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COMPARATIVE STUDY OF FIVE VARIETIES OF SPODUMENE THROUGH OPTICAL ABSORPTION

by

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ABSTRACT

A comparative study of five varieties of spodumene crystals from Brasil through optical absorption spectroscopy, classified according to the colours lylac, colourless I, colourless II, yellow and green is reported. This series shows a consistent increase of the [Fe]/[Mn] ratio. The principal bands in the yellow sample are at 7,000 and 9,000 cm^{-1}, and in the green sample besides these bands we observe a band at 16,000 cm^{-1}. In lylac, colourless I and colourless II samples, the principal bands are at 18,000 cm^{-1} and when irradiated two new bands appears at 15,700 cm^{-1} $(E \perp c)$ and 11,000 cm^{-1} $(k \perp c)$. We suggest that in green and yellow samples the bands are due to Fe^{2+} (at 7,000 cm^{-1} and 9,000 cm^{-1}) and due to $Fe^{2+}-Fe^{3+}$ charge transfer (at 16,000 cm^{-1}). In lylac and colourless I samples we apply the model for Mn^{3+} at two different sites. The colourless II corresponds to the case in which Mn^{3+} is at one site alone, being prohibited from occupying the second site due to higher Fe concentration.

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INTRODUCTION

We report here a comparative study by optical absorption spectroscopy of five varieties of spodumene. The spodumene is a silicate belonging to the inosilicate class of the formula $LiA\ell Si_2O_6$ (Dana and Hurlbut, 1978). The unit cell contains four chemical units, with the parameters a = 9.50 Å, b = 8.30 Å and c = 5.24 Å. It belongs to the spatial group $C_{2/c}$ with perfect cleavage plane (0 1 0) forming angles of 87° and 93° (Deer et al., 1966). There are four equivalent sites for Li^+ and $A\ell^{3+}$ with an axis of order 2 paralel to b. The figure 1 shows the projection of the unit cell in the plane (0 1 0).

Insert Figure 1

It is very common to find ions of Na^+ substitutive to Li^+. Other impurities usually found in spodumene are Fe, Mn, Cr and V. A relationship between the colour and the presence of impurities was observed. This relationship depends on the site occupied by these impurities in the crystal lattice, of their valence state, the coordination and their concentration.

The spodumene is a source for the production of Li salts. The transparent varieties of beautiful colouration are semi-precious stones. These are known as kunzite (lylac) hiddenite (green) and spodumene (colourless or yellow). The heat treatment as well as irradiation with γ-Rays, X-Rays, electrons and ultraviolet rays causes changes in colour and tonality. Extensive studies have already been done in spodumene (Claffy,1953; Manoogian et al., 1965; Holuj, 1968; Holuj and Manoogian, 1968; Gait and Michoulier, 1973; Leckebush et al., 1974; Schmitz et al., 1975 ;

Hassan and Labib, 1978; Ito and Isotani, 1983).

The kunzite, lylac variety of spodumene has an absorption band around 19,000 cm^{-1} and an ultraviolet band-edge from 25,000 cm^{-1}. When irradiated with ionizing radiation, there appears a strong band around 15,000 cm^{-1} and the ultraviolet band-edge shifts to 22,000 cm^{-1}. In this case the kunzite turns green. When heated to temperatures above 120°C the green colour disappears in few hours returning to the initial colour. The heating above 300°C bleaches the lylac colour, which can be restored by irradiation followed by heating at temperatures between 120°C and 300°C. Recently Ito and Isotani (1983) showed through thermal and irradiation dose kinetics of the absorption bands, that the 15,000 cm^{-1} (green) and 19,000 cm^{-1} (lylac) bands are independent. The result is sketched in figure 2.

Insert Figure 2

The Mn^{2+} EPR spectra of the natural kunzite cyrstals showed that they are substitutional to the $A\ell^{3+}$ and are changed on heating, passing from two main groups Mn^{2+} (I) and Mn^{2+} (II-V) to Mn^{2+} (I) (Holuj and Manoogian, 1968). However, after this treatment, nor irradiation nor heating, affect the EPR spectra of Mn^{2+} (I) (Ito and Isotani, 1983). Polarized optical absorption spectra of green and lylac bands was shown to be allowed for octahedral symmetry (Ito and Isotani, 1983).

The above observations, together with the observations of Holuj and Manoogian (1968) that the Mn^{2+} in a tetrahedral site (substitutional to Si) does not show heat nor irradiation effects, contradicts the previous models of Schmitz and Lehmann (1975) and Hassan and Labib (1978) based on valence charges of Mn in tetrahedral sites. So a new model was proposed in substitution to the previous ones based on the formation of radiation deffects (Ito and Isotani, 1983). It was suggested that the green and lylac bands are due to Mn^{3+} d-d transition enhanced by a charge trapped in an O ion of the MnO_6 group.

The Ito and Isotani studies were done in samples with low concentration of Fe and Cr, with Mn being the most important impurity. In the present report we present a comparative study of crystals of spodumene with different concentrations of Mn and Fe and with small concentrations of Cr.

EXPERIMENTAL

The samples were obtained in Minas Gerais, Brazil and were of different colours: colourless, lylac, yellow and green. They showed cleavage planes (1 1 0) and 93° angles between the planes ($\bar{1}$ 1 0). This morphology together with the known growth direction along the c axis allowed us to identify all crystalographic axis.

The samples were cut with a Buehler 12" thickness blade of low concentration in the Isomet of Buehler. We prepared two types of samples: (1) large in form of parallelopipeds with two faces perpendicular to the c axis and two faces parallel to the cleavage plane, with ~ 5 × 5 × 10 mm; (2) thin, with 0.2 to 0.8 mm of thickness, some with the faces perpendicular to c and the others parallel to c. The samples were polished with alumina in a Buehler Minimet.

The optical spectra were obtained in a Carl Zeiss DMR 21 spectrometer. The spectra were obtained with non-polarized light and reference beam in air. The measurements at liquid N_2 temperature were obtained in a cryostat (Fujii et al., 1983) made for this spectrometer.

The thermal treatments were done in air. The stability of the Forlabo furnace with useful volume 10 × 12 × 15 cm was improved to 1°C by diminishing the useful volume by 50% with brick materials and two metallic plates. All the samples to be treated were put between the previously heated metallic plates. With this set we obtained thermal equilibrium in the samples in about one minute, and the error in treatment time was about 20 seconds (Fujii and Isotani, 1982). The temperature were measured using a chromel alumel thermocouple with one junction at 0°C and a XT recorder of ECB and a digital multimeter of Keithley 160 B.

The samples were analysed by X-ray fluorescence for the determination of Fe, Mn and Cr. The results are shown in table I.

Insert Table I

RESULTS

Optical Absorption:- In Figure 3a we show the optical absorption of the lylac variety of spodumene. We observe a band

Insert Figure 3

at 18,600 cm^{-1} and a UV band-edge beyond 28,600 cm^{-1}. In figure 4 we show the spectrum of thin samples. We observe bands at

Insert Figure 4

29,000 cm^{-1}, 38,500 cm^{-1} and a band-edge beyond 45,000 cm^{-1}. The measurements in the UV region were possible only in this sample.

In figure 3b we show the spectrum of green spodumene. We observe bands at 6,000 cm^{-1}, 8,000 cm^{-1} and 16,000 cm^{-1}. We observe also 3 or 4 bands partially covered by the strong UV absorption between 20,000 cm^{-1} and 28,000 cm^{-1}.

In figure 3c we show the spectrum of yellow spodumene. We observe that the characteristic difference of the spectrum of this variety as related to that of green spodumene is in fact that the bands at 6,000 cm^{-1} and 8,000 cm^{-1} are larger and the one at 16,000 cm^{-1} is smaller than in yellow spodumene.

The colourless varieties of spodumene, which we call as colourless I and colourless II showed small absorption bands in the visible region. The difference between the two is that one absorbs in the UV from 24,000 cm^{-1} (I) and the other from 29,000 cm^{-1} (II).

Irradiation:- With the irradiation, the samples of original colour yellow and green do not show change of colour. The optical spectra showed changes in the UV region, with strong absorption from 24,000 cm^{-1} as shown in figures 5 and 6 and a small increase of 16,000 cm^{-1} band.

Insert Figures 5 and 6

With irradiation originally lylac coloured samples turn intensively green. In figure 7 we show the OA spectrum of the irradiated sample of the lylac variety. We observe the growth of a 16,000 cm^{-1} band and an infrared shift of the UV band-edge. Also, we obtained the spectrum of thin samples irradiated in the UV region. In figure 4 we show this spectrum. We see an increase in the intensity of the bands at 30,000 cm^{-1} and 38,500 cm^{-1} and appearance of others, partially covered, between 40,000 cm^{-1} and 43,500 cm^{-1}.

Insert Figure 7

The colourless samples showed two kinds of effects due to irradiation. The spectra of the colourless I variety are shown in figures 8 and 9. In figure 8 (E ⊥ c) we observed a weak absorption at 11,000 cm^{-1} and a strong absorption at 16,000 cm^{-1} and a shoulder at 18,000 cm^{-1}. In figure 9 (E//c) we observe that the bands 11,000 cm^{-1} and 16,000 cm^{-1} have their absorption of the same order of magnitude. This shows a strong dichroism in the absorption at the IR region.

Insert Figures 8 and 9

The spectra of the colourless II variety are shown in figures 10 (E ⊥ c) and 11 (E//c). The spectra are similar to that of colourless I, showing however the absence of the 18,000 cm^{-1} shoulder.

