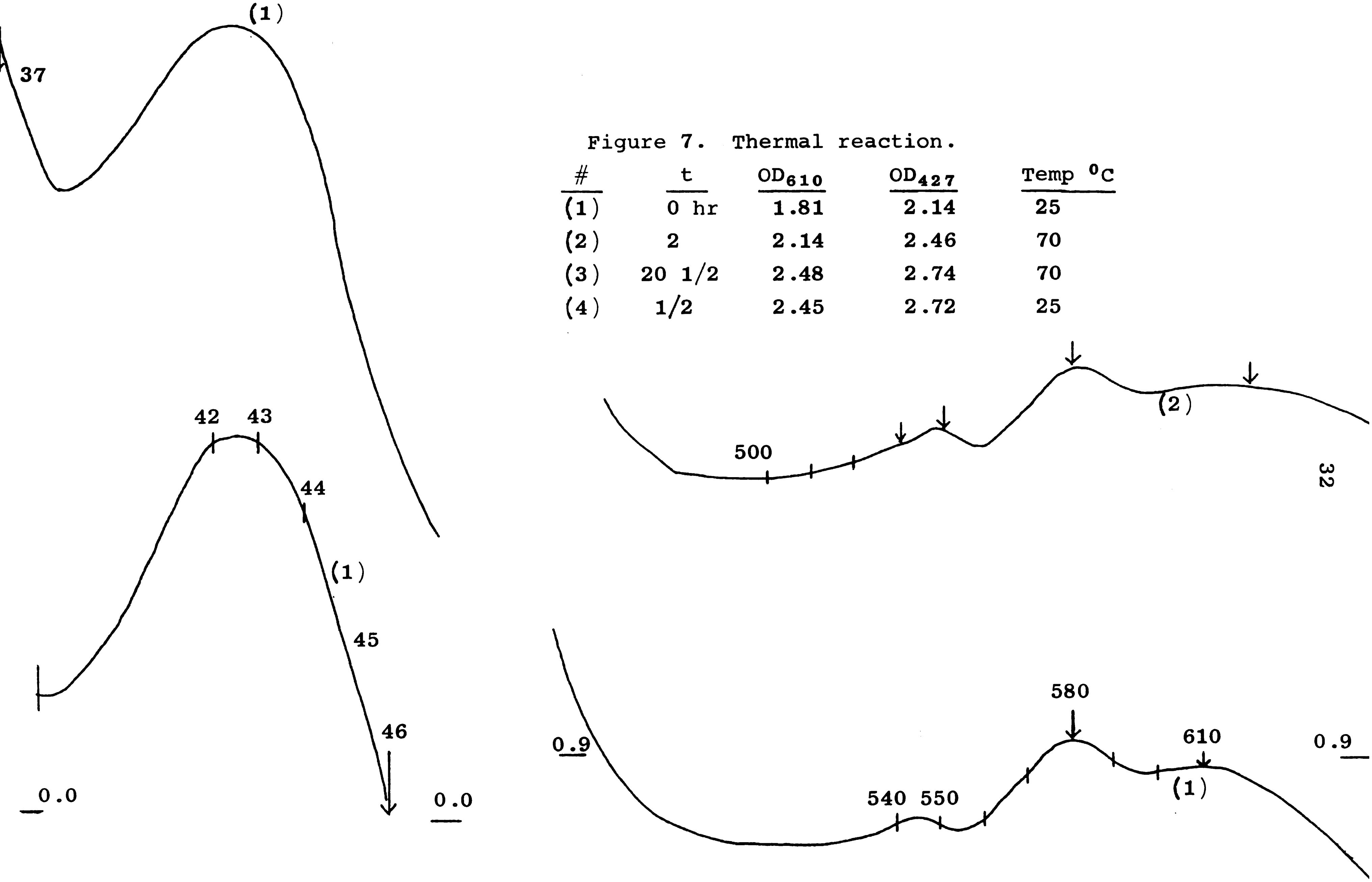


Figure 7. Thermal reaction.

#	t	OD_{610}	OD_{427}	Temp °C
(1)	0 hr	1.81	2.14	25
(2)	2	2.14	2.46	70
(3)	20 1/2	2.48	2.74	70
(4)	1/2	2.45	2.72	25

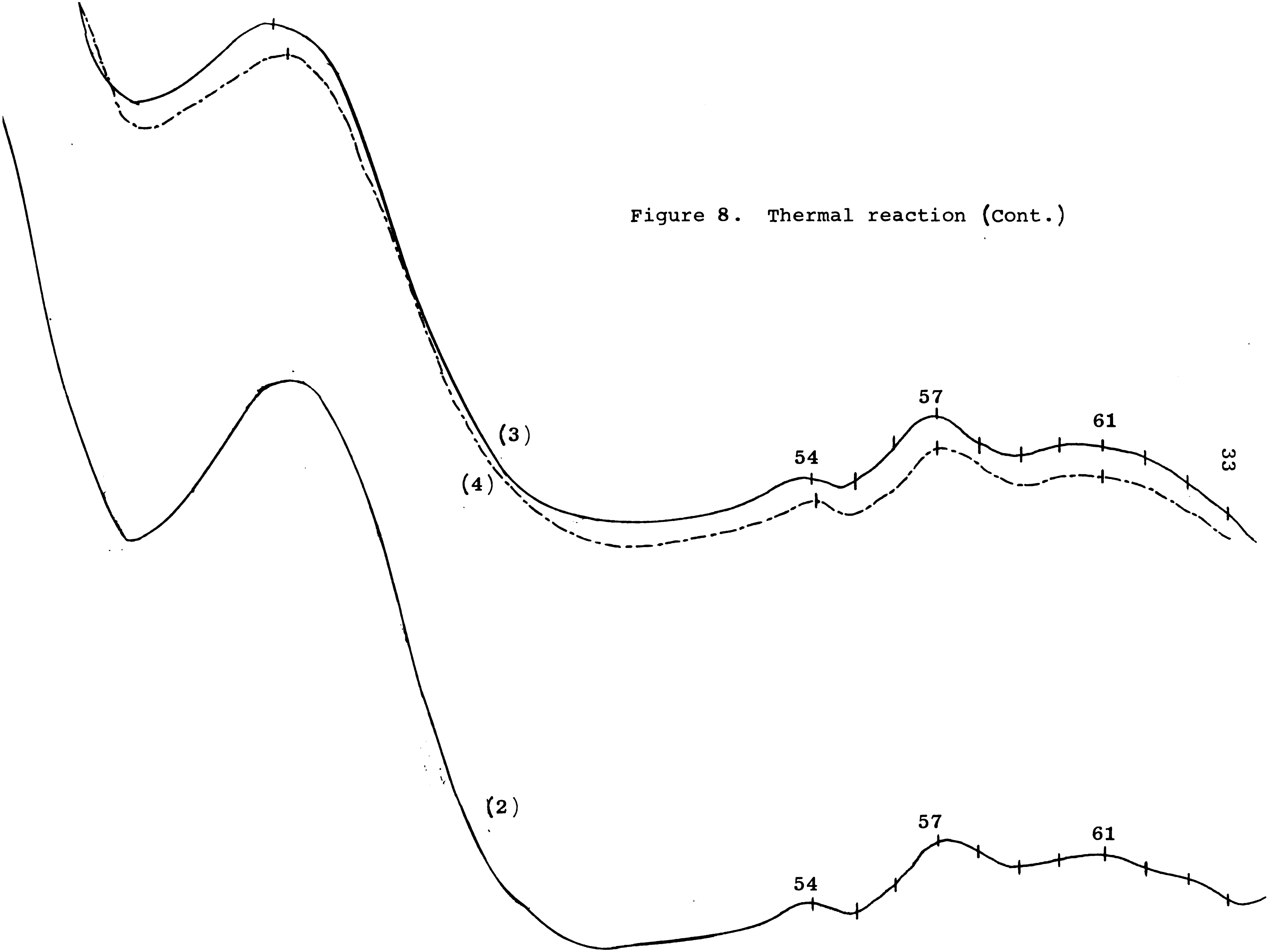


Figure 8. Thermal reaction (Cont.)

Assuming the cobalt compound to have the same structure, the formation of the hydrated electron on heating is likely. Its spectrum was determined by Hart[22]: ϵ^{7200}(max) = 15,800. At 600 mμ the extinction coefficient is around 10,000. The spectrum is suppressed by known electron scavengers such as H_3O^+, O_2, N_2O.[23]

To test this, air was flushed out with nitrogen and the test tube sealed, and heated to see if there were a change in the spectrum or an increase in the reaction rate. No noticeable difference was found when heating a sample for two hours in the presence, respectively absence of oxygen.

We conclude that the hydrated electron is absent, and the carbon dioxide radical, possibly because of its proximity to it, attacks another molecule of trisoxalatocobaltate(III) preferentially to oxygen.

This is the mechanism postulated for the photochemical decomposition too. While this work is definitely preliminary the results indicate that the thermal and photochemical reactions are identical.

Results Obtained by Irradiating at Different Wavelengths

(1) Change in the shape of the spectral bands.

(2) Polarization effects in orthoaxial spectra.

(3) Rate constants.

Irradiations were carried out at the following wavelengths (mμ):

white light - no filter	> 470
360-390	553
365	577
417	> 578
427	632.8

At the high energy side of the second ligand field band 360 mμ is the absorption minimum (Fig. 3). The low energy minimum is at 500 mμ. Energy between these limits is absorbed by the λ_{max} = 427 mμ band, while higher wavelengths are absorbed at the λ_{max} = 608 mμ band. The charge transfer band is at 242 mμ and is not directly effected.

Assuming that the initial optical density is due to trisoxalatocobaltate(III) alone, and that the first minimum in the OD *vs* time plot represents OD_∞, rate constants were calculated. As photochemical reactions are usually first order:

$$\ln[\text{trisoxalatocobaltate(III)}] = -kt + C$$

$$\therefore \quad \ln(OD_t - OD_\infty) = -kt + C$$

Plotting $\ln(OD_t - OD_\infty)$ *vs* time yields: $k = \frac{2.3}{t_2 - t_1} \log \frac{OD_1 - OD_\infty}{OD_2 - OD_\infty}$.

Unfortunately, in crystals of low trisoxalatocobaltate(III) concentration OD_∞ was reached before a sufficient number of measurements could be made. For these runs the rate constant was calculated from the difference between two concentrations.

For more concentrated crystals log $(OD - OD_\infty)$ *vs* time was plotted, and constants were calculated both ways. Calculation of constants from two concentration measurements were labeled A, and those calculated from the graph were designated B. For spectra and graphs see Figures 9-20. For rate constants see Table III.

The crystal section irradiated with 572 mμ light was orthoaxial, the others were axial. Half lives for decomposition ranged between 2.32-7.35 minutes. While the results are of the same order of magnitude they are not consistent enough to show the expected increase in magnitude with increasing light intensity.

Reaction rates are essentially identical at both ligand field bands.

Polarization of the Ligand Field Band Spectra of the Decomposition Products

Spectra of crystals containing a low concentration, about 1% by weight, of trisoxalatocobaltate(III) show the presence of two visible absorption bands absent in the more concentrated crystal. These bands are centered at 535-540 mμ and at 567-570 mμ. Their intensities are low relative to that of the two ligand field bands of trisoxalatocobaltate(III) and upon irradiation their intensities change. The change is dependent on the orientation of the crystal for an orthoaxial section. See Figures 21-30 in Appendix.

We attribute these bands to a low symmetry decomposition product. This compound could be formed in one or both of two ways.

(1) By a slow thermal reaction during crystal growth.

(2) By a photochemical decomposition during irradiation.

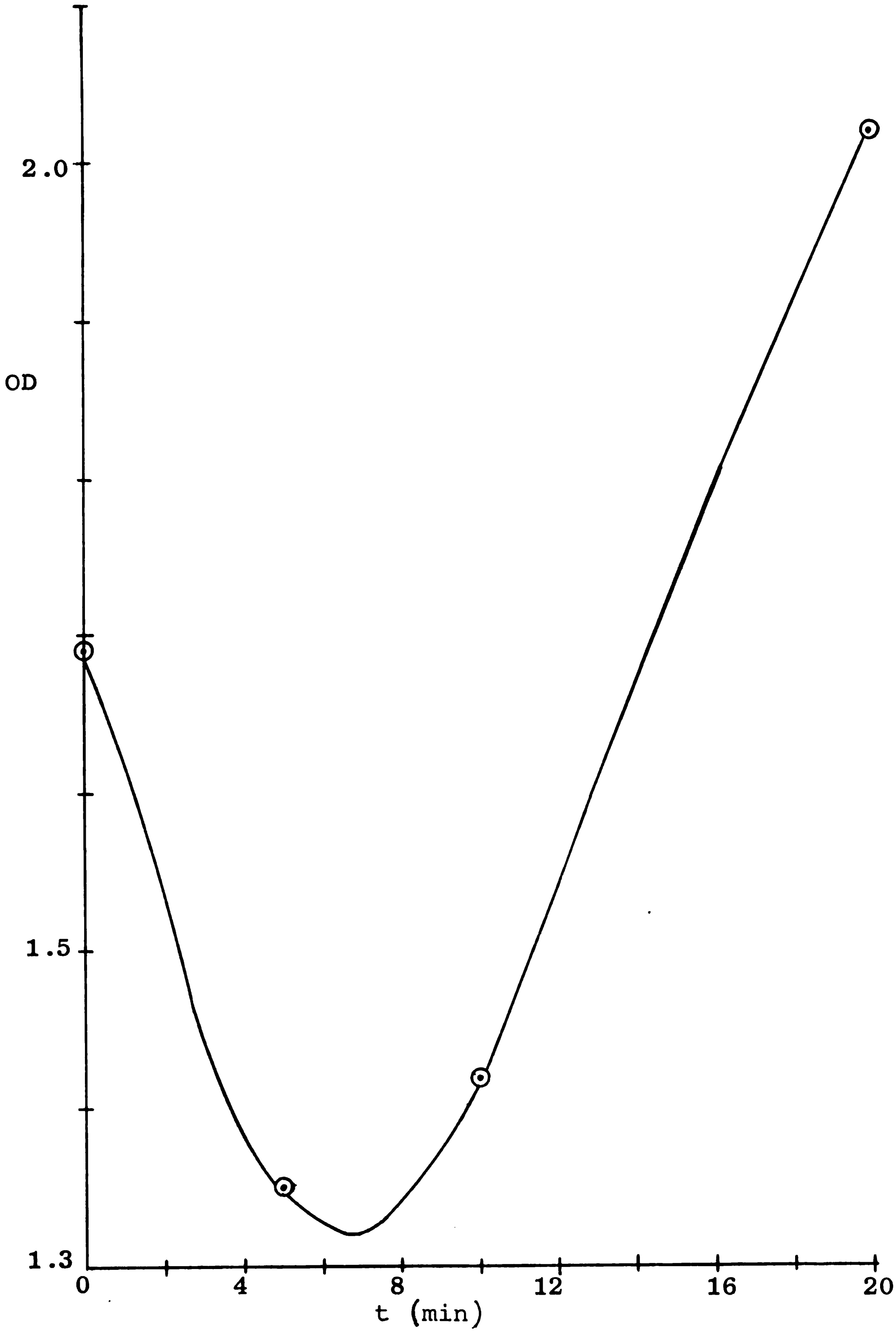


Figure 9. Irradiation with white light. Axial section, 610 band.

