AD-A244 464

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 10, 1991	Technical Report- 1Aug90 - 31 Jul 91

4. TITLE AND SUBTITLE

Laser Assisted CVD Growth of AlN and GaN

5. FUNDING NUMBERS

F49620-89-C-0108
Proc. Inst No.

FQ8671-89-01458 2306/B1 Req. No.

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Washington, DC 20059

AFOSR-TR-

8. PERFORMING ORGANIZATION REPORT NUMBER

210

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

USAF/AFSC
AirForce Office of Scientific Research
Building 410
Bolling AFB, DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

F4920-89-C-0108

2306/B1

11. SUPPLEMENTARY NOTES

DTIC ELECTE JAN 1 6 1992 S D D

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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This is the second annual report of a project for investigating the laser induced CVD growth of AlN and GaN (Gallium Nitrogen). In the second year significant progress has been made in the growth of AlN. AlN films have been produced by laser ablation. A new LI CVD source for Al atoms has been characterized and verified by growth of Al films. Additionally, some progress has been made in the understanding and characterization of alkyl aluminum-amino adducts which may be used for the growth of AlN.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
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INTRODUCTION

The goal of this project is to design, test and verify advanced laser induced chemical vapor deposition processes (LI-CVD), specifically for the growth of AlN. In the past year we have made progress in three areas:

a: Rapid growth of AlN thin films by laser ablation of AlN powders.

b: Demonstration of an advanced LI-CVD method for deposition of Al films from trimethylaluminum (TMAl). This method was designed to be used as the aluminum atom source in AlN growth, but also has utility for laser deposition of aluminum interconnects, an area of current interest..

c: Synthesis and characterization of a number of stable alkylaluminum-nitrogen containing adducts for future use in film growth.

A. GROWTH OF AlN THIN FILMS BY LASER ABLATION

We have grown AlN thin films by laser ablation of powdered AlN compressed into a pellet. AlN powder (98% purity from Strem Chemicals, Inc.) was compressed into tablets in a die used to prepare powdered samples for IR

92 1 13 002

analysis. The die was placed in a hydraulic press and a small powder tablet, 13 mm in diameter, was pressed.

The tablet was placed in a vacuum chamber and oriented at 45° or 90° angles to the laser beam, as shown in Figure A1. Initially, the substrate was placed below the powder pellet, but for some later runs the substrate was placed above the pellet. The later orientation minimizes the spillage of ablated fragments on the substrate. KrF or ArF laser beams of between 50 and 200 mJ per pulse were softly focussed onto the AlN powder tablet from a distance of 300 mm. Both the long focal length and the large divergence of the laser beam result in a relatively soft focal condition.