Insert Figures 10 and 11

Heating:- The heating of the green and yellow samples to 600°C does not change their colours. In figures 12 and 13 we show the spectra of the samples treated at 500°C. Only the UV band-edges are shifted to higher energies.

Insert Figures 12 and 13

The lylac sample when heated at 400°C for longer enough times turns colourless. In figure 14 we show the effects of heat treatments at 200°C and 400°C of the irradiated samples. The lylac spodumene when irradiated turns intensely green. At 200°C the 16,000 cm^{-1} band is bleached, leaving unchanged the 18,000 cm^{-1} band. With the bleaching of the 16,000 cm^{-1} band the spodumene turns lylac. At 400°C the 18,000 cm^{-1} band is bleached and the spodumene turns colourless.

Insert Figure 14

The samples colourless I and colourless II when irradiated turn intensely green. With the heating at 200°C the colourless I spodumene turns lylac and the colourless II spodumene turns colourless. In figures 15 (E ⊥ c) and 16 (E//c) we show the results of heat treatments in colourless I sample. At 200°C we observe the bleaching of the bands 16,000 cm^{-1} (E ⊥ c) and 11,000 cm^{-1} and 16,000 cm^{-1} (E//c). The remaining lylac colouring is due to the 18,000 cm^{-1} band which remains almost unchanged with a heat treatment at 200°C. In figures 17 (E ⊥ c) and

Insert Figures 15 and 16

18 (E//c) we show the results of heat treatment in colourless II spodumene. At 200°C the 16,000 cm^{-1} (E ⊥ c) and 11,000 cm^{-1} and 16,000 cm^{-1} (E//c) bands are bleached leaving a very weak absorption at 18,000 cm^{-1} explaining the change of irradiated colourless II sample from green to colourless.

Insert Figures 17 and 18

OA at Liquid N_2 Temperature:- The liquid N_2 temperature measurements of green and yellow spodumene are shown in figures 19 and 20. We see that the 6,000 cm^{-1} , 9,000 cm^{-1} and 16,000 cm^{-1} bands do not show changes in absorption. On the other hand they showed changes in the position of maximum of the bands. The 6,000 cm^{-1} and 9,000 cm^{-1} became closer at liquid N_2 temperature. The 16,000 cm^{-1} band in the green sample showed an infrared shift.

Insert Figures 19 e 20

The spectra at liquid N_2 temperature of lylac, colourless I and colourless II samples are shown in figures 21, 22, 23 and 24. In these samples the stronger bands at 16,000 cm^{-1} and 18,000 cm^{-1} turn sharper with negligible shifts. The 9,000 cm^{-1} (E//c) band in colourless II sample shows a small IR shift, but here the effect is seen to be caused by the decrease of the mixture with the 16,000 cm^{-1} band. In colourless samples we see a 21,500 cm^{-1} weak band.

Insert Figures 21, 22, 23 and 24

DISCUSSION

An inspection of the OA spectra obtained at room and liquid N_2 temperatures showed that the green and yellow samples have bands whose absorbances are insensitive to temperature, while in lylac, colourless I and II the absorbances are temperature sensitive. This suggests that the OA centers in green and yellow samples are different from those in lylac, colourless I and II samples.

The concentration of Cr is of the same order in lylac, colourless I and II and yellow samples. Due to the differences observed in the OA spectra of natural, heated and irradiated samples we assume that Cr is not responsible for the colours. In green sample the concentration of Cr is twice that in others, but the OA spectra are similar to those of yellow sample. So, in the green sample we do not assign the colour to Cr .

The Fe appears with higher concentration in green and the Mn in lylac. So, it seens reasonable to assign the OA bands of green and yellow samples to Fe and those of lylac, colourless I and II to Mn .

The 6,000 cm^{-1} and 9,000 cm^{-1} bands in green and yellow samples are characteristic of Fe^{2+} in distorted octahedral M_2 sites (Burns, 1970). The energy diagram of this center is shown in figure 25. In green spodumene the concentration of Fe is 4 - 8 times higher than in other samples. This concentration possibly allows a $Fe^{2+} - Fe^{3+}$ charge transfer interaction being responsible for the 16,000 cm^{-1} band.

Insert Figure 25

The bands 10,500 cm^{-1} and 16,000 cm^{-1} in lylac, colourless I and II samples were assigned to d - d Mn^{3+} bands (Ito and Isotani, 1983). These transitions are shown in figure 26.

Insert Figure 26

The 11,000 cm^{-1} band in colourless I and II samples are characteristic of Fe^{2+} in distorted octahedral M_1 site (Burns, 1970). The energy diagram of this center is shown in figure 27.

Insert Figure 27

By comparing the UV absorptions we observe the band-edge at about 24,000 cm^{-1} in lylac, yellow and colourless I samples and at 29,000 cm^{-1} in green and colourless II samples. By comparing the [Fe]/[Mn] ratios, we see that the UV band-edge at higher energies occur for large ratios. In the spectrum of thin sample of lylac we observe a band at 29,000 cm^{-1}. This suggests that in colourless I and yellow samples the band-edge at 24,000 cm^{-1} is due to the 29,000 cm^{-1} band. In green and colourless II this band does not exist.

The above observation suggests that the lylac band at 18,000 cm^{-1} is related to the 29,000 cm^{-1} band. In fact this band is observed in lylac, colourless and yellow samples but not in green and colourless II. So we assign tentatively the 29,000 cm^{-1} band to a hole center in an oxygen neighbour to Mn^{2+}. Also, we suggest that with increase of [Fe]/[Mn] ratio, the Mn^{3+} (lylac) type of site is inhibited.

In a study by Claffy (1953) of the luminescent and tenebrescent properties, examining samples of spodumene of different colours and origin it was proposed a classification of spodumene in two types: chromian (hiddenite) and non-chromian. However, we suggest in the present report that in green spodumene it is more reasonable to assign the 16,000 cm^{-1} band to Fe^{2+}-Fe^{3+} charge transfer band. This type of band was also observed in tourmaline with high Fe concentration (Smith, 1978). So we suggest that Claffy's classification must be revised.

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TABLE I

Concentration of Fe, Cr and Mn in spodumene

Sample	[Fe] (ppm)	[Mn] (ppm)	[Cr] (ppm)
lylac			
Colourless I	190	180	100
Colourless II	390	110	90
Yellow	320	200	90
Green	1720	500	190

FIGURE CAPTIONS

Figure 1 - Projection of the unit cell in the plane (0 1 0).

Figure 2 - Sketch of the process of transformation of colour of spodumene by heating and irradiation.

Figure 3 - Optical absorption spectra of green, yellow, colourless I, colourless II and lylac varieties of spodumene.

Figure 4 - OA spectra of natural and irradiated thin sample of lylac spodumene.

Figure 5 - Radiation effect in green spodumene.

Figure 6 - Radiation effect in yellow spodumene.

Figure 7 - Radiation effect in lylac spodumene.

Figure 8 - Radiation effect in colourless I spodumene for $E \perp c$.

Figure 9 - Radiation effect in colourless I spodumene for E//c.

Figure 10 - Radiation effect in colourless II spodumene for $E \perp c$.

Figure 11 - Radiation effect in colourless II spodumene for E//c.

Figure 12 - Heating effects in green spodumene.

Figure 13 - Heating effects in yellow spodumene.

Figure 14 - Heating effects in lylac spodumene.

Figure 15 - Heating effects in colourless I spodumene for $E \perp c$.

Figure 16 - Heating effects in colourless I spodumene for E//c.

Figure 17 - Heating effects in colourless II spodumene for $E \perp c$.

Figure 18 - Heating effects in colourless II spodumene for E//c.

Figure 19 - OA spectra of green spodumene at liquid N_2 temperature.

Figure 20 - OA spectra of yellow spodumene at liquid N_2 temperature.

Figure 21 - OA spectra of lylac spodumene at liquid N_2 temperature.

FIGURE 22 - OA spectra of irradiated and 200°C heated colourless I spodumene at liquid N_2 temperature.

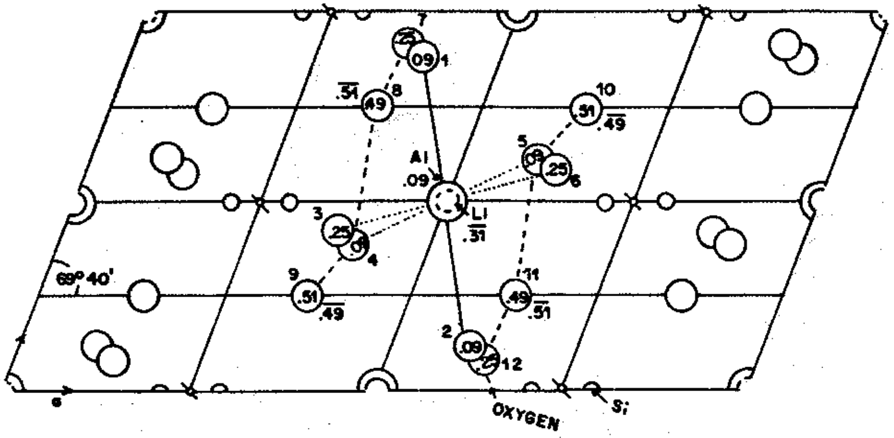
Figure 23 - OA spectra of irradiated colourless II spodumene for $E \perp c$ at liquid N_2 temperature.