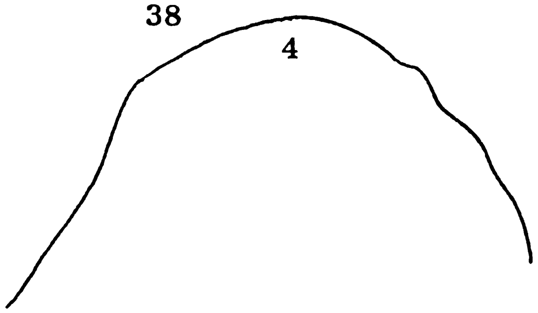


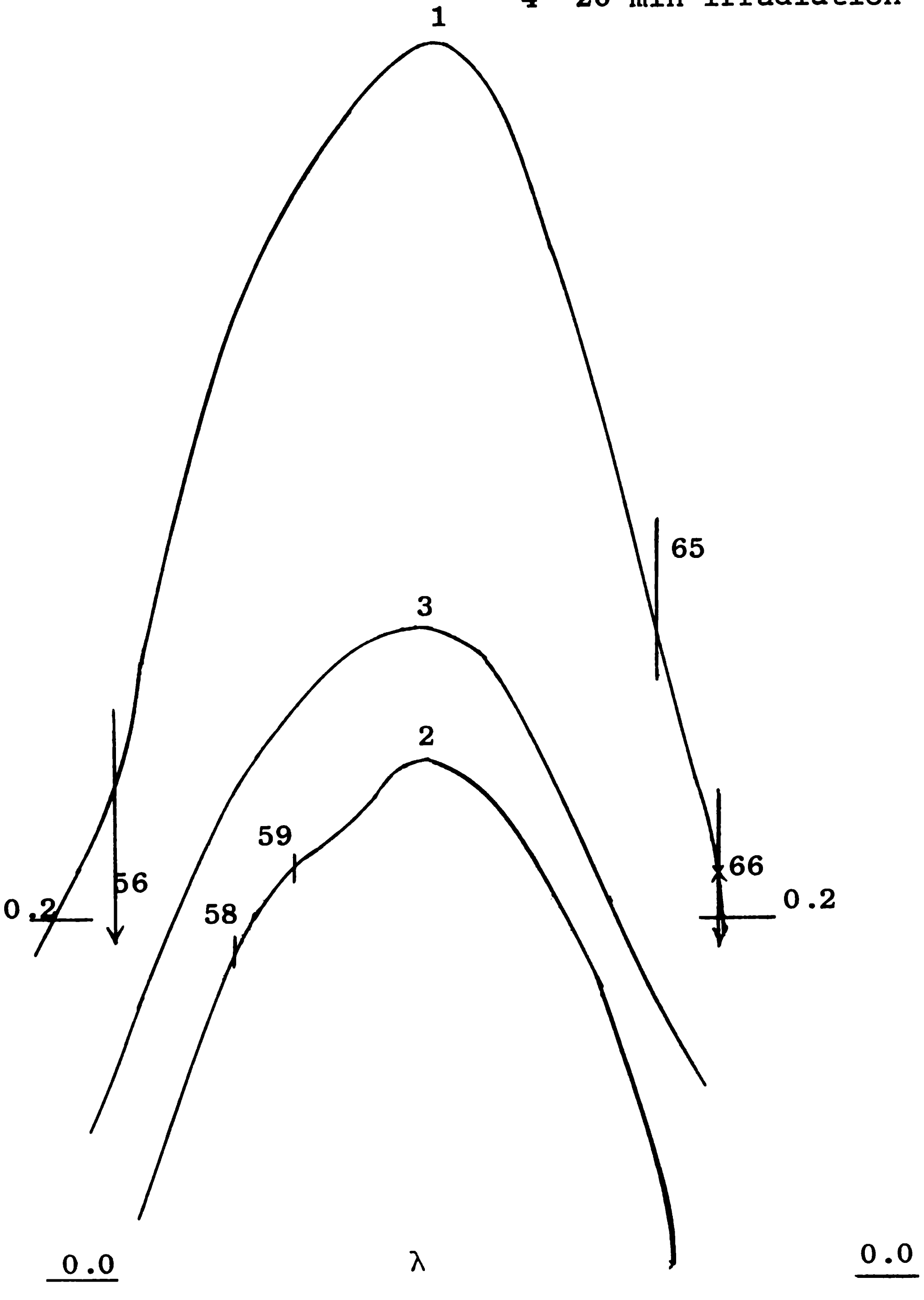
Figure 10. Spectrum for Figure 9.

1 Original

2 5 min irradiation

3 10 min irradiation

4 20 min irradiation



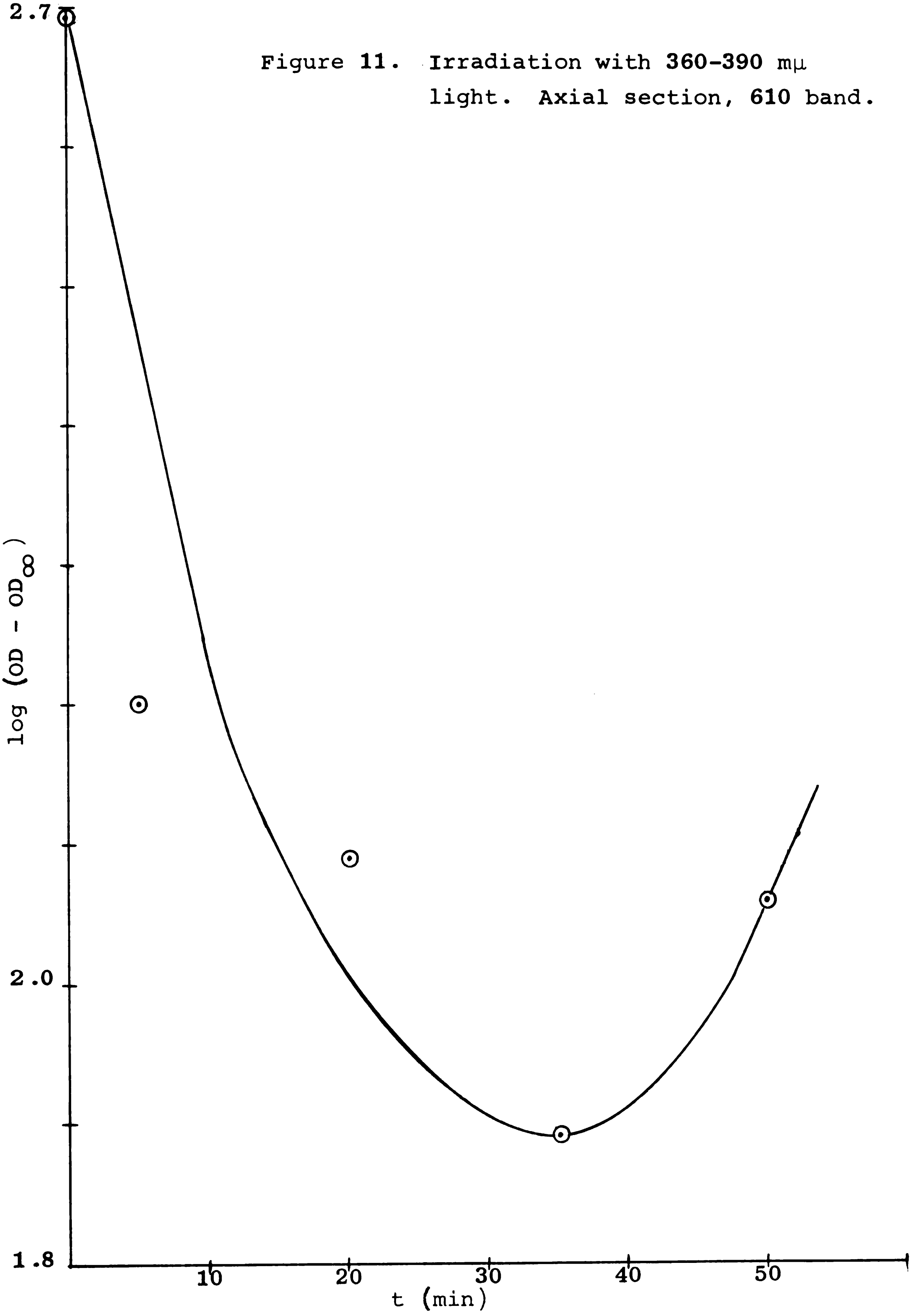


Figure 11. Irradiation with 360-390 mμ light. Axial section, 610 band.

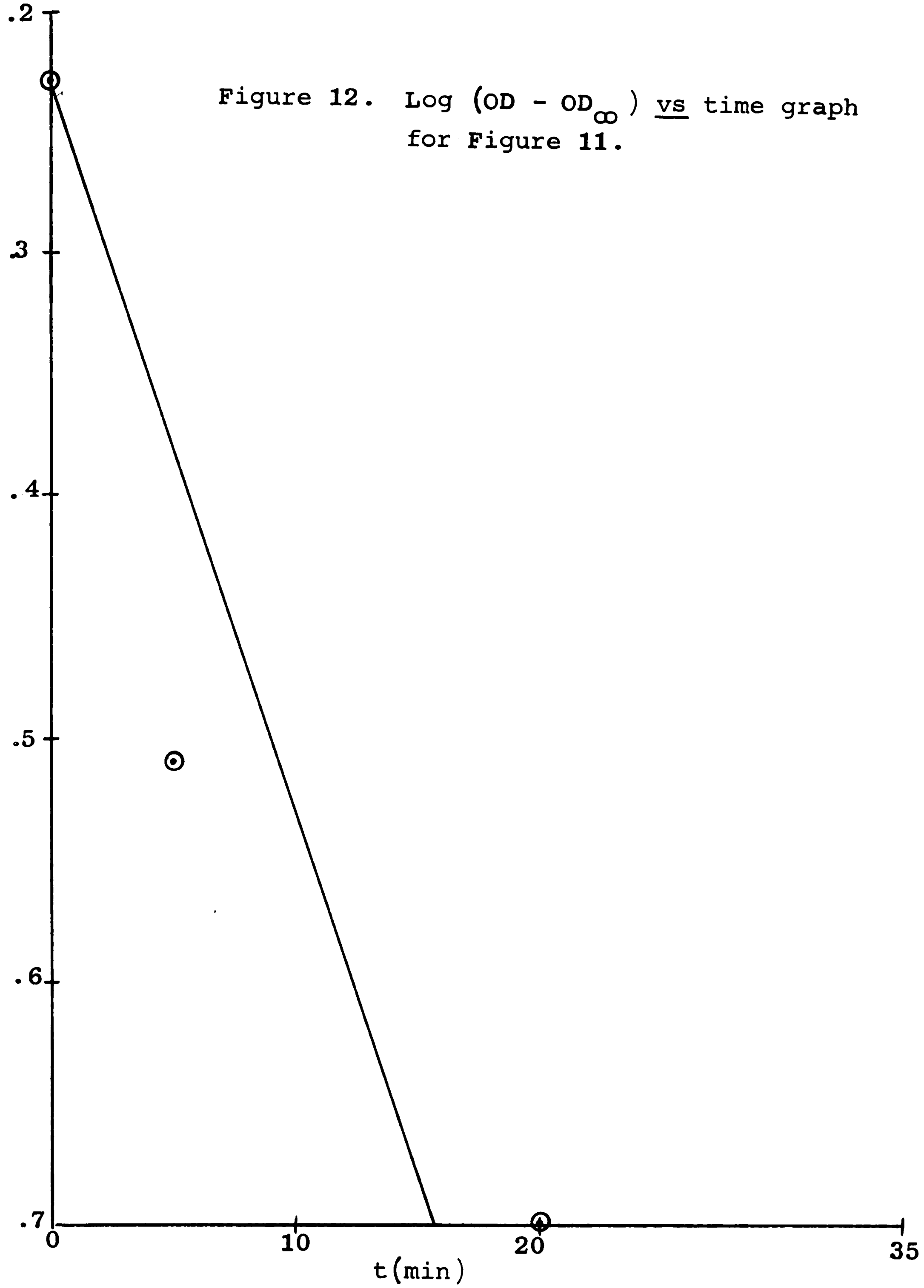


Figure 12. Log $(OD - OD_{\infty})$ *vs* time graph for Figure 11.

	OD_{610}	
(1) Before irradiation	2.69	(off scale)
(2) 5 min. irradiation	2.20	
(3) 20 min. irradiation	1.87	
(4) 50 min. irradiation	1.67	
(5) 200 min. irradiation	1.74	

Not all points were plotted
to make spectrum clearer.