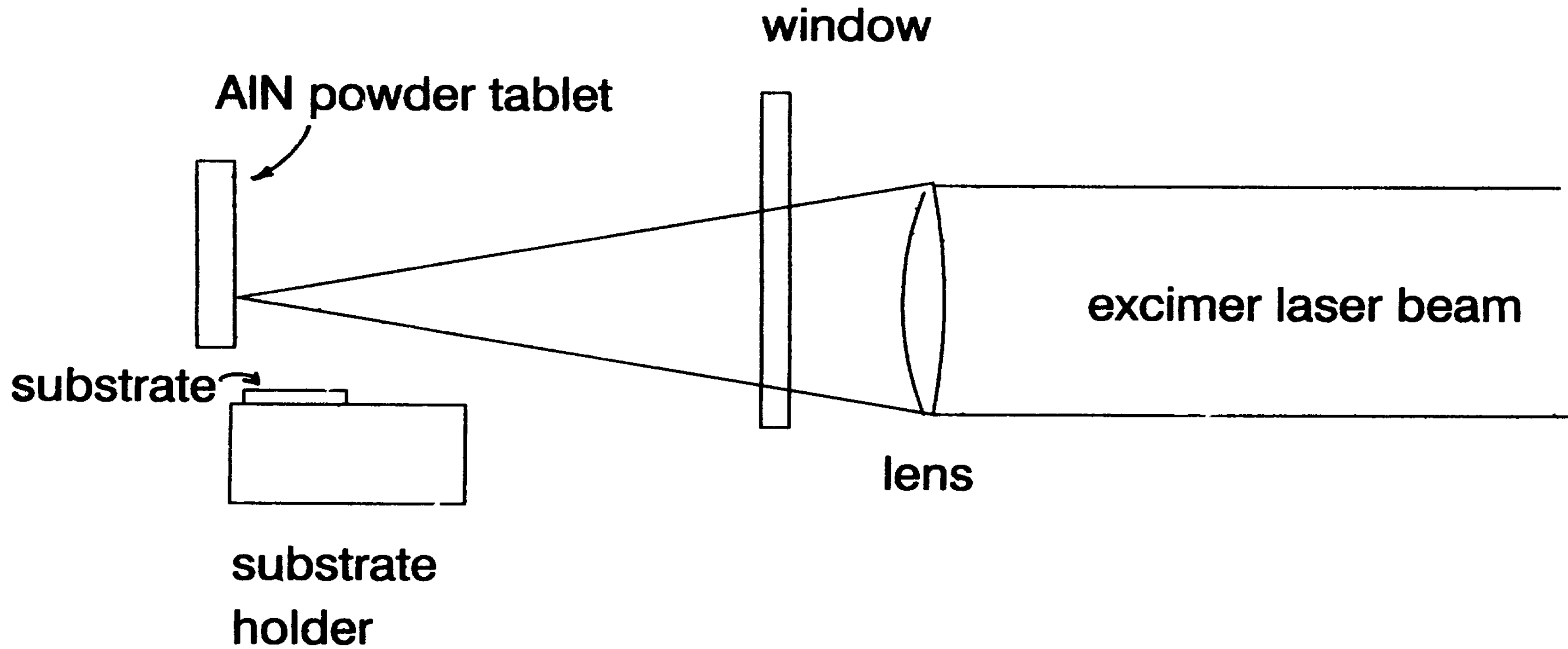
The laser beams ablate the powder, and we observed a rapid film growth on substrate material of diverse composition. Films have been grown cn KBr, supracil quartz and GaAs substrates.

Figure A2 shows the IR spectrum of an AlN thin film ablated onto a KBr substrate. This is identical with the reference IR spectrum of AlN [1]. Figure A3 is a UV spectrum of an AlN thin film sample sputtered onto supracil quartz. The peak of the spectrum is at 200 nm or 6.20 eV [2]. The band absorption extrapolates to zero at about 245 or 5.06 eV. These are compatible with the measured bandgap of AlN. Note the small peak at 260 nm which may be due to

Dist A-1

Figure A1:

Apparatus for Laser Ablation Growth of AlN Films



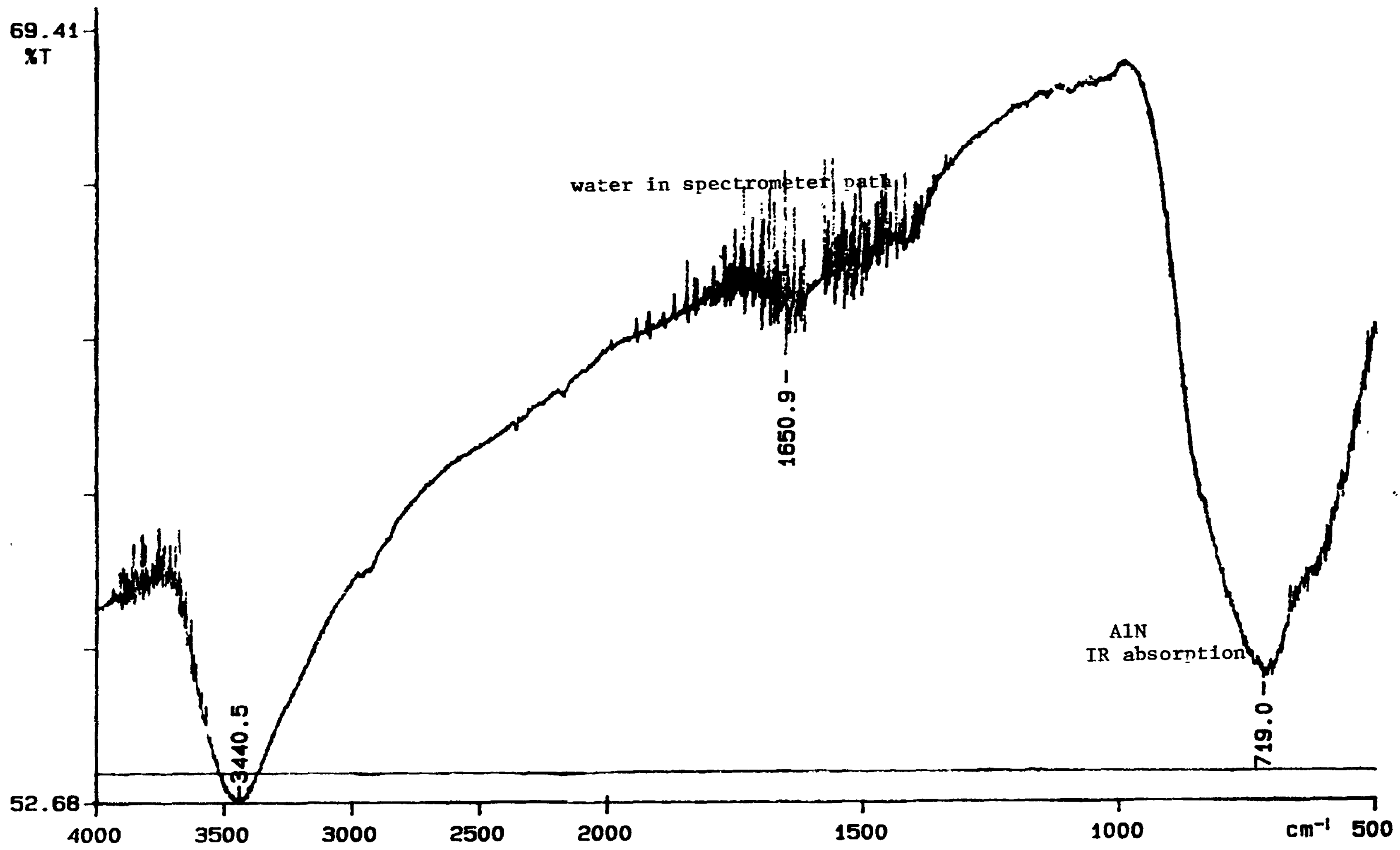


Figure A2: IR Absorption of AlN Film Grown by Laser Ablation on KBr

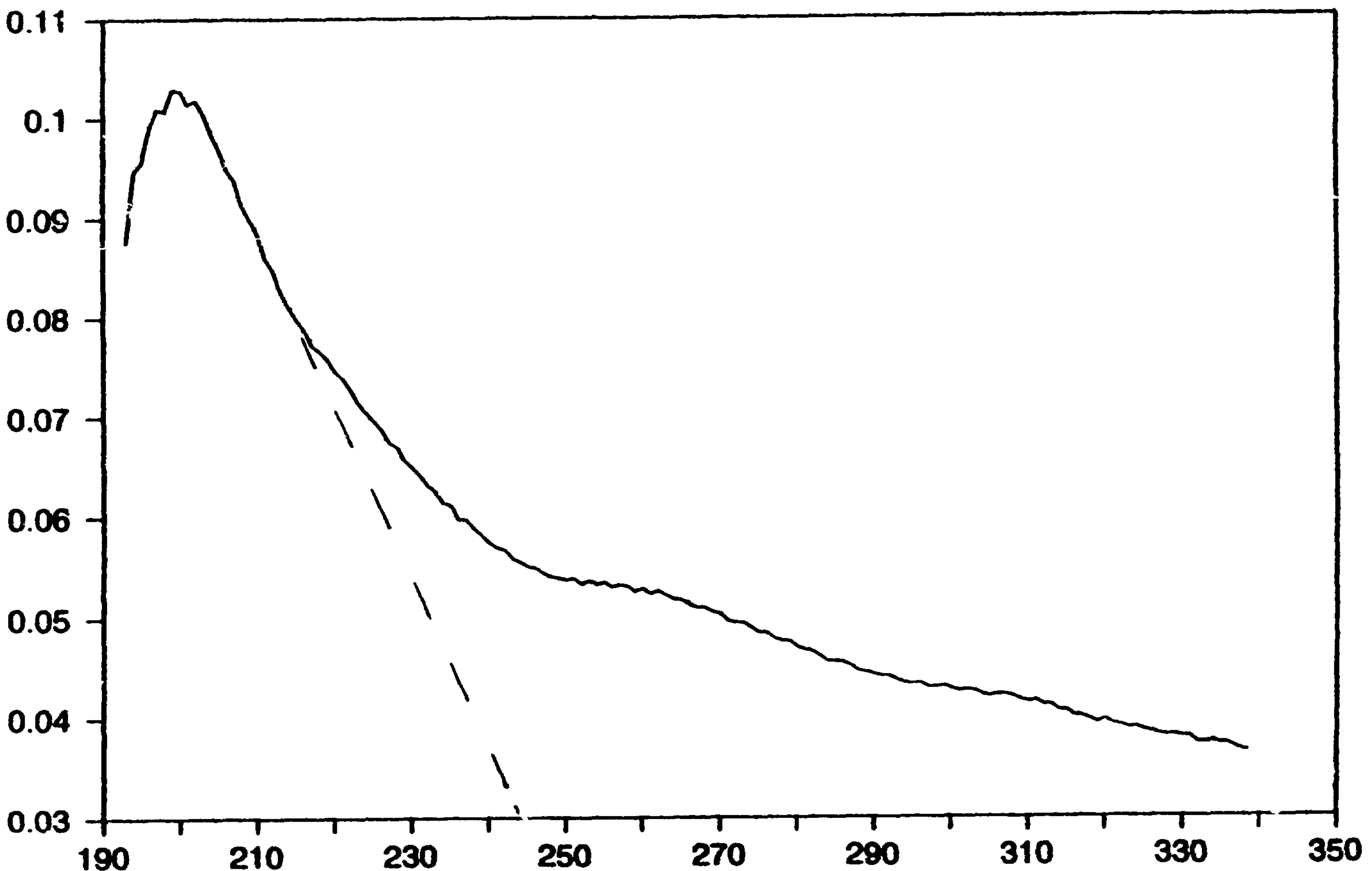


Figure A3: UV Absorption of AlN Film Grown by Laser Ablation on Quartz

an impurity peak. The continuous rise of the spectrum from 330 nm is due to diffuse scattering from the sample.

Photomicrographs of a samples grown on GaAs are shown in Figure A4. The first shows a poor film, which has incomplete coverage. On this one can see the islands of AlN on the GaAs substrate. The second film is generally smooth with an average thickness of 0.45 microns, and a variation of less than 0.05 microns. Little variation can be seen on the picture. We believe that most of the small pieces on the film are ablation ejecta. Orientation of the substrate above the powder tablet minimizes this problem. It should be noted that we have grown less than 20 samples at this time and have not optimized growth rates or condition for production of good films, nor have we yet grown films with heated substrates, which also might result in more uniform surface coverage. Figure A5 shows photographs of SEM pictures of the same sample, at two magnifications.

Figure A6 is an Auger depth profile of a thick sample grown on GaAs. The film was sputtered for ten minutes before the Auger profiles were recorded. This was a relatively thick film of over 1 micron, and there was a significant problem with charging of the sample, especially at longer sputtering times. Oxygen content is low throughout. We note a segregation of carbon on the surface which decreases rapidly with depth. The carbon is probably a result of handling or, more likely, of photolysis of

Figure A4: 1000x photomicrograph of a poor AlN thin film grown by photoablation showing platelets of AlN and the underlying GaAs substrate.