Figure 24 - OA spectra of irradiated colourless II spodumene for $E//c$ at liquid N_2 temperature.

Figure 25 - Energy diagram for Fe^{2+} in M_2 site.

Figure 26 - Energy diagram for Mn^{3+} in "green" site.

Figure 27 - Energy diagram for Fe^{2+} in M_1 site.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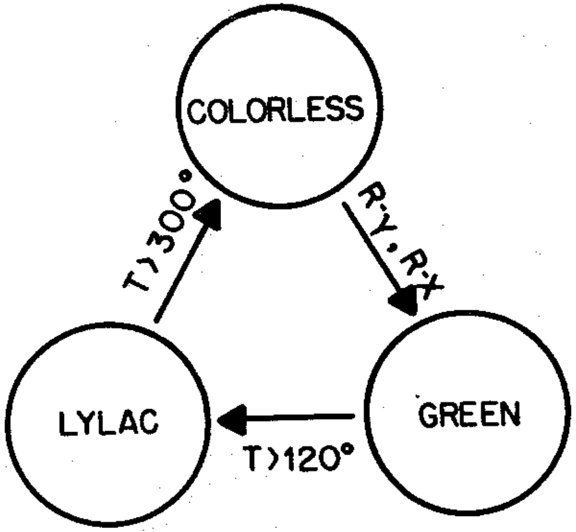
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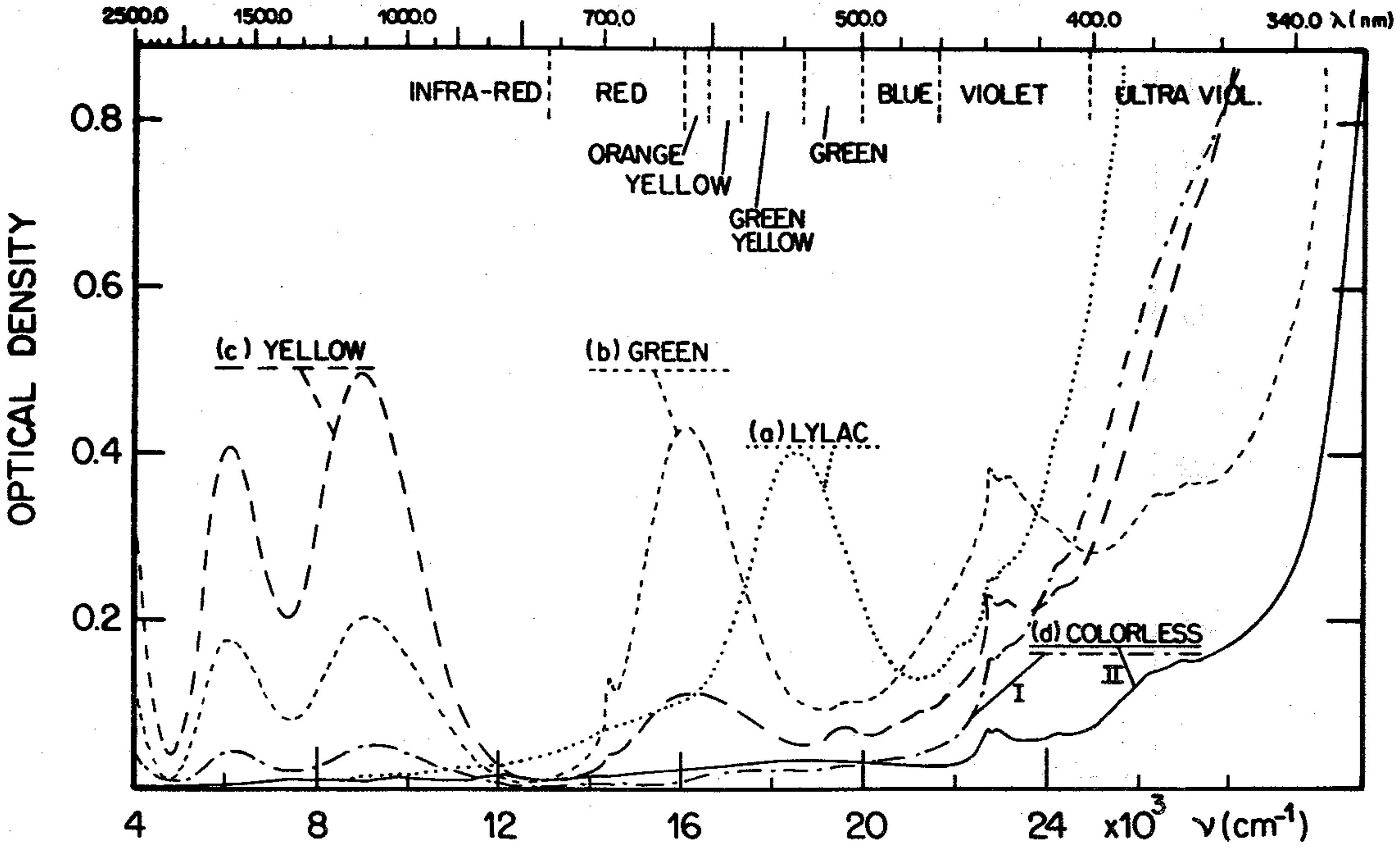