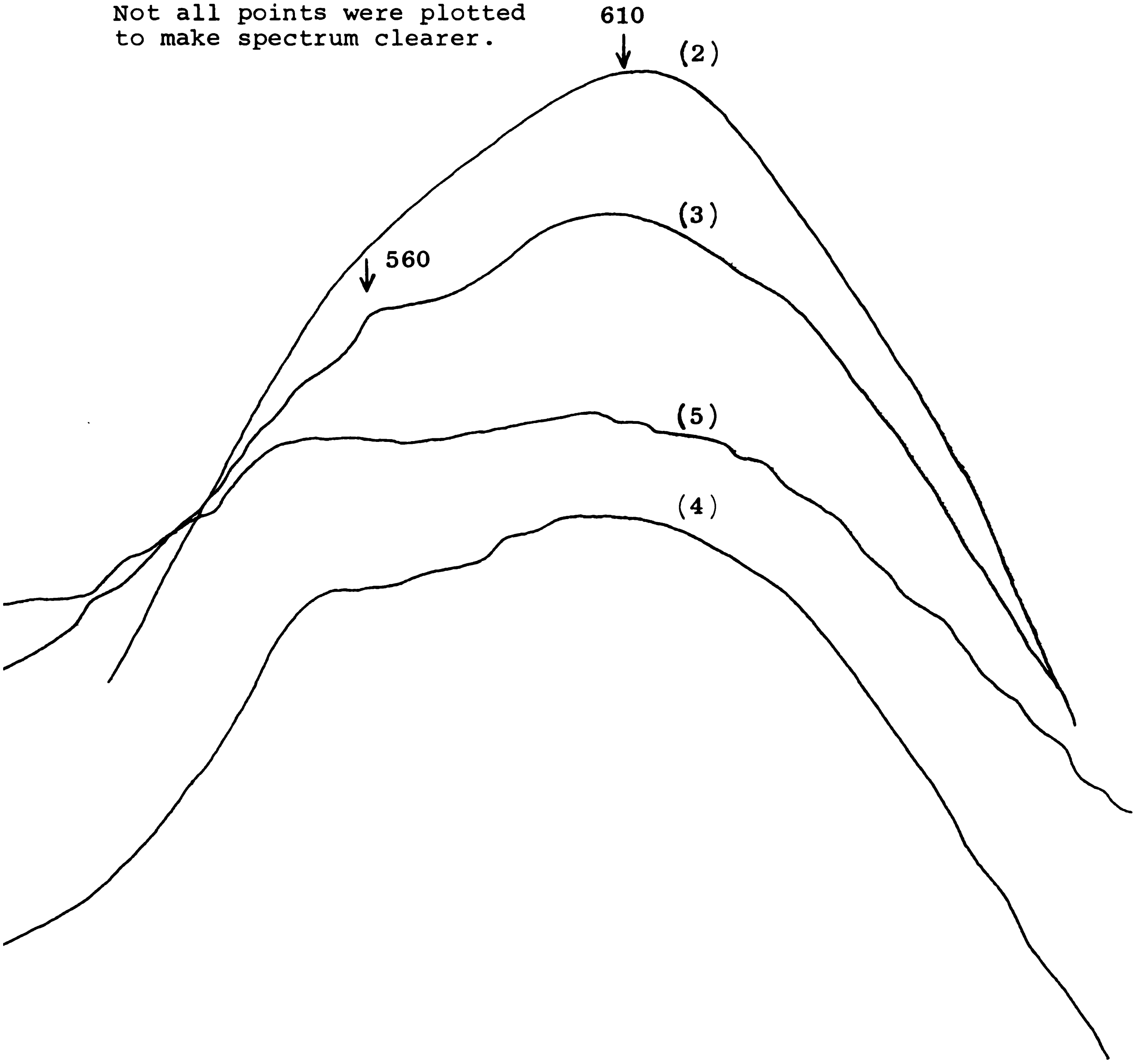


Figure 13. Spectrum for Figure 11.

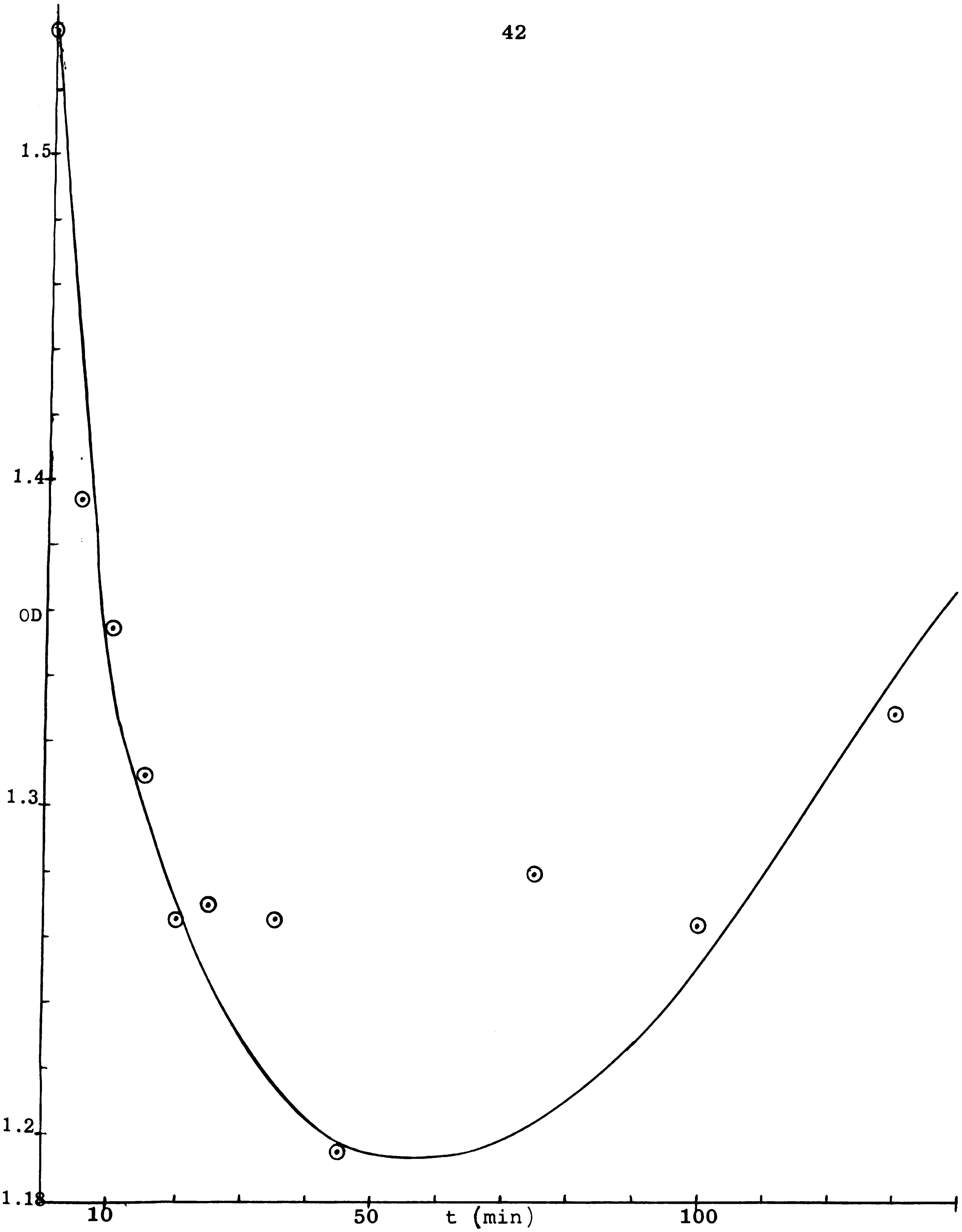


Figure 14. Irradiation #2 with 360-390 mμ light. Axial section at 610 mμ band.

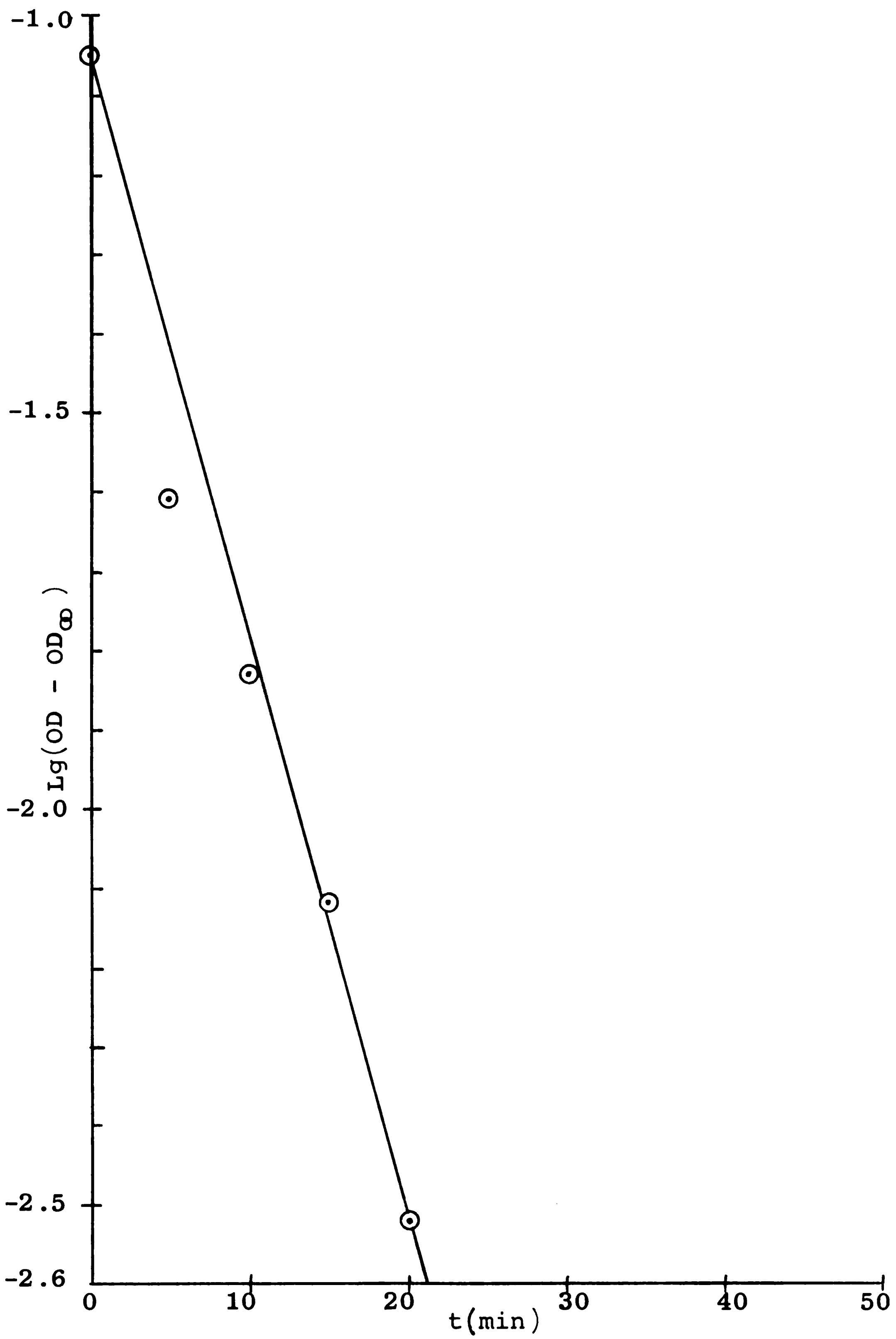


Figure 15. Log (OD - OD$_\infty$) vs time graph for Figure 14.

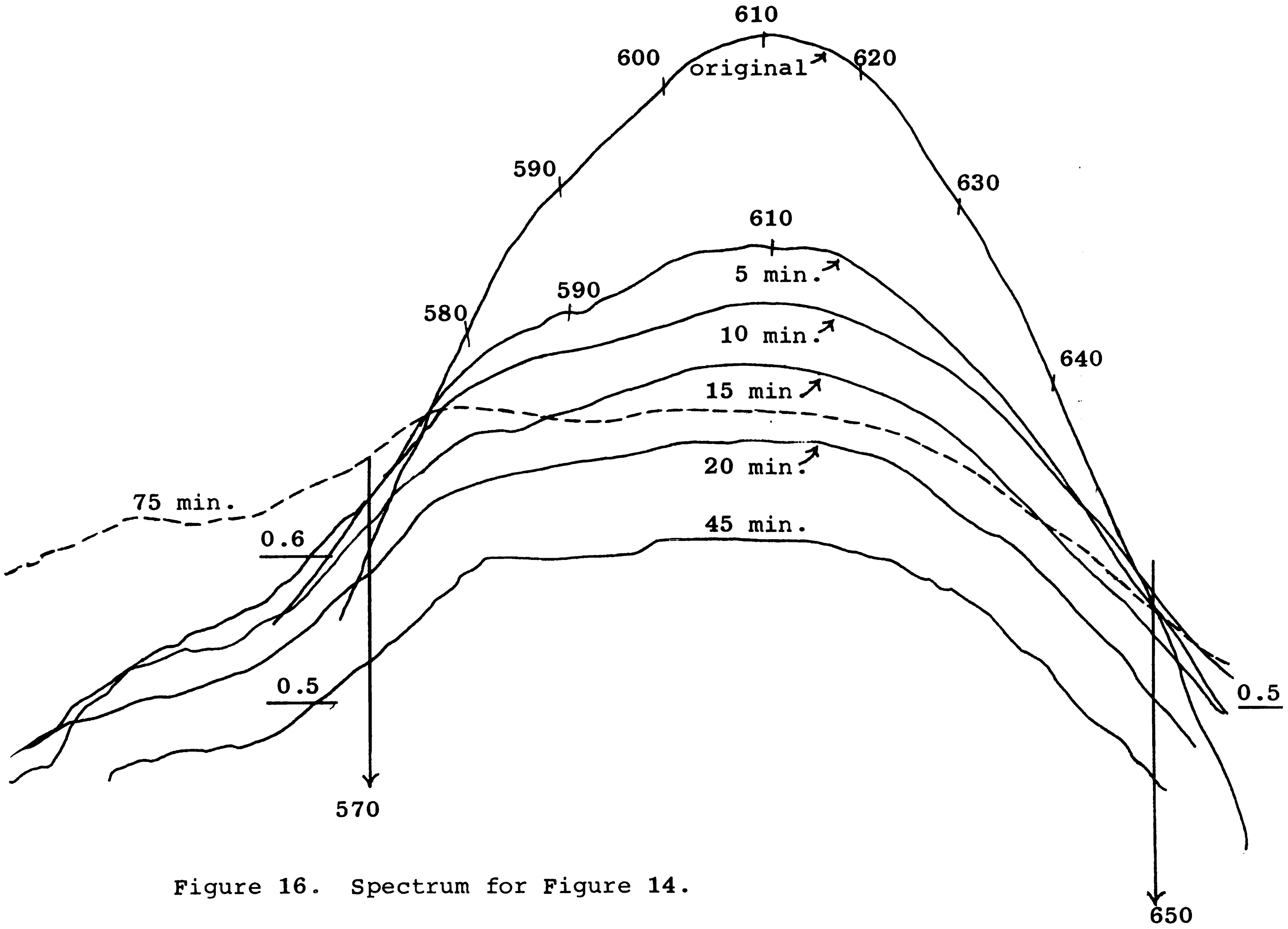


Figure 16. Spectrum for Figure 14.