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(b) GREEN
(a) LYLAC
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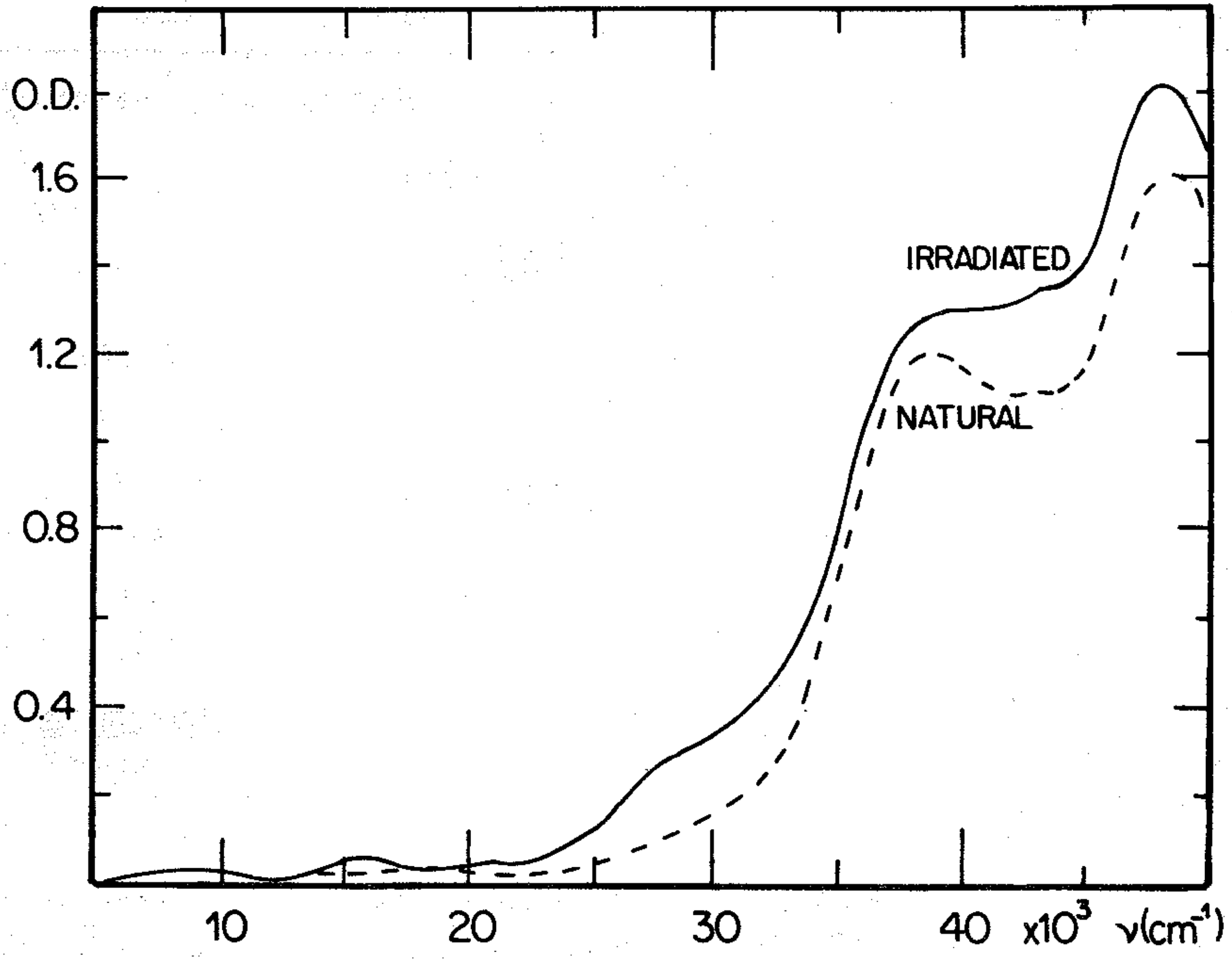
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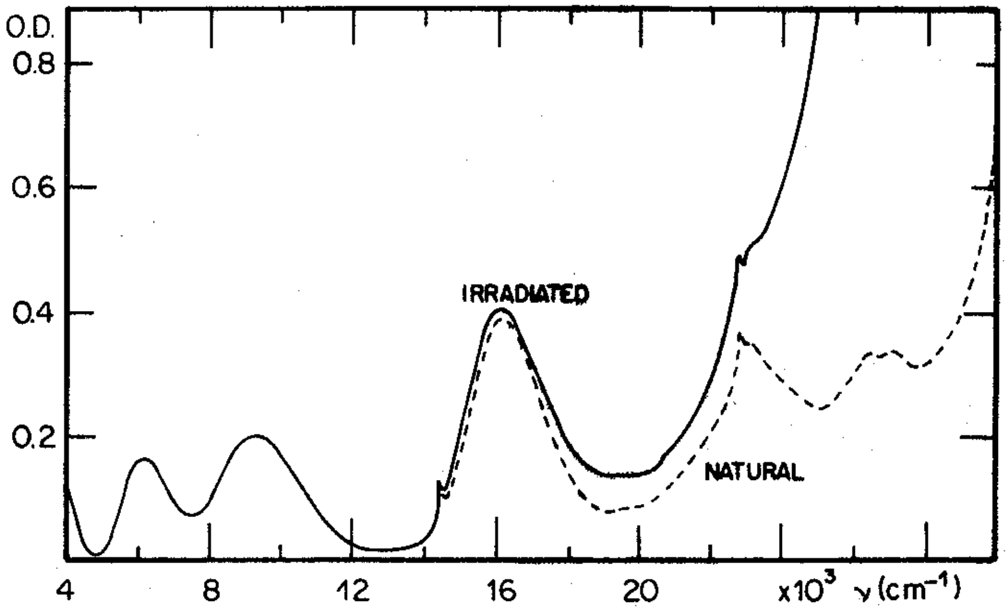
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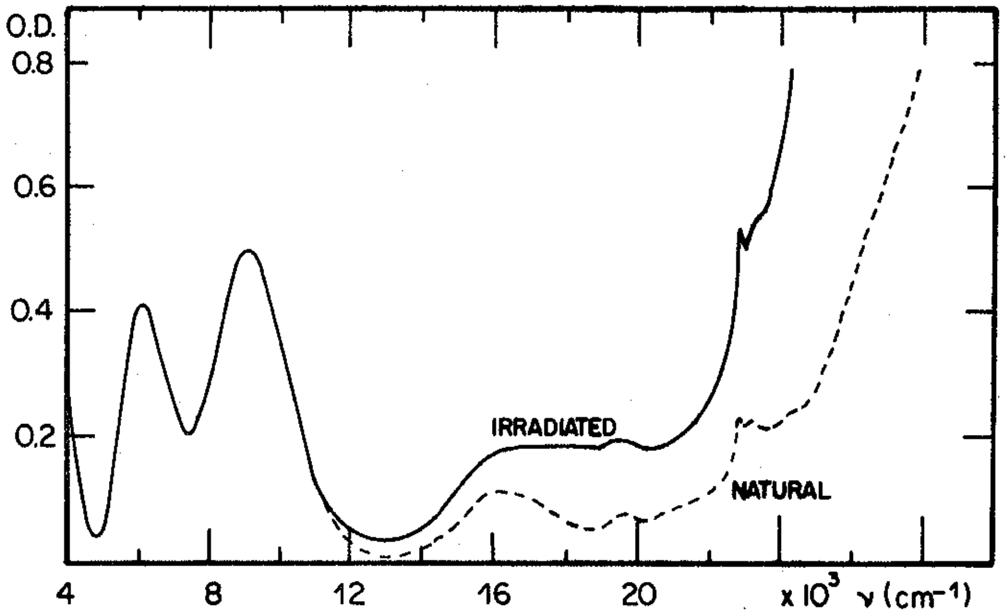
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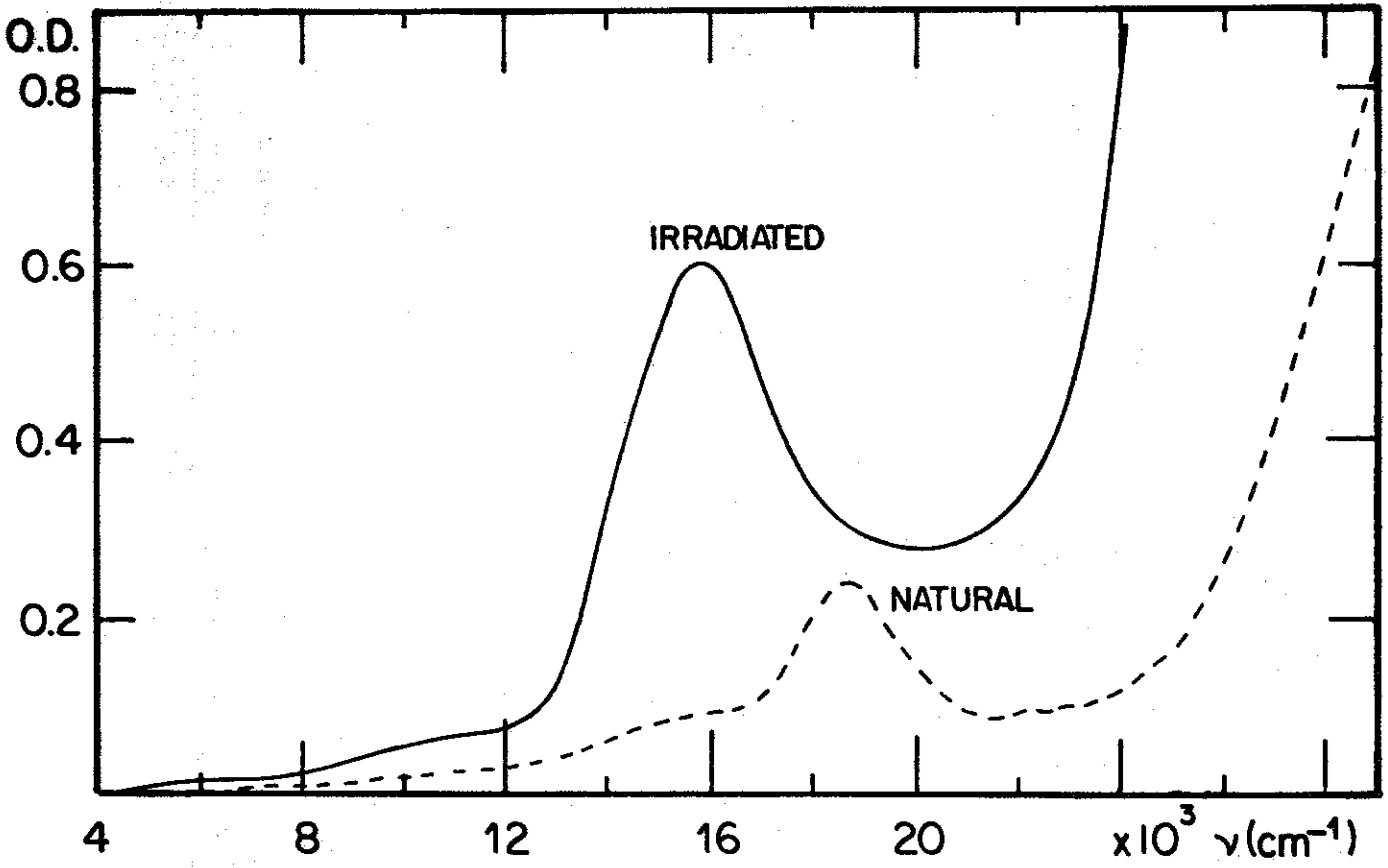