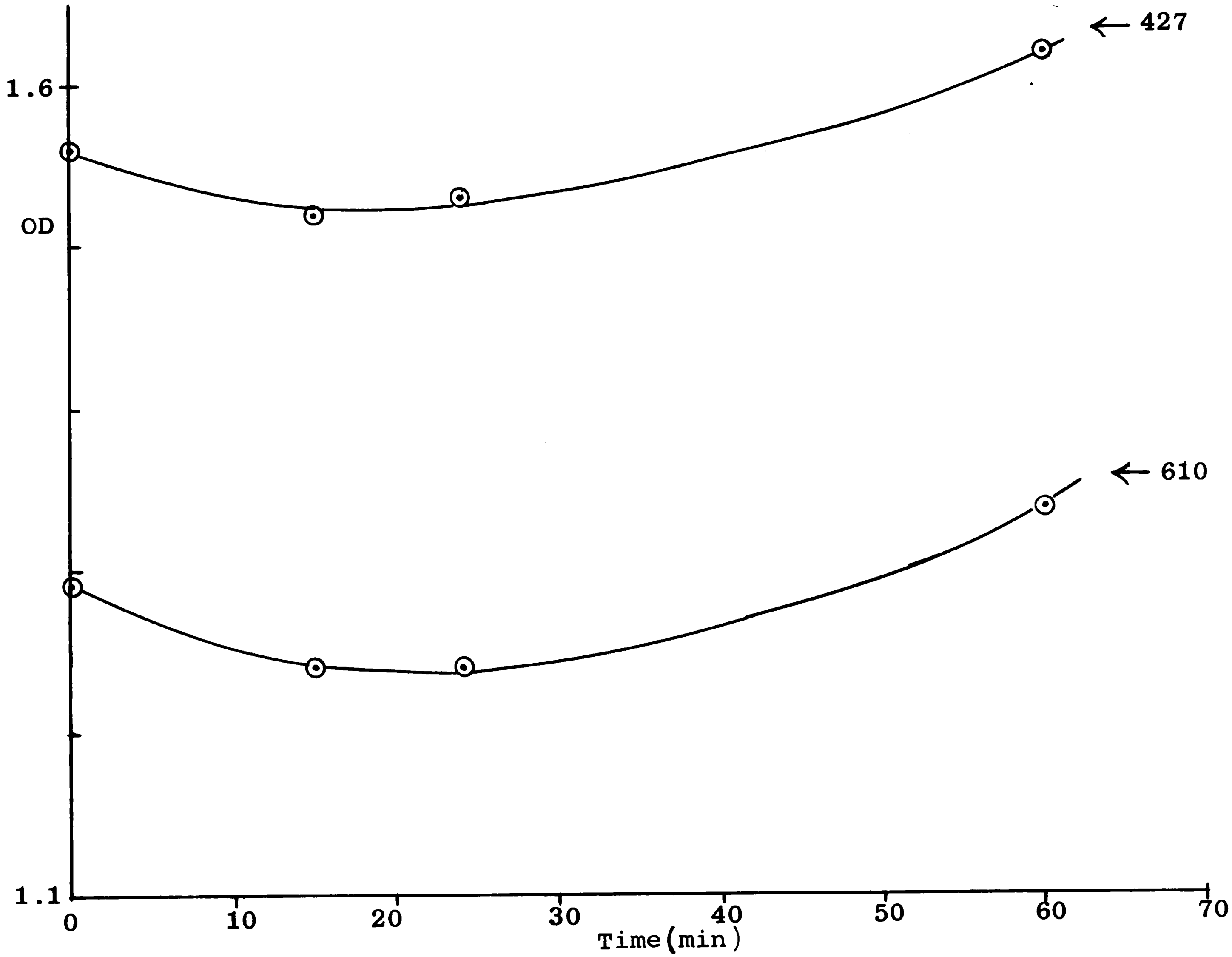


Figure 17. Irradiation at 417 mμ, monitored at 610 mμ and 427 mμ. Axial section.

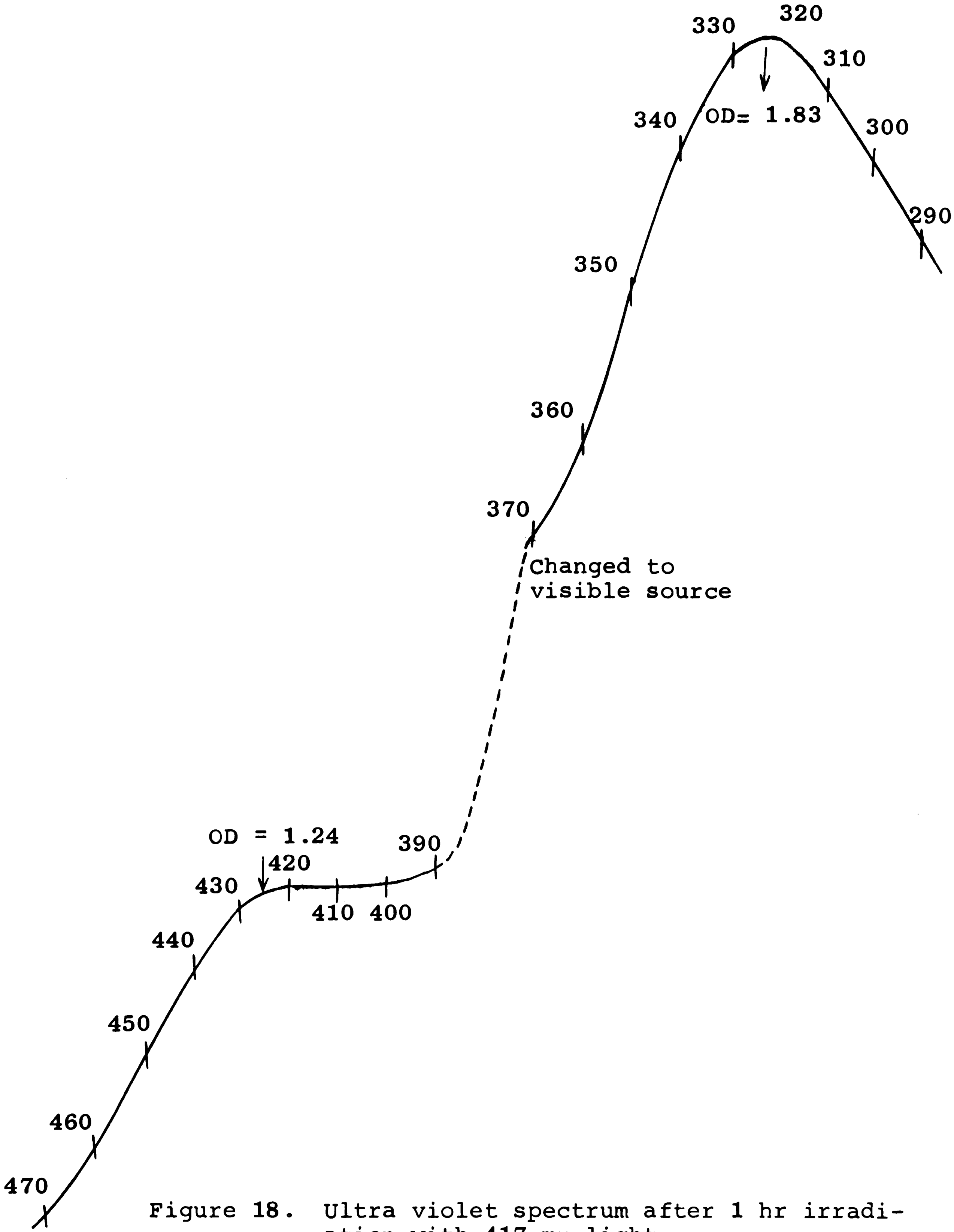
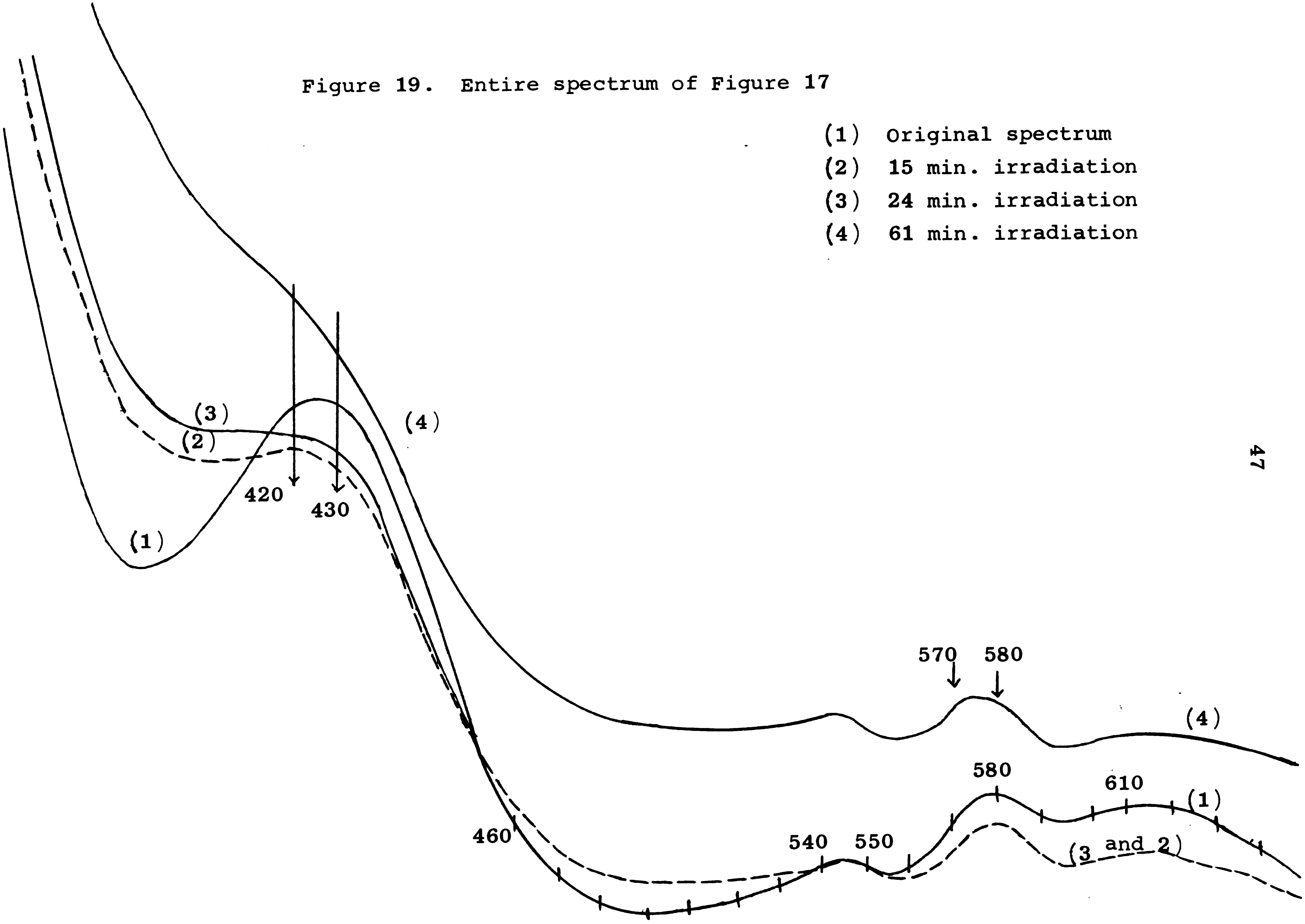


Figure 18. Ultra violet spectrum after 1 hr irradiation with 417 mμ light

Note: Different crystal from Figure 17.

Figure 19. Entire spectrum of Figure 17



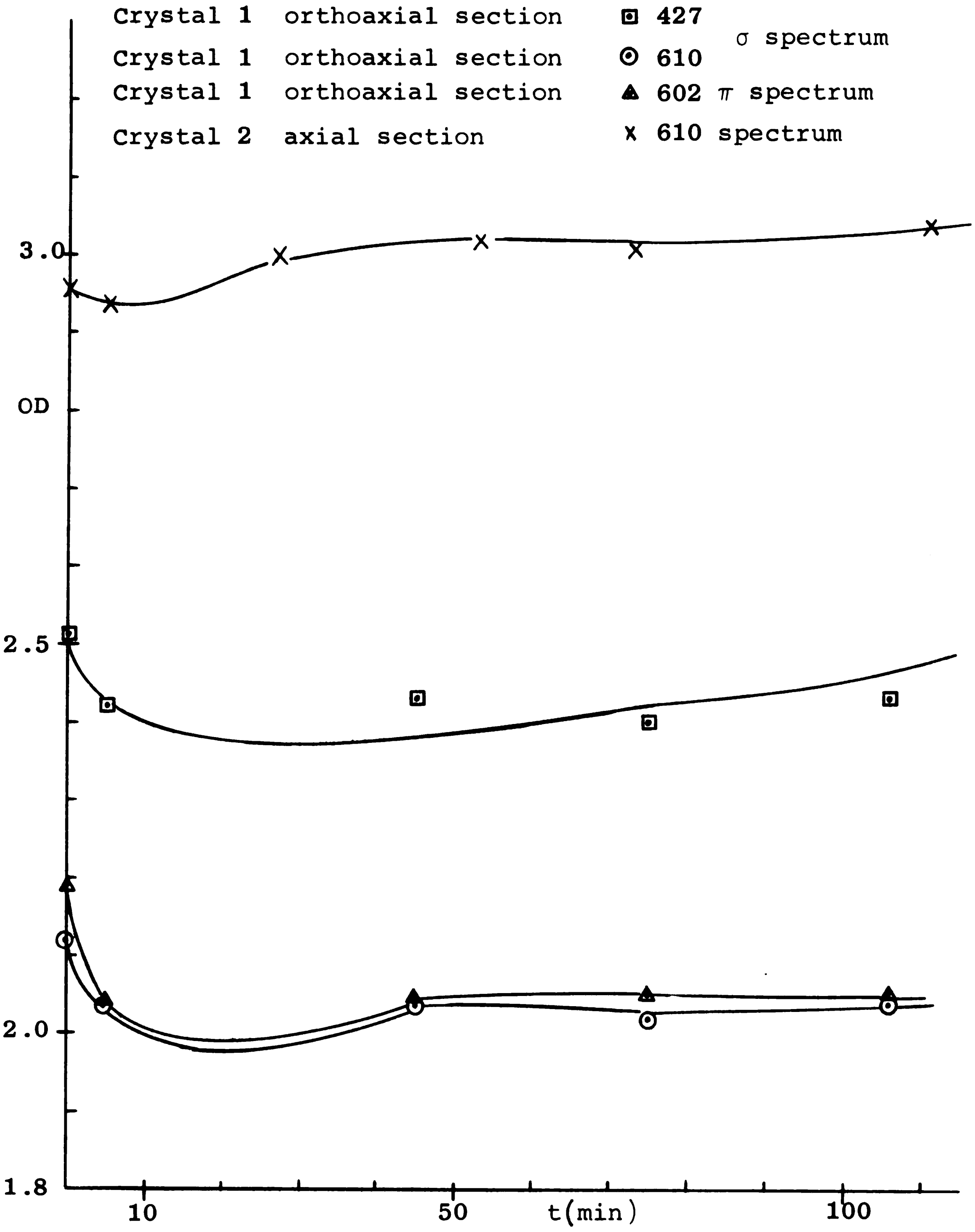


Figure 20. Irradiation at 572 mμ.

Table III. Rate constants for the photodecomposition.

Time (sec)	OD	log $(OD - OD_\infty)$	k(sec^{-1})	τ (min)	I (einsteins/sec)
Figure 9.	Irradiation with white light, monitored at the 610 mμ band				
0	1.69	- .43	2.17×10^{-3} (A)	5.3	Not determined
5	1.35	-1.52			
7	1.32	OD_∞			
Figure 11.	Irradiation with 360-390 mμ, monitored at 610 mμ				
0	2.69	-0.10	1.86×10^{-3} (A)	6.15	3×10^{-6}
5	2.20	-0.51			
20	2.09	-0.70	1.13×10^{-3} (B)		
35	1.89	OD_∞			
Figure 14.	Same as above, different crystal				
0	1.59	-0.46	6.4×10^{-3} (A)	3.96	2.34×10^{-6}
5	1.39	-0.70	2.9×10^{-3} (B)		
10	1.35	-0.80			
15	1.31	-0.92			
20	1.27	-1.10			
45	1.19	OD_∞			
Figure 17.	Irradiation at 417 mμ, monitored at 610 mμ				
0	1.29	-1.22	1.56×10^{-3} (A)	7.35	5.65×10^{-8}
15	1.24	-2.00			
20	1.23	OD_∞			

Table III. (Continued)

Time (sec)	OD	log $(OD - OD_{\infty})$	$k(\text{sec}^{-1})$	τ (min)	I (einsteins/sec)
Figure 17. Irradiation at 417 mμ, monitored at 427 mμ					
0	1.56	-1.3	$1.67x10^{-3}$ (A)	6.9	$5.65x10^{-8}$
15	1.52	-2.0			
18	1.51	OD_{∞}			
Figure 20. Irradiation at 572 mμ, monitored at 610 mμ					
0	2.12	-0.96	$4.8x10^{-3}$ (A)	2.38	$2.32x10^{-6}$
5	2.04	-1.52			
7	2.01	OD_{∞}			
Figure 20. Irradiation at 572 mμ, monitored at 427 mμ					
0	2.51	-0.89	$4.95x10^{-3}$ (A)	2.32	$2.32x10^{-6}$
5	2.42	-1.38			
8	2.38	OD_{∞}			

The compound could not be seen in the more concentrated crystal as it would be obscured by the intense 610 mμ band.

The polarization for an orthoaxial section of the ligand field transitions for the decomposition products were as follows:

Table IV. Polarized spectra of the irradiated crystals

Irradiation(mμ)		570 band - π	580 band - σ	540 band - σ
360-390	Run 1	OD incr.	Marked incr.	Marked incr.
	Run 2	OD incr.	Marked incr.	Marked incr.
427		OD incr.	Slight incr.	Slight incr.
> 450		OD incr.	Marked incr.	Marked incr.
572		Slight incr.	Slight incr.	Slight incr.
577		Unchanged	Unchanged	Unchanged

The 427 mμ transition is allowed for the σ ($\perp$) spectrum only. The 540 mμ transition which is polarized is allowed in the same direction, and is absent in the π spectrum.

Light absorbed at the long wavelength 610 mμ band does not effect the spectrum noticeably, probably because the energy absorbed is too small.

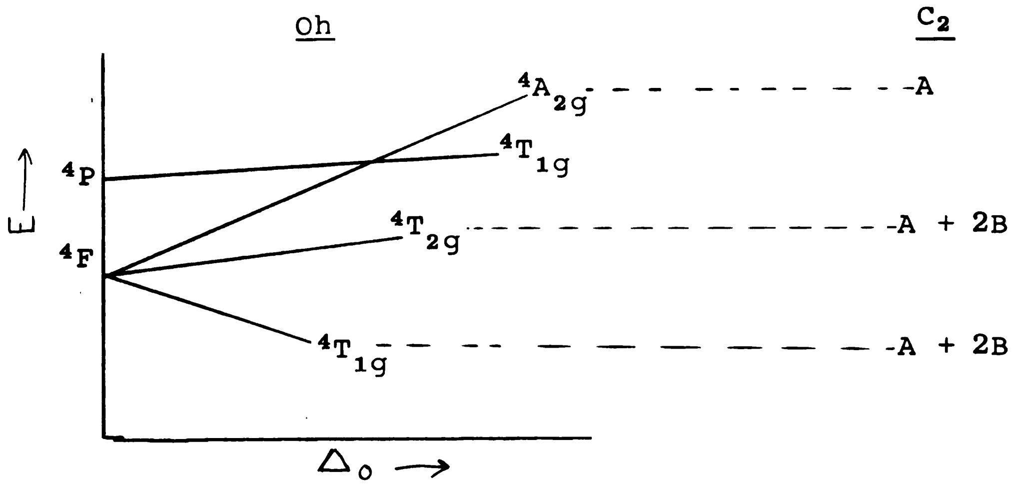
The decomposition product absorbing in this region could be either bisoxalatodiaquocobaltate(II) or trisoxalatocobaltate(II). The former could be either the <u>cis</u> or the <u>trans</u> isomer or both, as cobalt(II) complexes are labile. The cis isomer is the prevalent one formed from trisoxalatocobaltate(III) by loss of a ligand. This isomer has C_2 symmetry. It is a likely product as the unit cell structure of the complex in the diluent crystal contains six moles of noncoordinated water.

However, calculations and spectra support the D_3 symmetry of trisoxalatocobaltate(II). The reaction mechanism postulated by us presupposes the presence of both compounds. The aquo complex could presumably undergo anation by oxalate and form the trisoxalato complex, which would then be the final product of the reduction.

Calculations for cis- bisoxalatodiaquocobaltate(II). C_2.

(1) For a d^7 ion the ground state Russell-Saunders term is ^4F.

(2) Crystal field splits this state.[24]



(3) in C_2 the representations are as follows:[25]

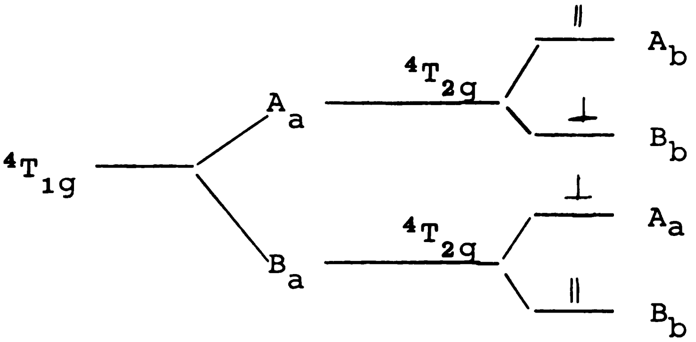
$$\left\{\begin{array}{r} z = A \\ (x,y) = B \end{array}\right\}$$ Taking the triple products the following selection rules are found:

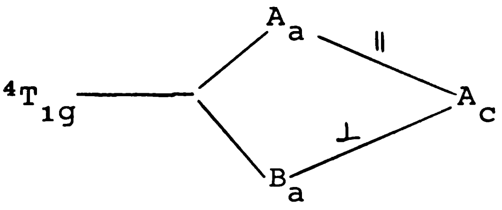
$$A \xrightarrow{\parallel} A$$

$$A \xrightarrow{\perp} B$$

$$B \xrightarrow{\parallel} B$$

Since the ground state T_{1g} is split and this splitting is probably too small to notice the spectrum would not appear to be polarized:





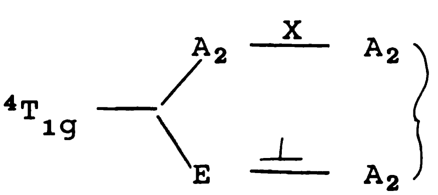
In the case of D_3 symmetry the selection rules are of course, the same as for the cobalt(III) ion but the states are split differently for the d^7 ion, <u>i.e</u>.:

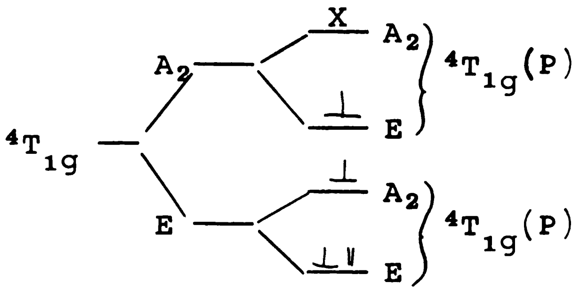
Oh		D3
$^4T_{1g}$	=	$A_2 + E$
$^4T_{2g}$	=	$A_1 + E$
$^4A_{2g}$	=	A_2

$A_2 \xrightarrow{\parallel} A_1$ $\quad$ $E \xrightarrow{\perp} A_1$

$A_2 \xrightarrow{\perp} E$ $\quad$ $E \xrightarrow{\parallel\perp} E$

$A_2 \xrightarrow{X} A_2$ $\quad$ $E \xrightarrow{\perp} A_2$





The $^4T_{1g} \longrightarrow {}^4T_{2g}$ transition is in the infrared region and its polarization was not investigated. A wide band of low molar extinction was found at 1210 mμ in solution, and was attributed to this transition.

The $^4T_{1g} \longrightarrow {}^4A_{2g}$ transition is polarized in the same direction as the $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition (427 mμ) in the reactant. Its polarization was therefore easy to find.

The spectrum was interpreted as follows:

ν_1 : $^4T_{1g} \longrightarrow {}^4T_{2g}$ at 1210 mμ

ν_2 : $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ at 570-580 mμ

ν_3 : $^4T_{1g} \longrightarrow {}^4A_{2g}$ at 535-540 mμ

Values for D_q, B, and ν_2 were calculated from ν_1 and ν_3.[26]

$$D_q = [(2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1\nu_3 - \nu_1^2)^{1/2}]/20$$

$$B = (\nu_3 - 2\nu_1 + 10\ D_q)/15$$

ν_1 = 1210 mμ or 8260 cm^{-1}

ν_3 = 535 mμ or 18,700 cm^{-1}

D_q = 935 cm^{-1} B = 770 cm^{-1}

$\nu_2 = \nu_1 + 10\ D_q$ = 17,610 cm^{-1} or 567 mμ.

The ν_2 value is in excellent agreement with our experimental value. B is lower than the value found for it in the Tanabe and Sugano diagrams, where B = 970 cm^{-1} for Co(II). This is due to the fact that the separation between the Russel-Saunders terms is less in the complex than in the free ion, but the diagrams do not consider the nephelauxetic effect. The D_q value is of the magnitude usually found for oxalate in the literature.

Calculating ν_1, ν_2 and ν_3 for the above values of D_q and B, we get from the Tanabe and Sugano diagrams:

$$\frac{\Delta_0}{B} = \frac{9350}{770} = 12.2$$

$$^4T_1 \longrightarrow {}^4T_2 = 9250\ cm^{-1}$$

$$^4T_1 \longrightarrow {}^4A_2 = 16900\ cm^{-1}$$

$$^4T_1(F) \longrightarrow {}^4T_1(P) = 18,500\ cm^{-1}$$

The assignment for the latter two transitions are interchanged from our assignments but the two states differ only slightly in energy, in this region. The primary reduction product is expected to be low spin Co(II), $t_{2g}^6\ e_g$, and evidence for the existence of hexacoordinated low spin Co(II) products has recently been reported in the literature.[27] Due to the high pairing energy of 22,500 cm^{-1} [19] the final oxalate compound is expected to be high spin i.e. $t_{2g}^{5}\ e_{g}^{2}$. Thus the spectrum of the hexaquocobalt(II) ion with excess oxalate should be identical to the product of the photodecomposition. There are, however, two visible bands in the spectrum of the solid and one in the solution.

The hexaquocobalt(II) ion spectrum shows the absence of the $^4T_{1g} \longrightarrow {}^4A_{2g}$ transition which is expected to be weak. This may be the case with the oxalate in solutions, too.

Conceivable too, in the solid the trisoxalatocobaltate(II) ion responsible for the absorption is only present in trace amounts in solution because the low K value. This also accounts for the fact that the spectrum of a 4:1 ligand-metal solution is identical to that of a 3:1 solution.

Additional support for the existence of the reduced oxalate complex is Wendland's[9] work. Reflectance spectrophotometry established the disappearance of the high energy ligand field band and a subsequent decrease in reflectance at 540 mμ.

We were unsuccessful in incorporating bisoxalatodiaquocobaltate(II) into the diluent crystal. Its volume and that of trisoxalatoaluminate are sufficiently different to make substitution difficult.