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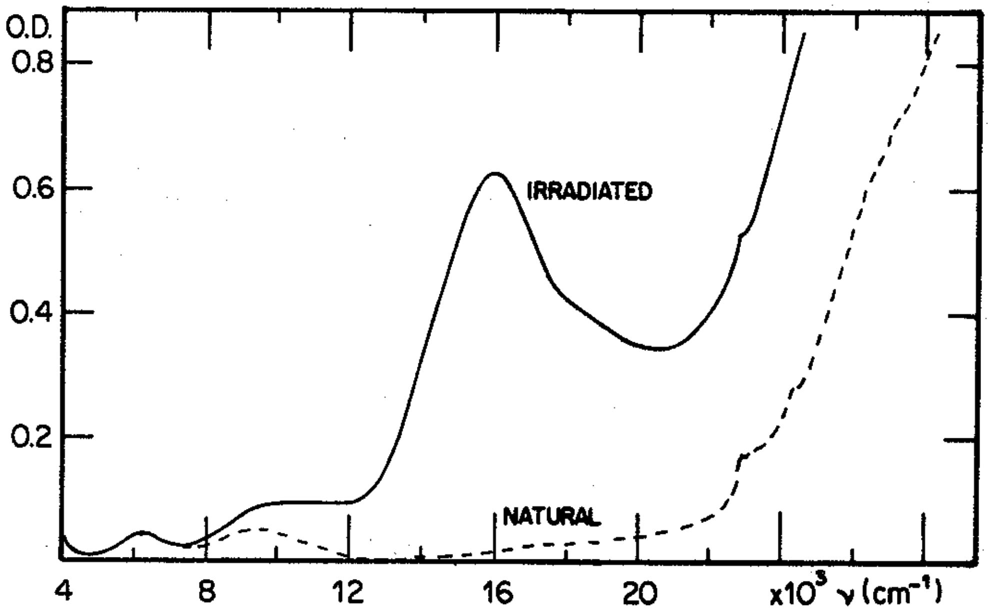
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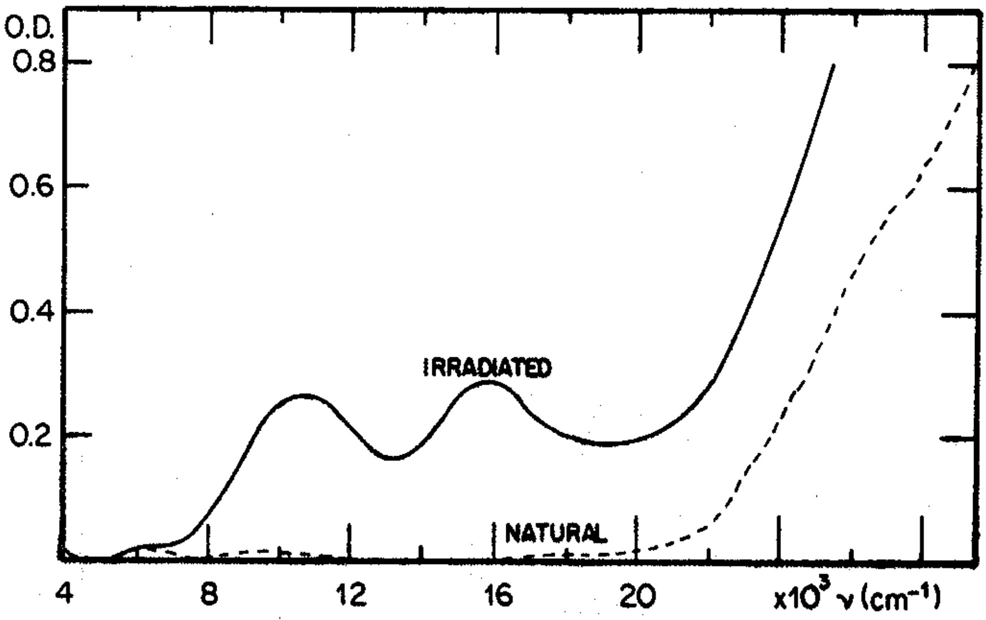
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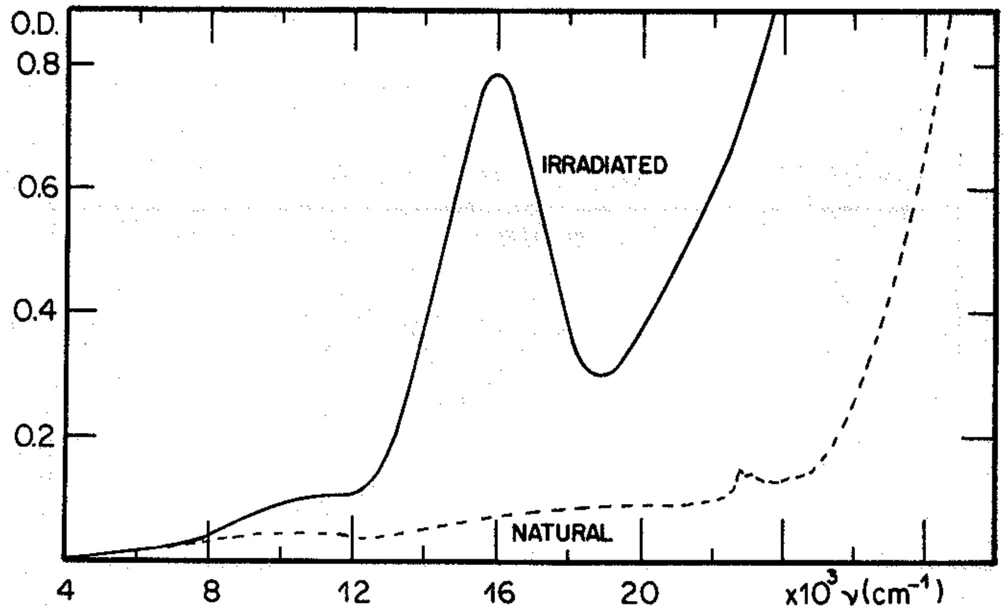
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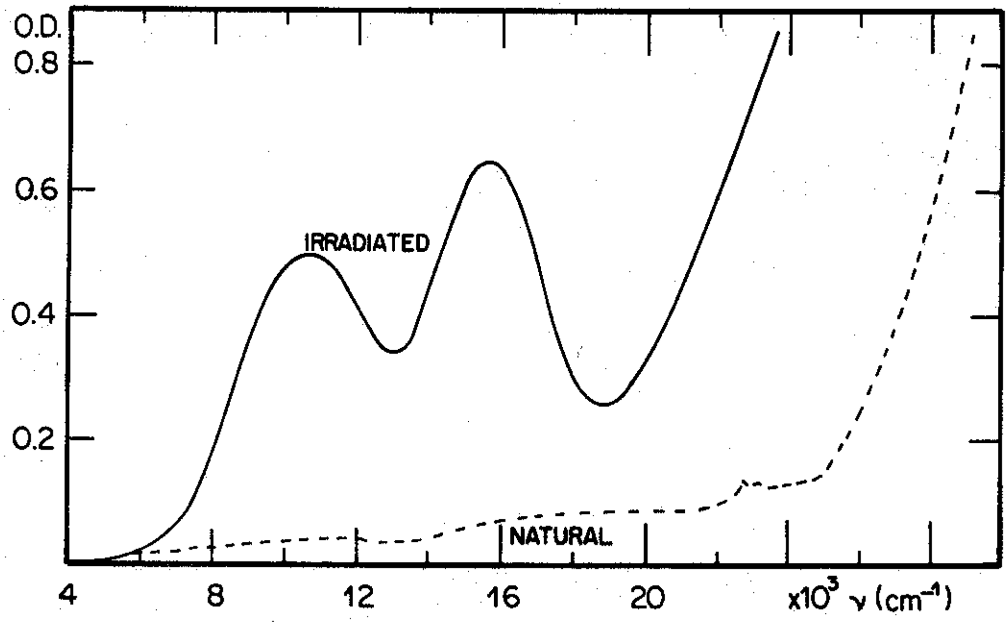