An attempt was made to investigate the other decomposition products CO_2, and $CO_2^{\overline{\cdot}}$. A mull made of potassium trisoxalatocobaltate(III) was irradiated and a gas was produced. The spectrum could not be determined as the mull was rearranged. This could be due either to CO_2, or to a decomposition product of the mineral oil (Nujol).

Another mull, made up between NaCl plates, this time of the dilute crystal, was irradiated and its IR spectrum was analyzed to identify the gas. The IR spectra were run from 650 cm^{-1} to 4000 cm^{-1}. The CO_2 fundamentals are:

$$\nu_1 = \begin{matrix} 1286\ cm^{-1} \\ 1388\ cm^{-1} \end{matrix}, \quad \nu_2 = 667\ cm^{-1}, \quad \nu_3 = 2449\ cm^{-1}.$$[25]

All three peaks were present before irradiation. 360-390 mμ light was centered on the mull for 25 minutes.

After the irradiation, when the spectrum was retraced, no new peaks were found. There was a five percent decrease in transmittance at ν_1 and ν_3; none at ν_2. We hoped that as $CO_2^{\overline{\cdot}}$ is isoelectronic with NO_2 some of the IR peaks could be identified in the new peaks after irradiating.

More work would have to be done to assure that the mull is tight. The sample in the mull was rearranged on irradiation. If this is due to thermal decomposition of the Nujol possibly cooling, during photolysis, is necessary.

The photodecomposition is undoubtedly reversible as cobalt(II) is readily oxidized by molecular oxygen in the presence of complexing ligands, but the increased optical density cannot be accounted for by this reaction. Upon irradiating for twenty minutes with uv light the crystal surface is covered with the pink decomposition product but the optical density is still increasing at the ligand field bands of trisoxalatocobaltate(III). As discussed previously, this is attributed to $CO_2^{\overline{\cdot}}$.

SUMMARY

The postulated mechanism for the photodecomposition was supported by tentative spectrophotometric identification of some of the decomposition products i.e., $CO_2^{\overline{\cdot}}$ and $Co(C_2O_4)_3^{4-}$.

Cause of the high intensity band as a $CO_2^{\overline{\cdot}}$ transition was fairly well established. The fact that a long lived radical intermediate is present was suggested by others. Parker and Hatchard's[7] flash photolysis experiment with trisoxalatocobaltate(III) and trisoxalatoferrate(III) assumed it to be $HCO_2^{\cdot}$ or $HC_2O_4^{\cdot}$.

E.s.r. studies on trisoxalatocobaltate(III) in the diluent crystal show a number of resonances which disappear on irradiation.[26] In place of them a large, narrow signal, typical of an organic radical, and not present initially, grows in.[26] As Co^{3+} is diamagnetic, and octahedral Co^{2+} gives no detectable esr spectrum at room temperature, the system is particularly amenable to esr study. This will be the next step in the identification of the $CO_2^{\overline{\cdot}}$ radical.

Work with solutions containing the hydrated electron show CO_2 to react with e_{aq}^{-} at $k = 7.7 \times 10^9$ $\underline{M}^{-1}$, sec^{-1}.[28] When CO_2 is added to de-aerated water the intensity of absorption, due to the hydrated electron decreases.[23] This suggests that in our system of oxalate cages $CO_2^{\overline{\cdot}}$ ion, rather than e^-_{aq} is the stable radical product of the photodecomposition.

Ultra violet spectra of solids have not been studied in detail, and our method has been rather makeshift. A clear, plastic mount which would hold the crystal in a definite orientation could help to pin the $CO_2^{\overline{\cdot}}$ spectrum down exactly.

Further work is suggested by Eaton and Stuart[8], who did esr work on frozen, acidified solution of trisoxalatocobaltate(III). On irradiation their primary products were $H^{\cdot}$ and $HC_2O_4^{\cdot}$. They tentatively identified $CO_2^{\overline{\cdot}}$ as a secondary product, resulting from further attack by $H^{\cdot}$. If aqueous, non-acidified solutions were studied $H^{\cdot}$ would not be expected to be a primary product, also, the system would be free of interference from sodium resonance from the diluent crystal.

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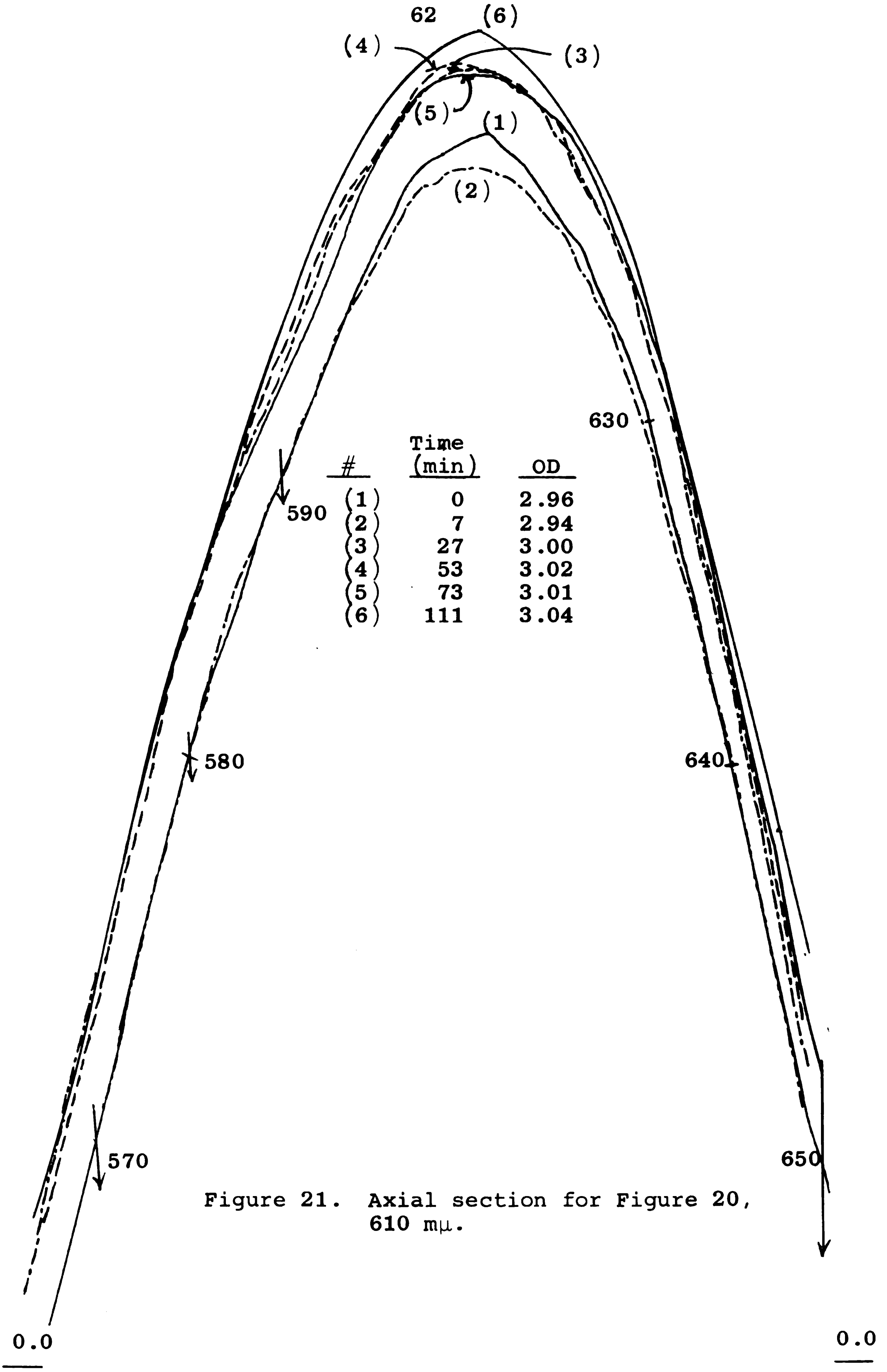
APPENDIX



#	Time (min)	OD
(1)	0	2.96
(2)	7	2.94
(3)	27	3.00
(4)	53	3.02
(5)	73	3.01
(6)	111	3.04

Figure 21. Axial section for Figure 20, 610 mμ.

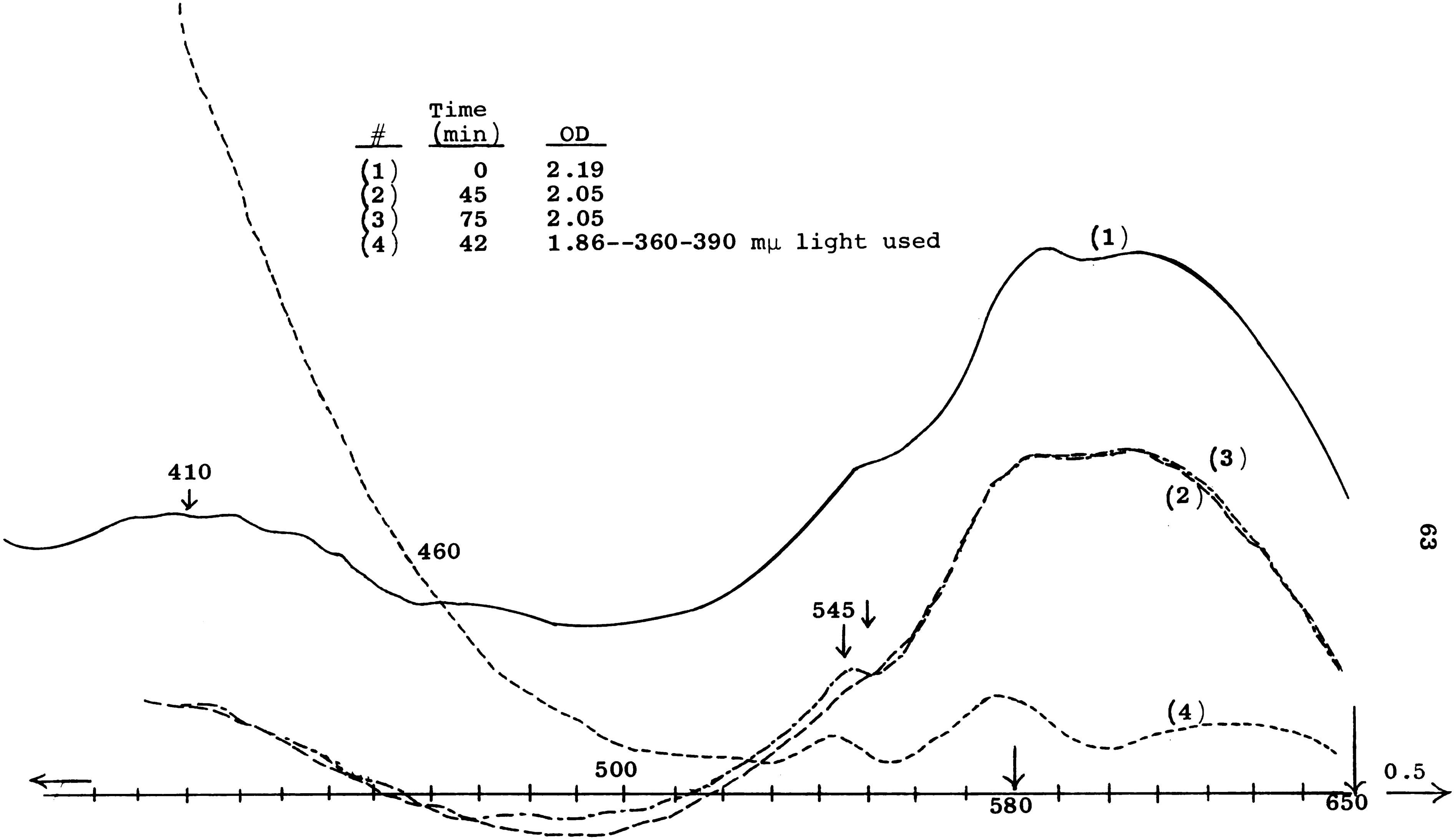


Figure 22. Orthoaxial section for Figure 20, π spectrum.