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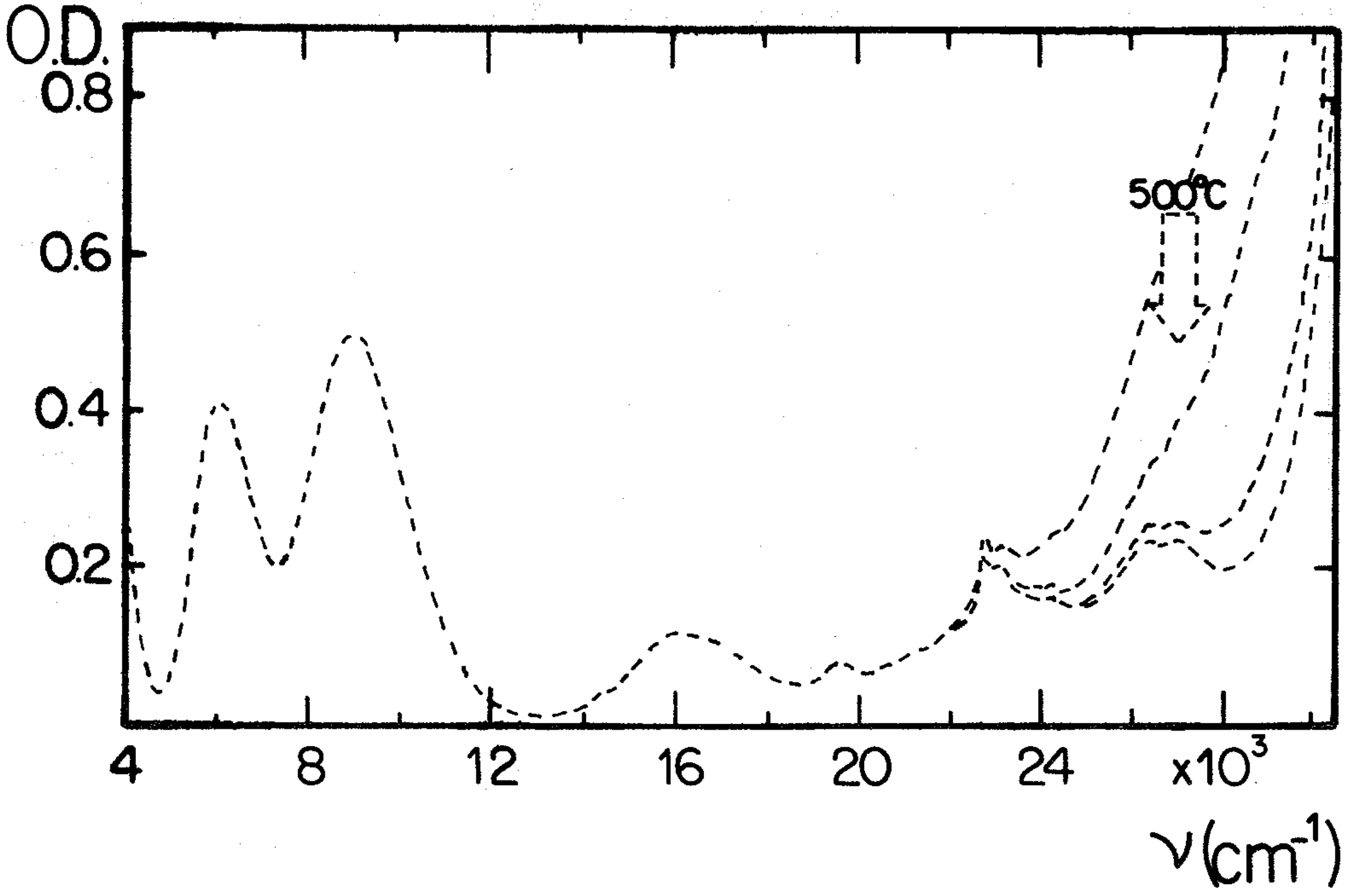
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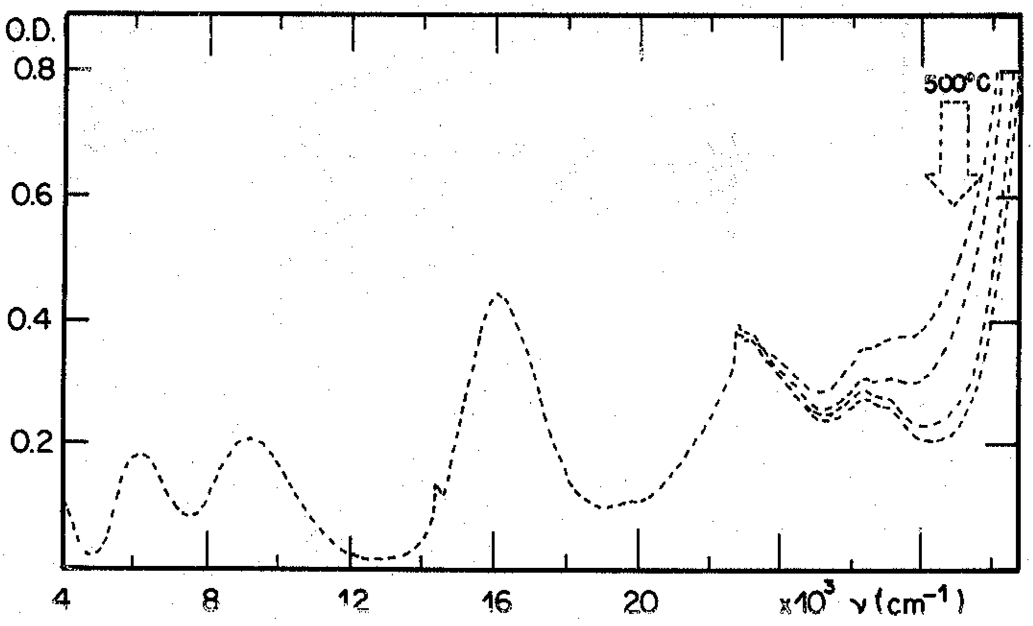
ν(cm^{-1})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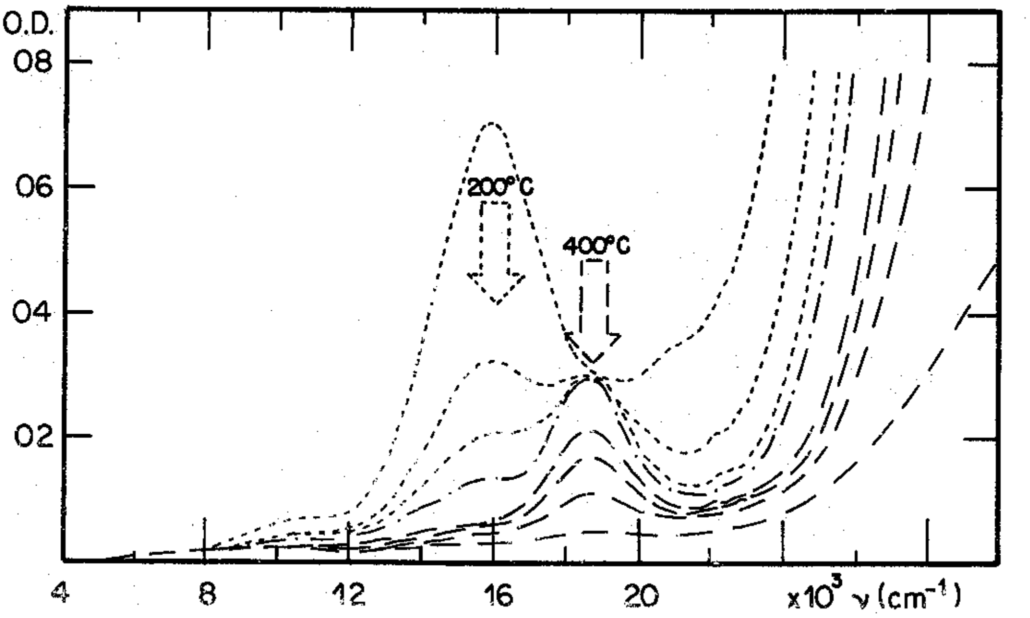
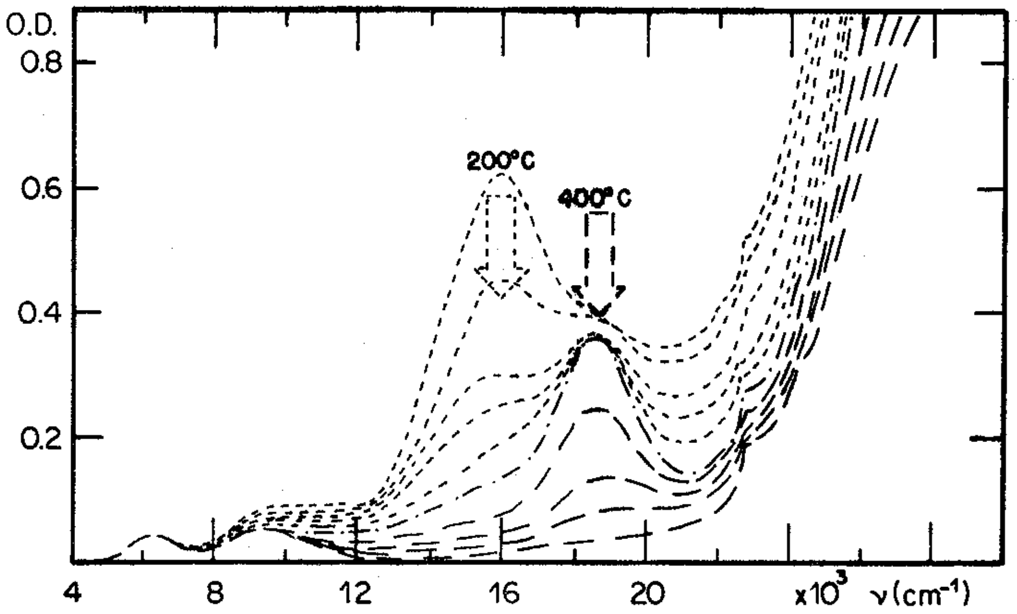
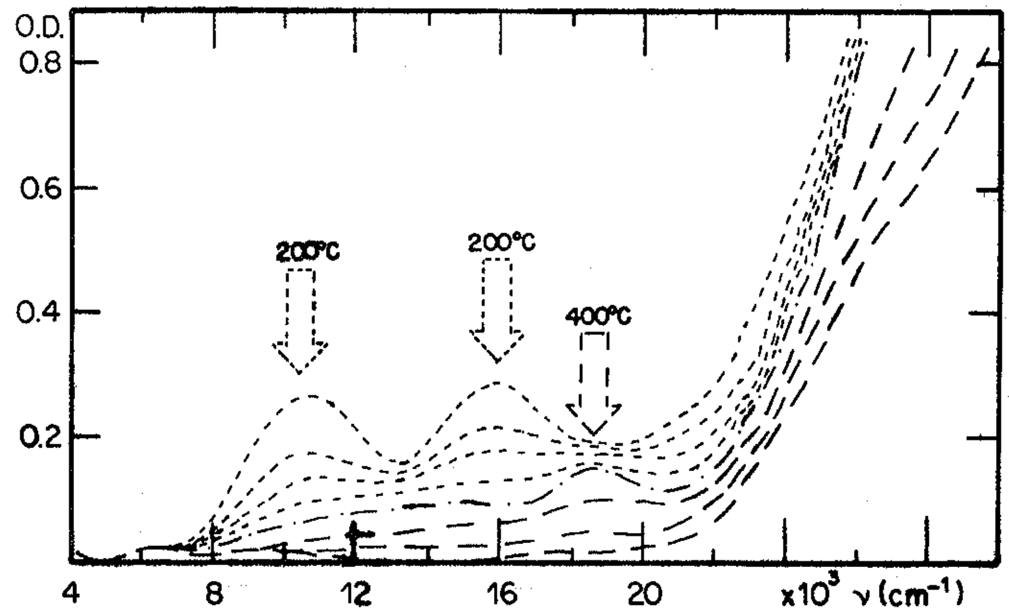
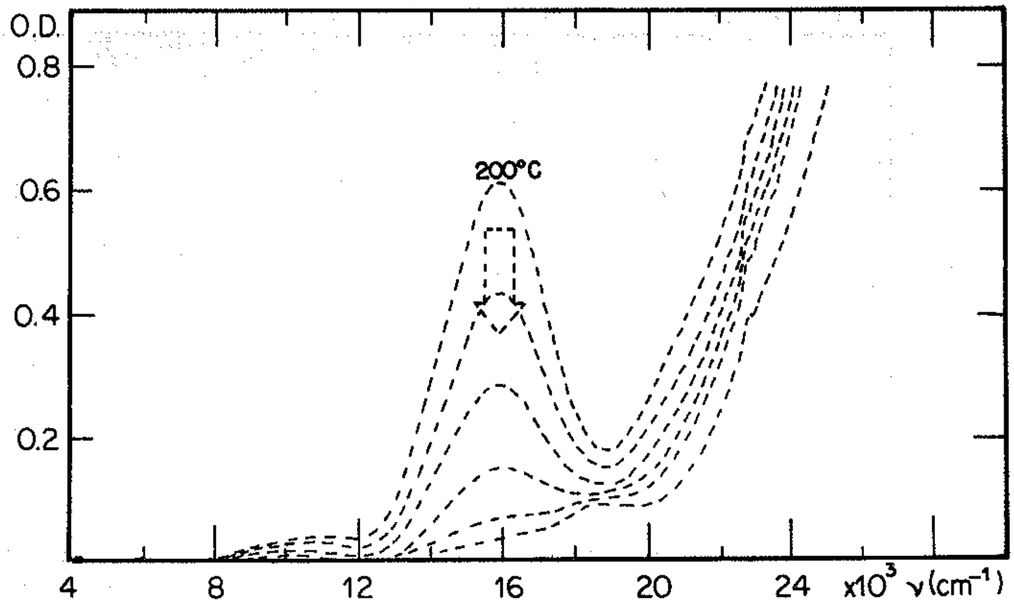
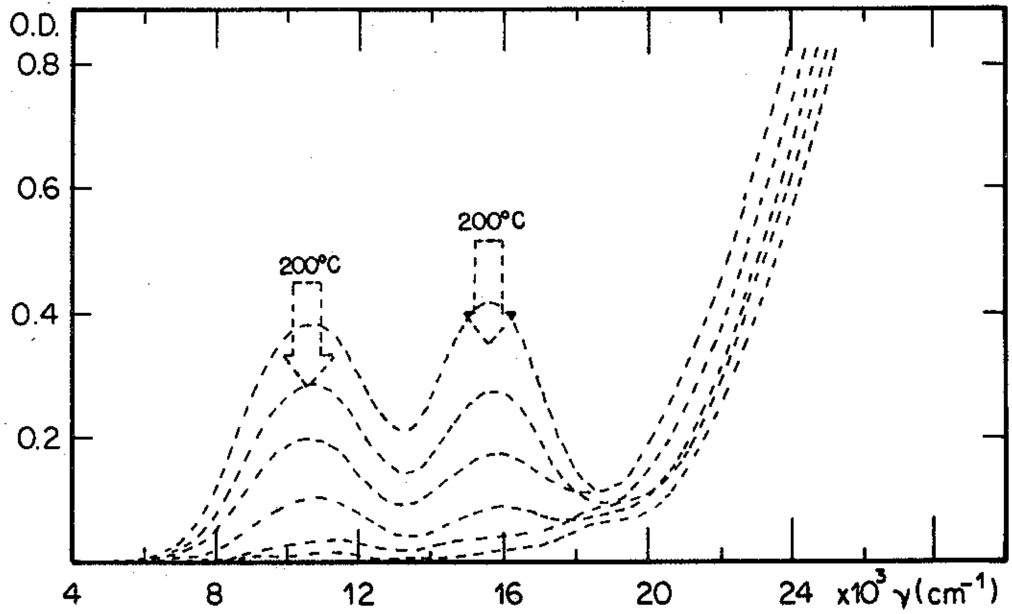
x10³ ν (cm⁻¹)
500°C