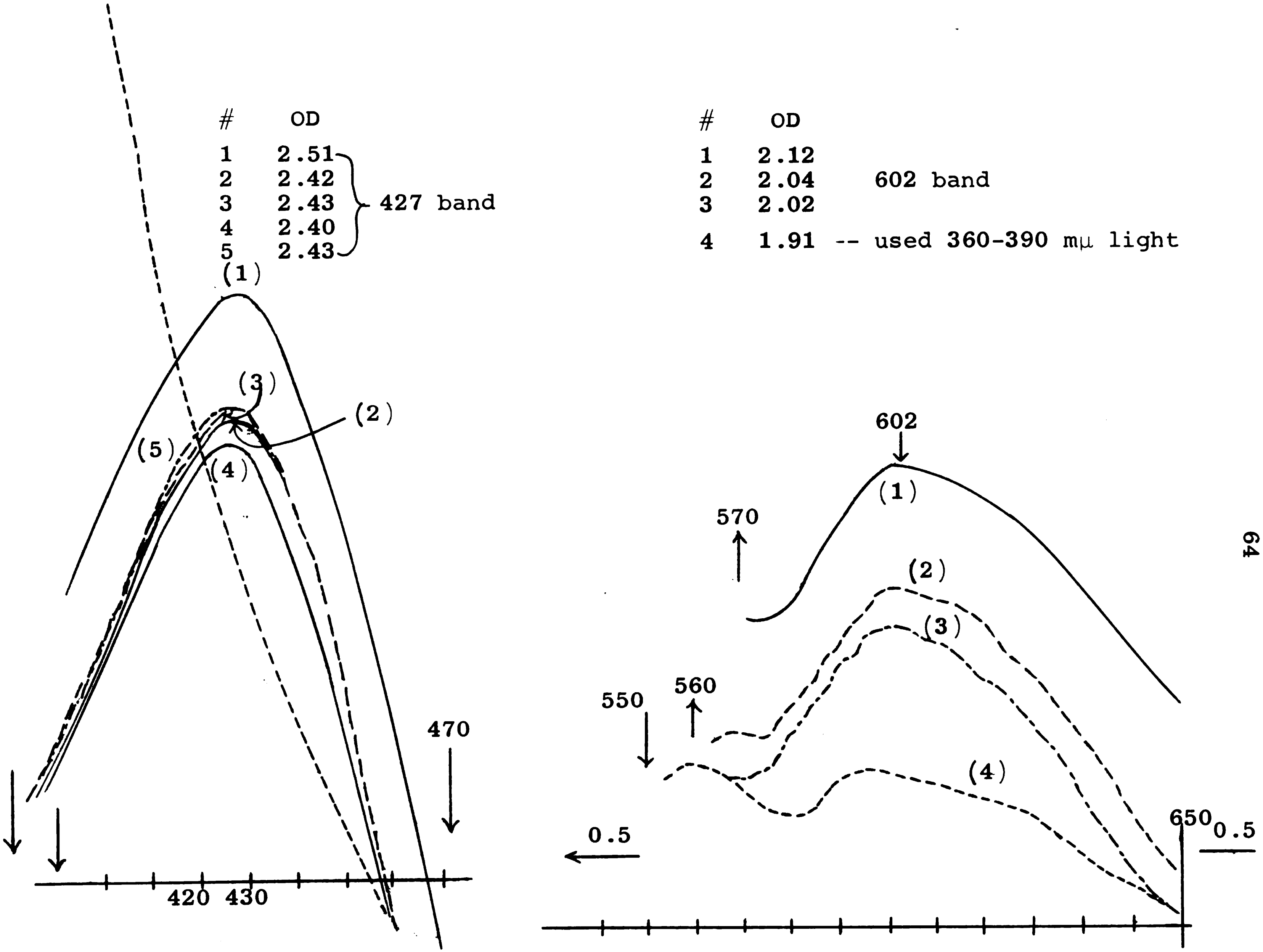
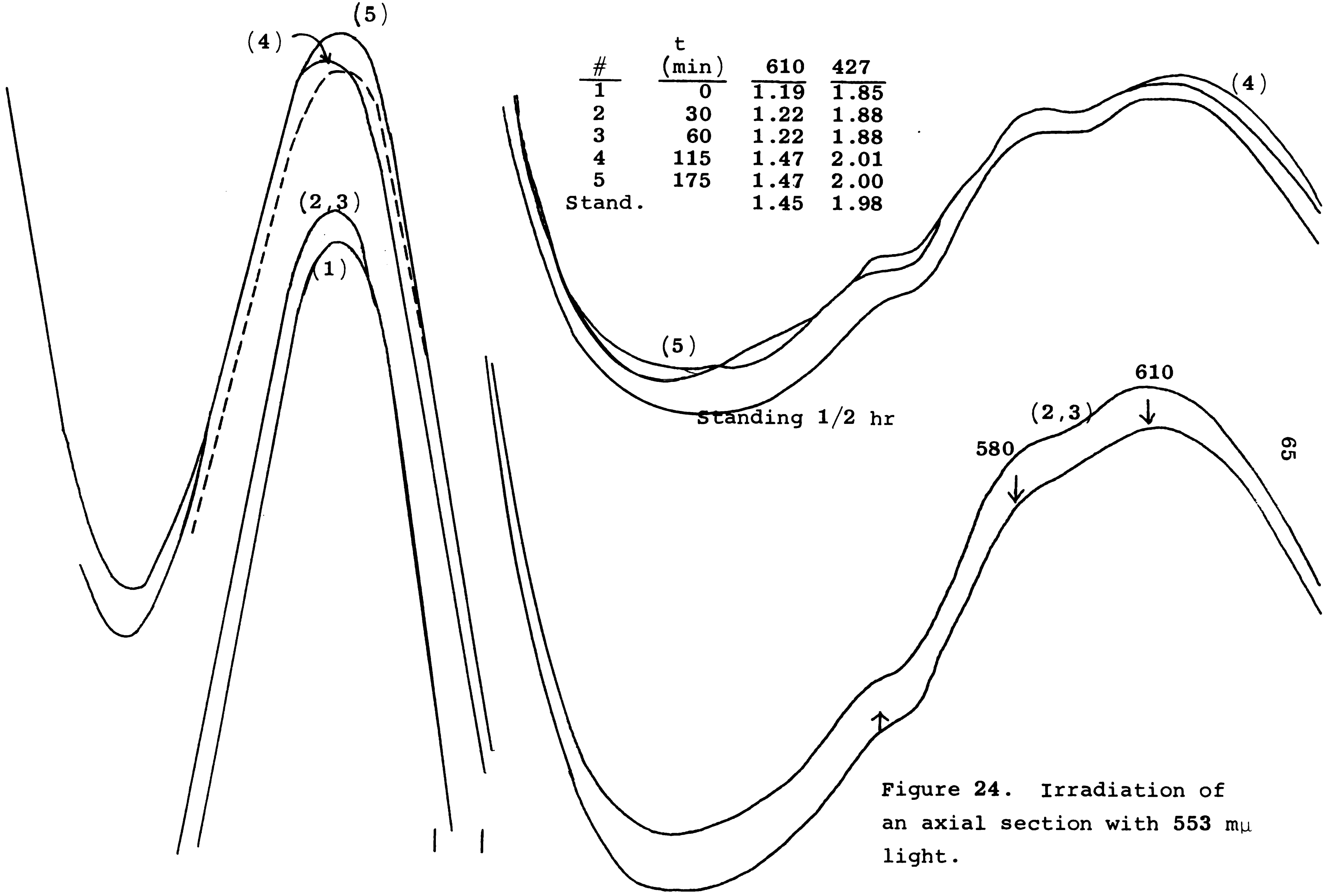


Figure 23. Orthoaxial section for Figure 20, σ spectrum.



#	t (min)	610	427
1	0	1.19	1.85
2	30	1.22	1.88
3	60	1.22	1.88
4	115	1.47	2.01
5	175	1.47	2.00
Stand.		1.45	1.98

Figure 24. Irradiation of an axial section with 553 mμ light.

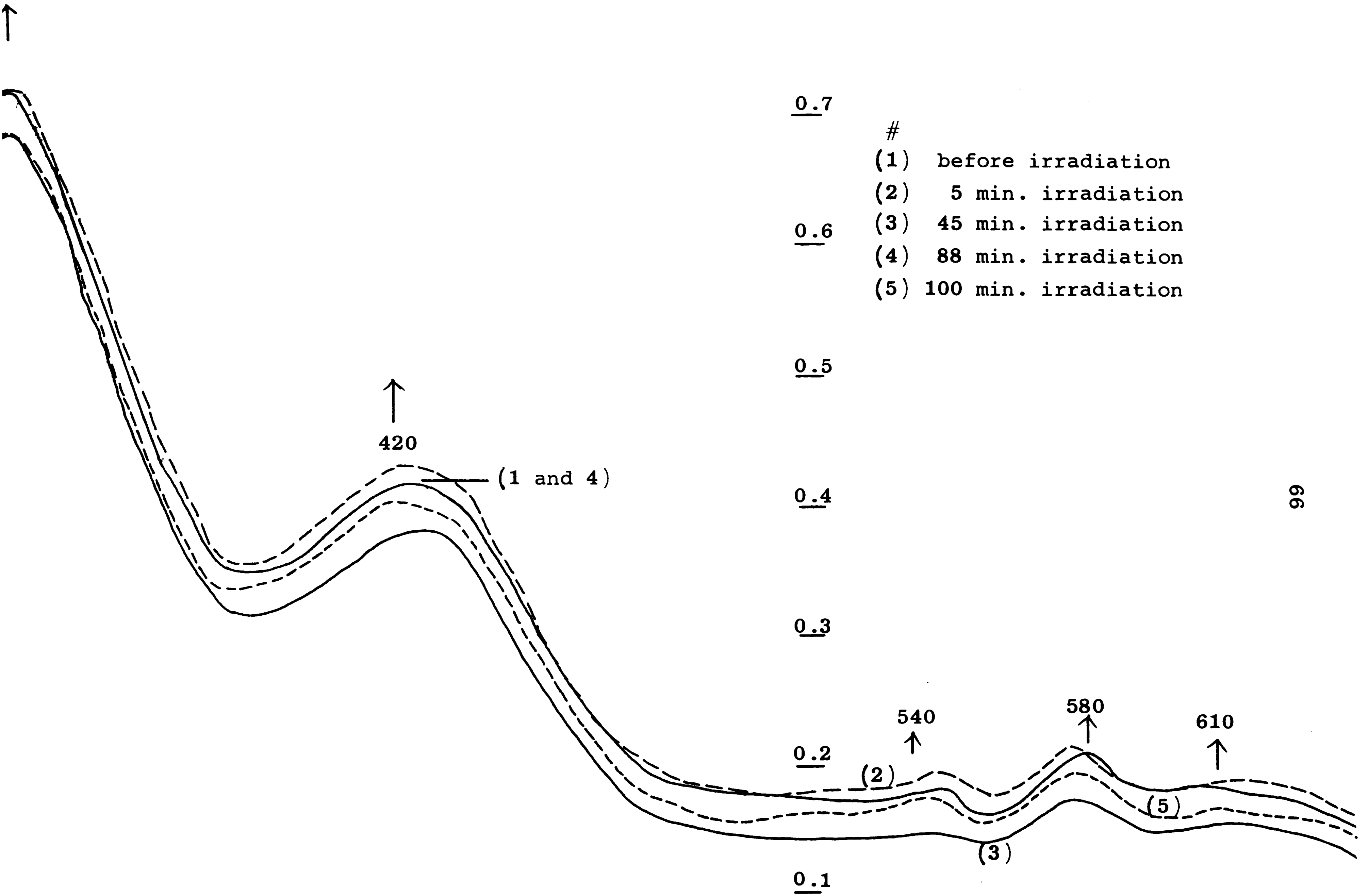


Figure 25. Irradiation of an axial section with light of $\lambda > 578$ mμ.

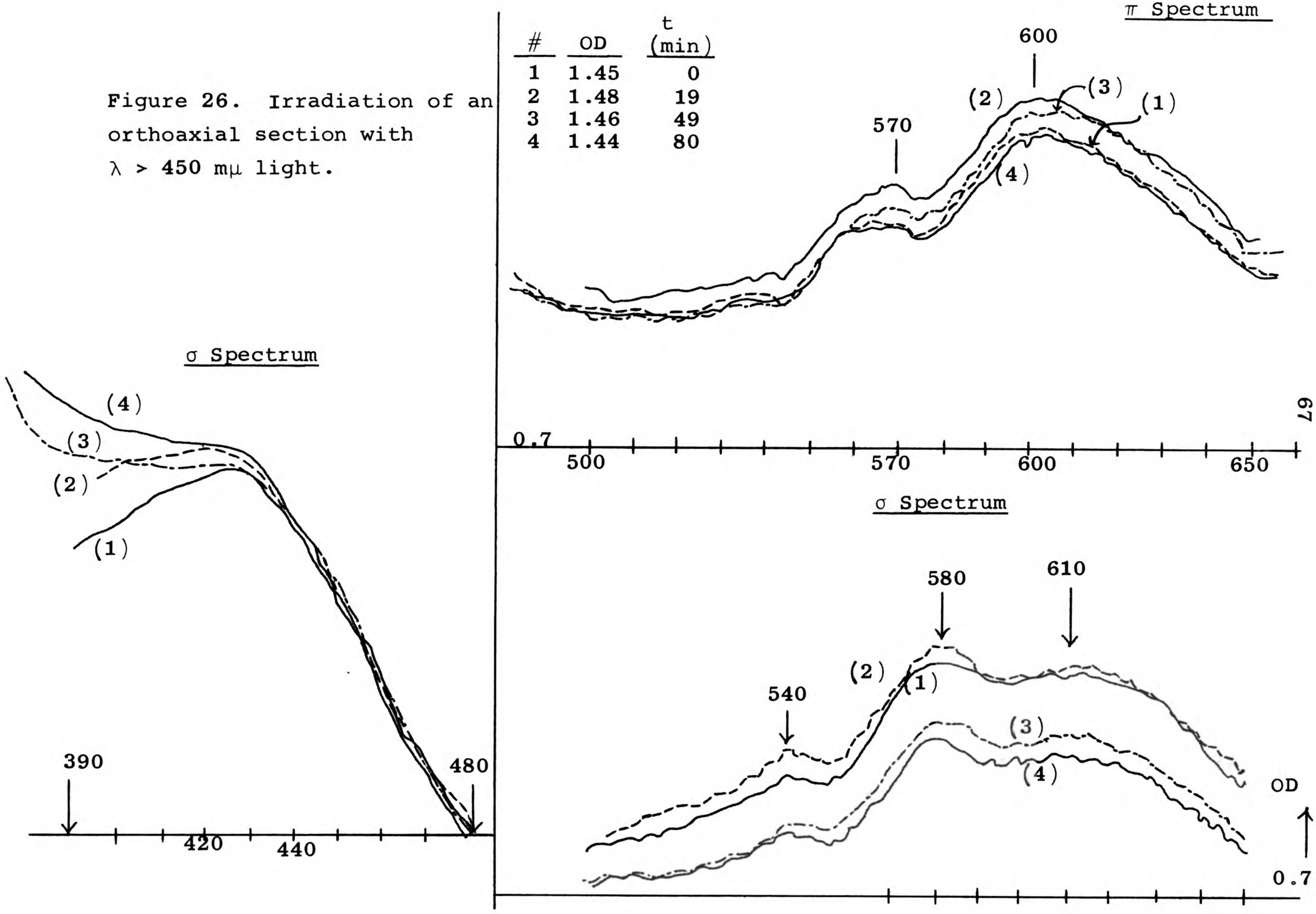


Figure 26. Irradiation of an orthoaxial section with λ > 450 mμ light.