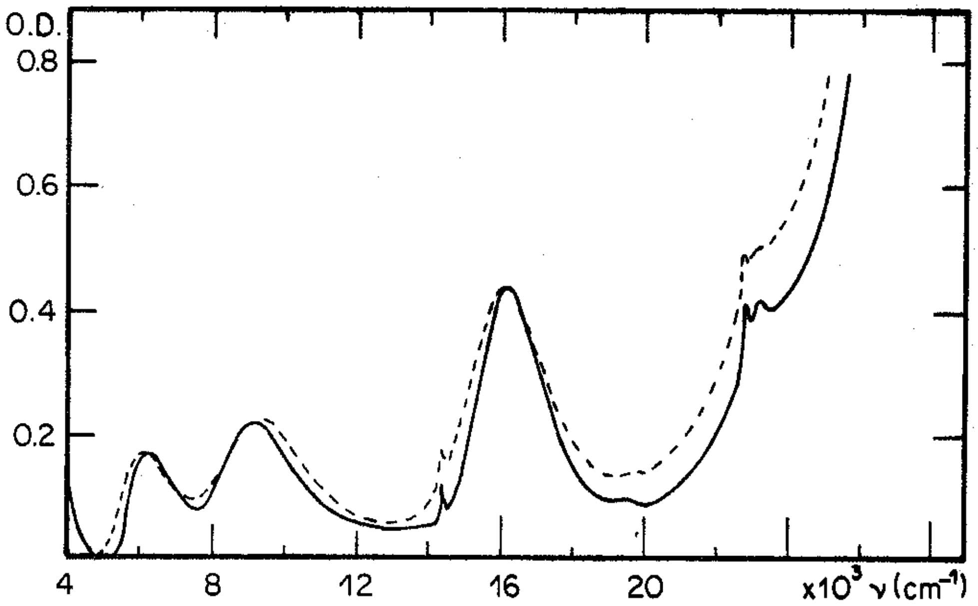

O.D.
08
06
04
02
4
8
12
16
20
x10³ ν (cm⁻¹)
200°C
400°C

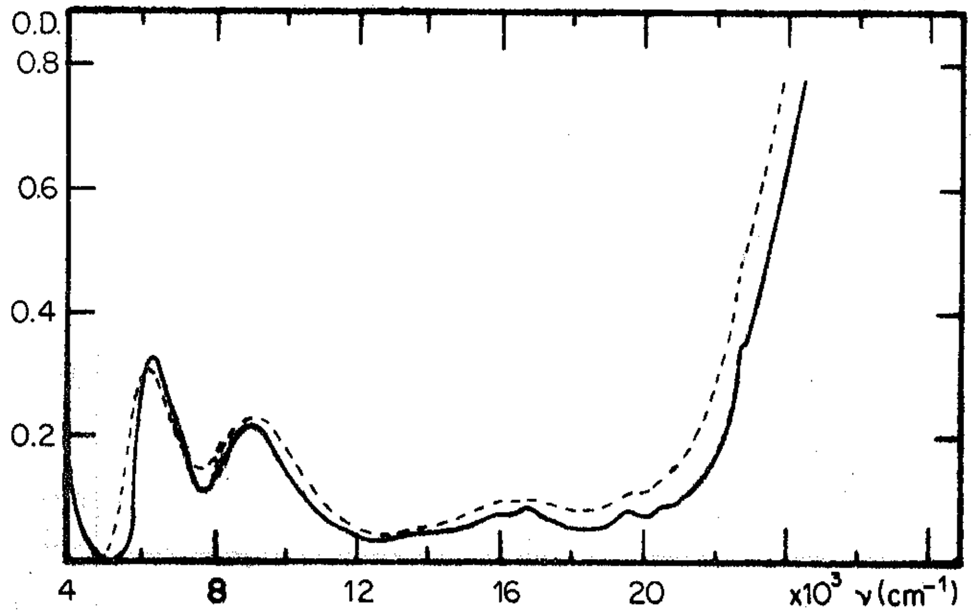

O.D.
0.8
0.6
0.4
0.2
200°C
400°C
4
8
12
16
20
x10³ ν (cm⁻¹)

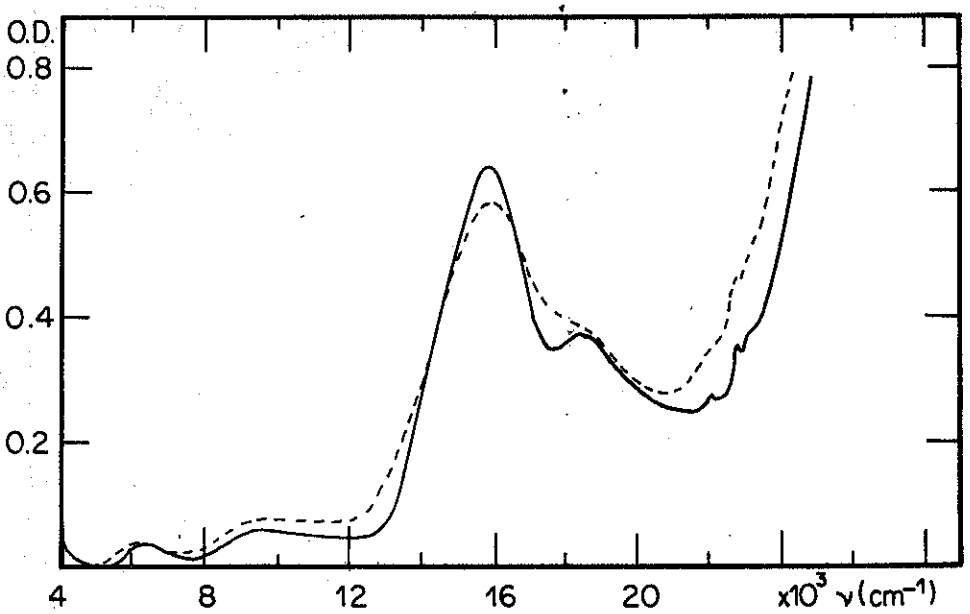

O.D.
0.8
0.6
0.4
0.2
200°C
200°C
400°C
4
8
12
16
20
x10³ ν (cm⁻¹)