#	OD	t (min)
1	1.45	0
2	1.48	19
3	1.46	49
4	1.44	80

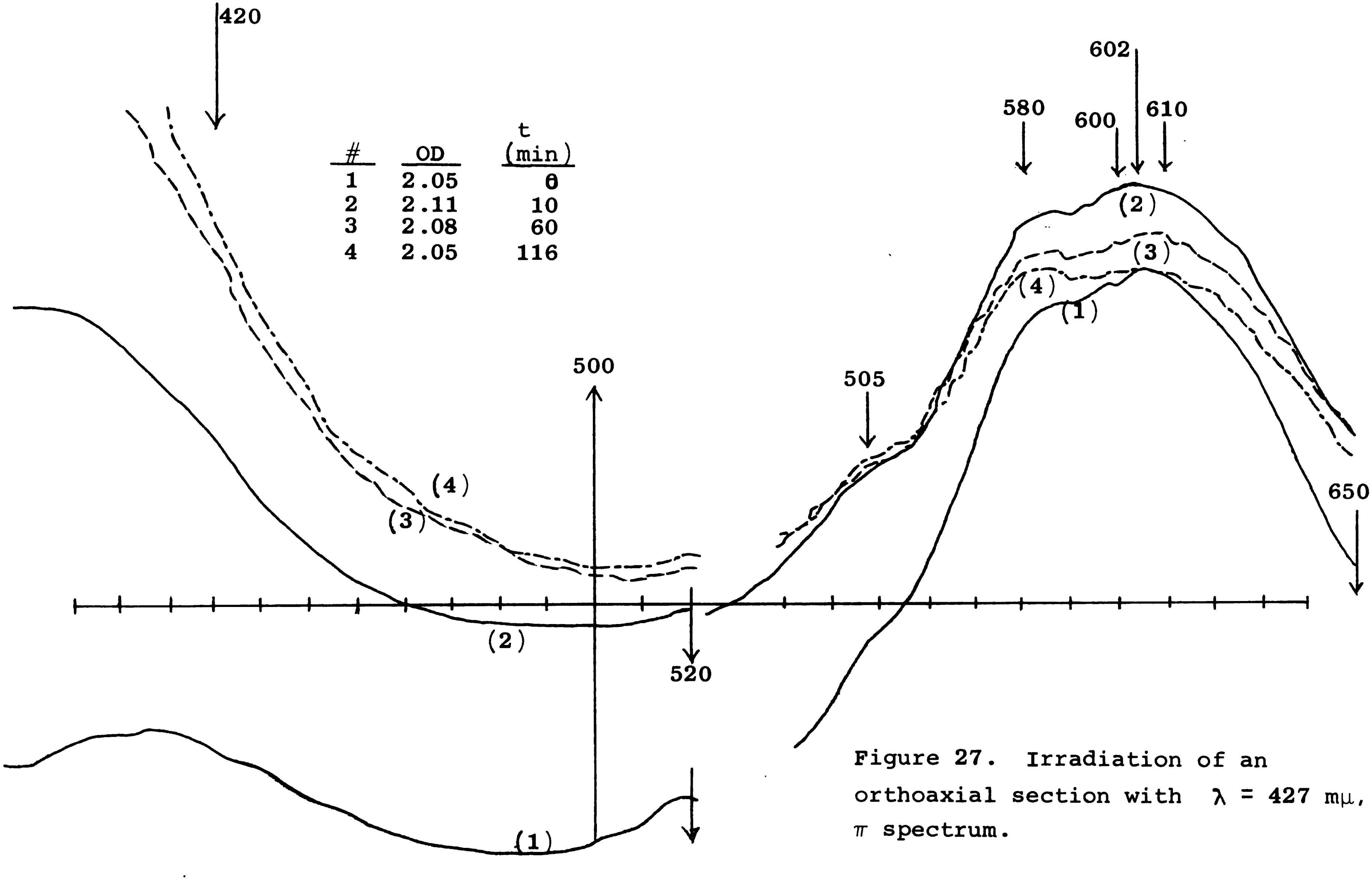


Figure 27. Irradiation of an orthoaxial section with $\lambda = 427$ mμ, π spectrum.

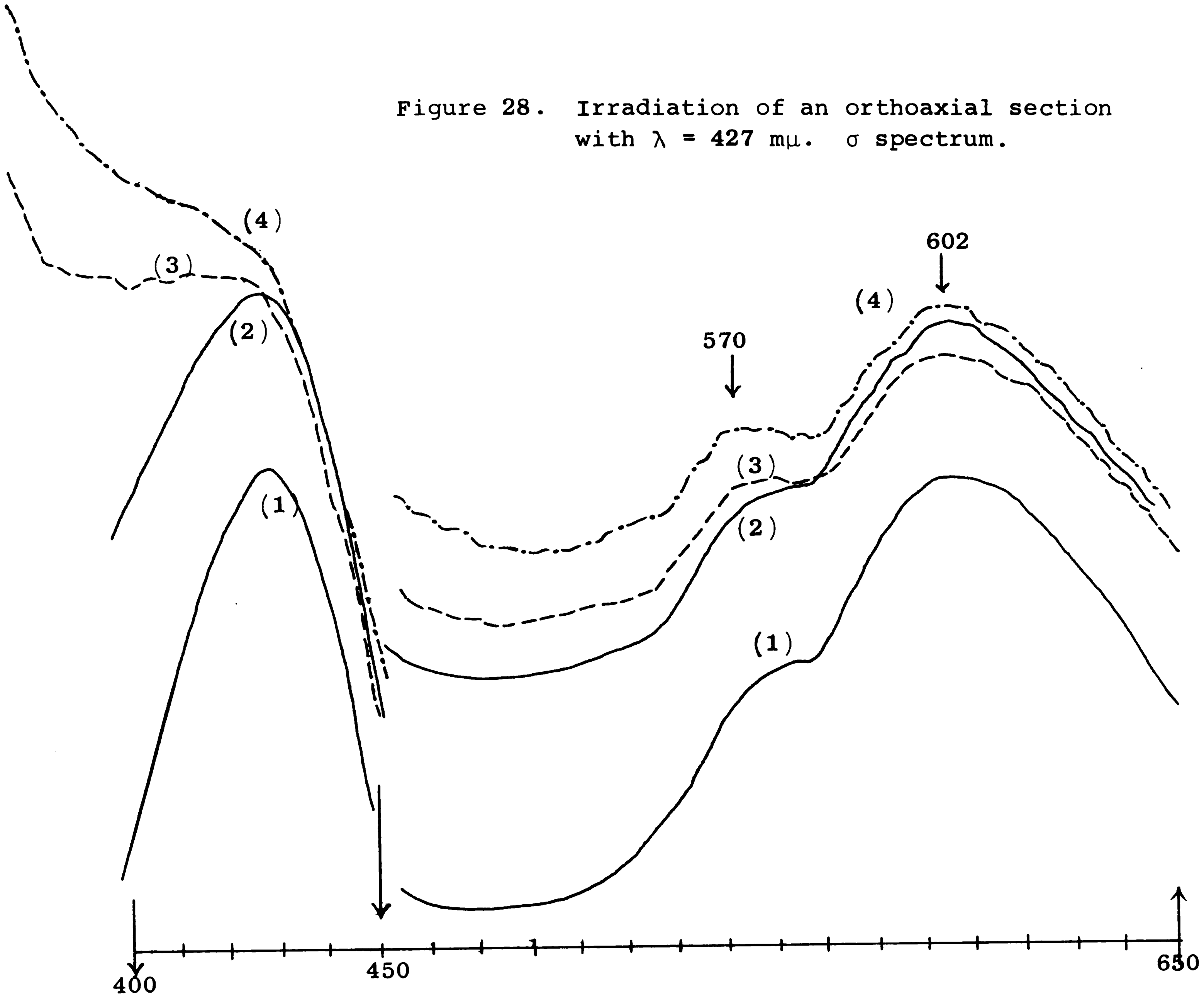


Figure 28. Irradiation of an orthoaxial section with λ = 427 mμ. σ spectrum.

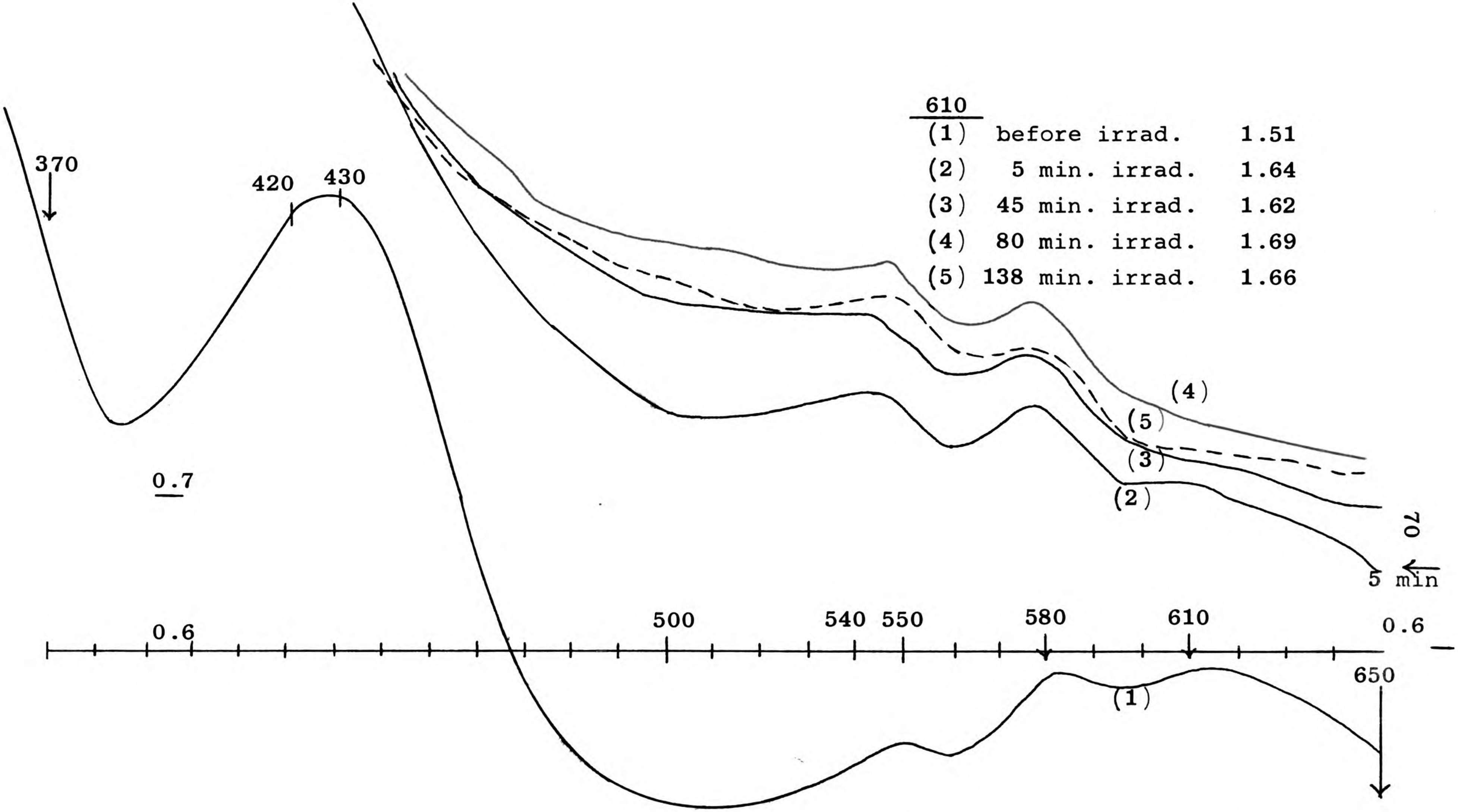


Figure 29. Irradiation of an orthoaxial section with λ = 360-390 mμ. σ spectrum.

(1)	1.85
(2)	1.82
(3)	1.81
(4)	1.69
(5)	1.66

Max. decrease $\frac{.19}{1.85} = 10$

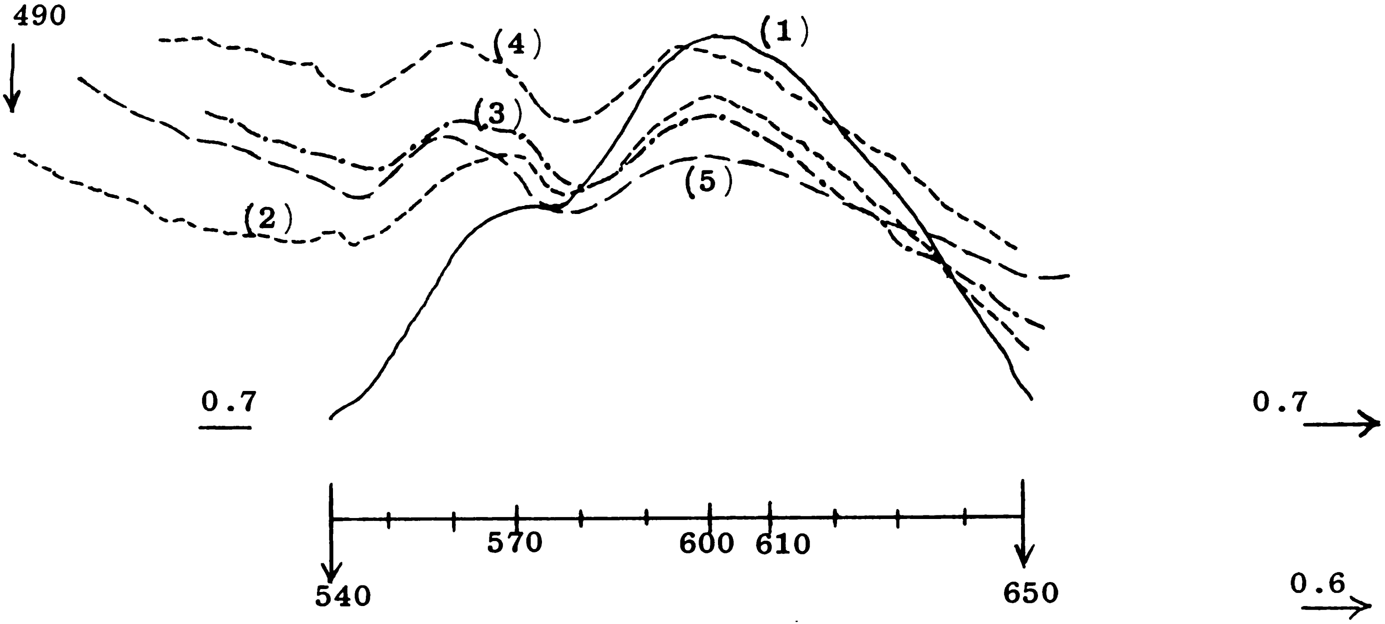


Figure 30. Irradiation of an orthoaxial section with λ = 360-390 mμ, π spectrum.