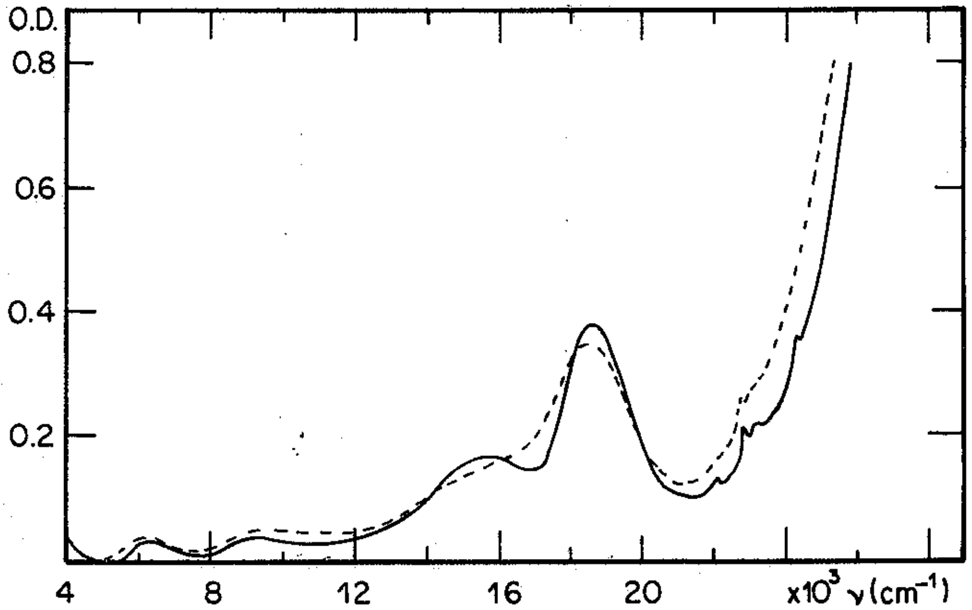

O.D.
0.8
0.6
0.4
0.2
200°C
4
8
12
16
20
24
x10³ ν(cm⁻¹)

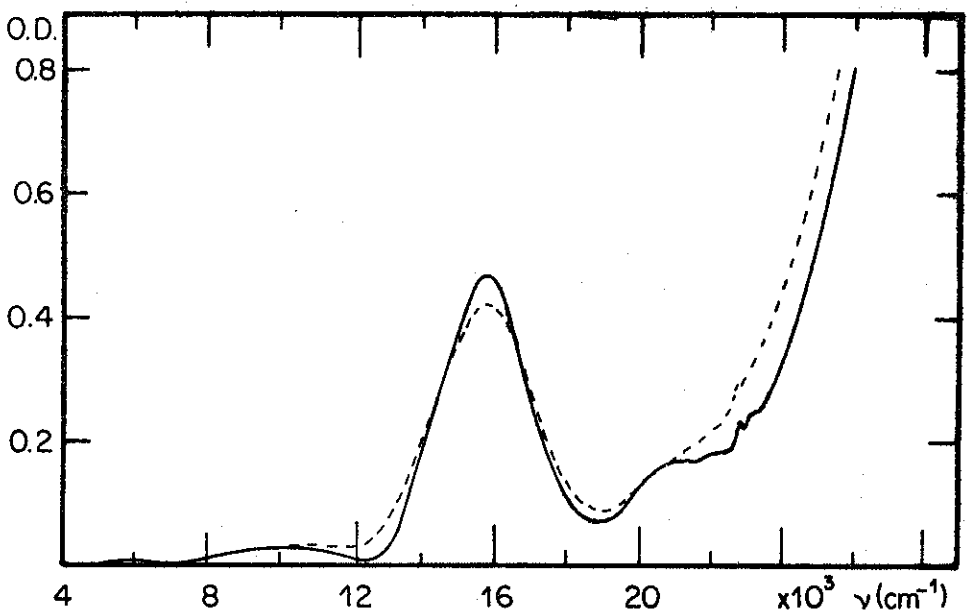

O.D.
0.8
0.6
0.4
0.2
200°C
200°C
4
8
12
16
20
24
x10³ γ(cm⁻¹)

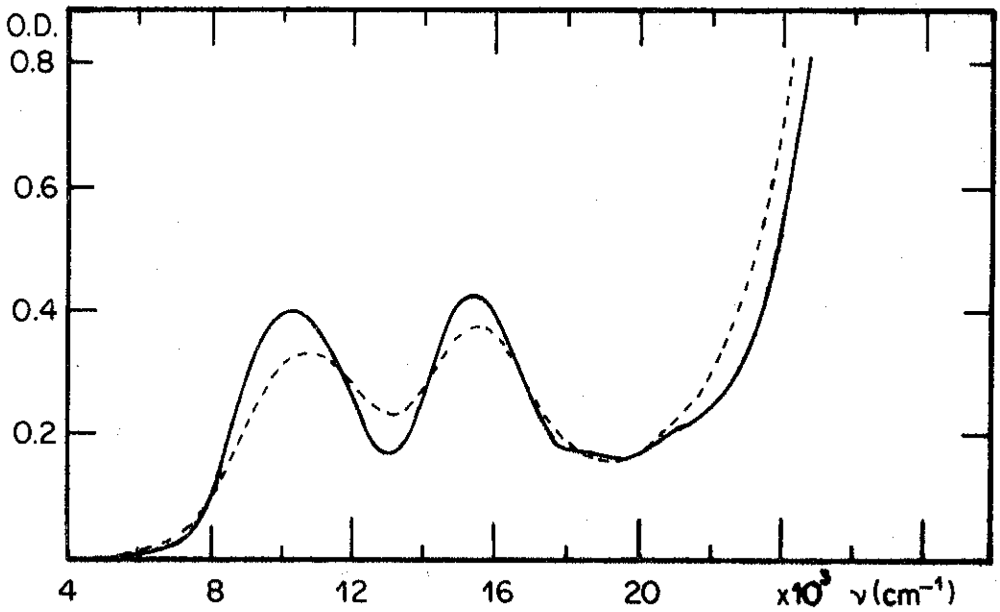

O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10³ ν (cm⁻¹)

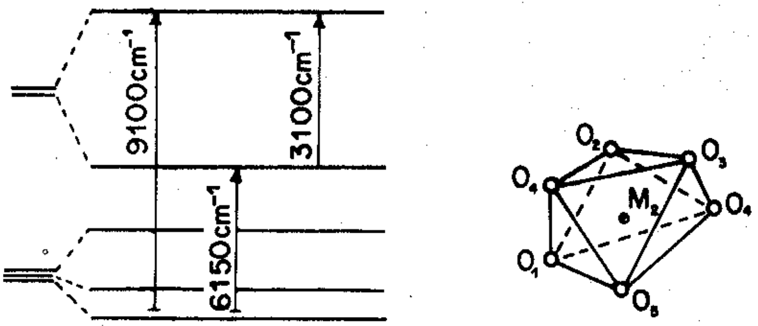

O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10³ ν (cm⁻¹)

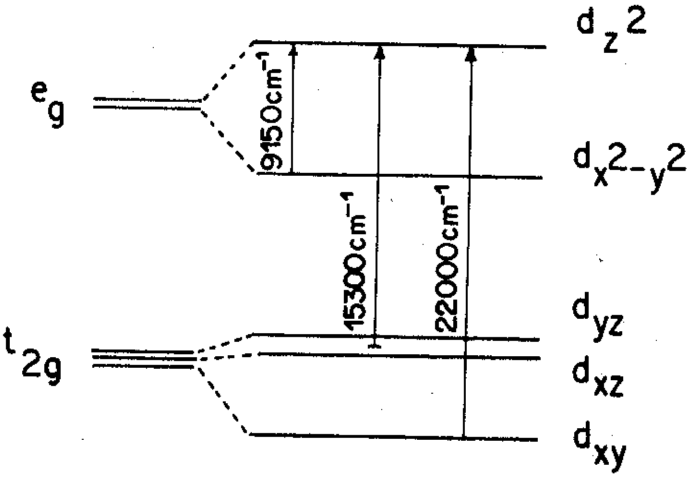

O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10^3 ν(cm^{-1})

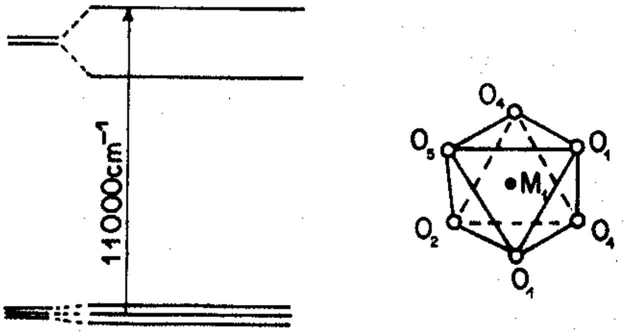

O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10^3 ν(cm^{-1})


O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10^3 ν (cm^{-1})


O.D.
0.8
0.6
0.4
0.2
4
8
12
16
20
x10^3 ν (cm^{-1})


9100cm-1
3100cm-1
6150cm-1
O2
O3
O4
M2
O4
O1
O5


eg
t2g
9150cm-1
15300cm-1
22000cm-1
dz2
dx2-y2
dyz
dxz
dxy


11000cm-1
O4
O5
O1
M1
O2
O4
O1