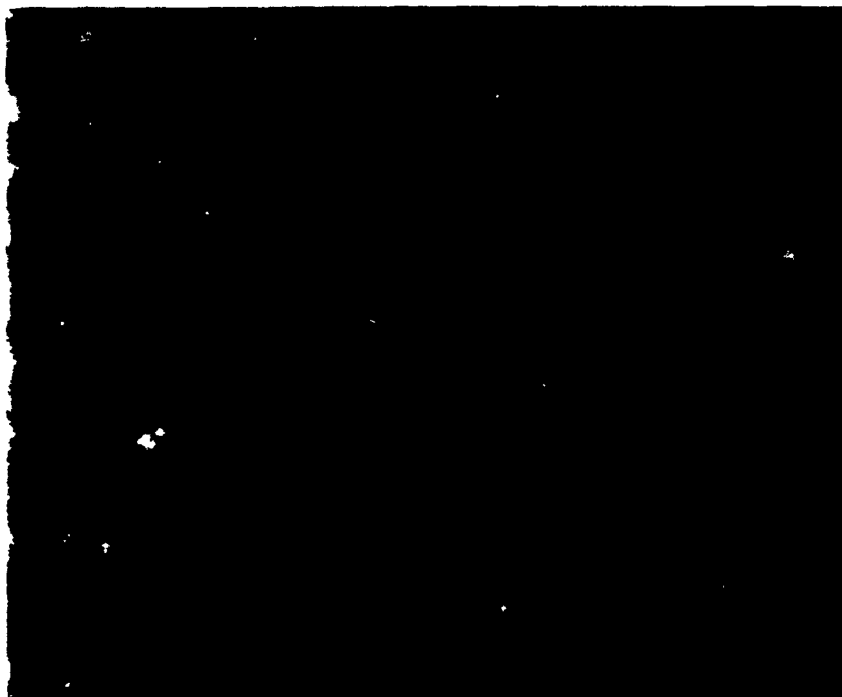


Figure A4: 1000x photomicrograph of a better AlN film.

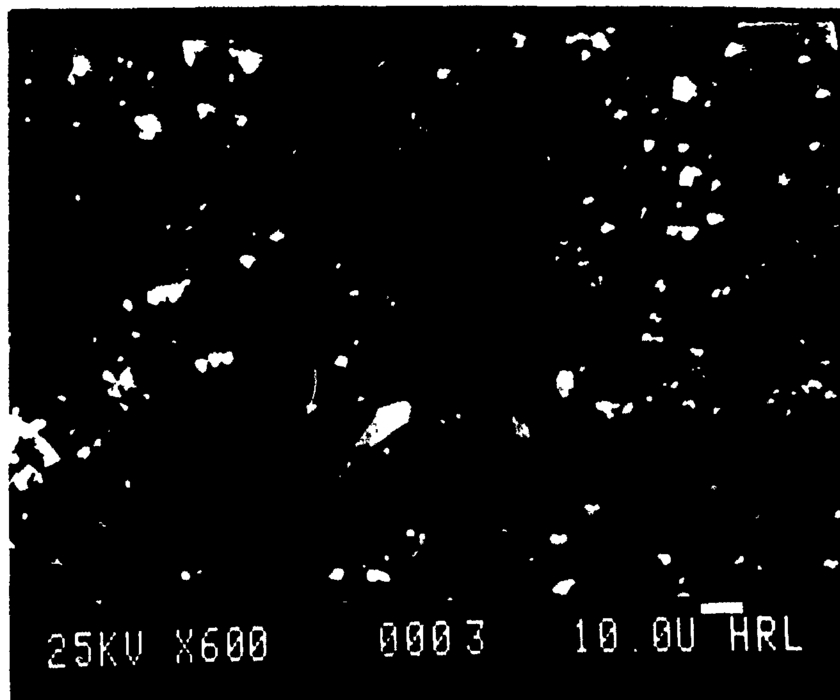
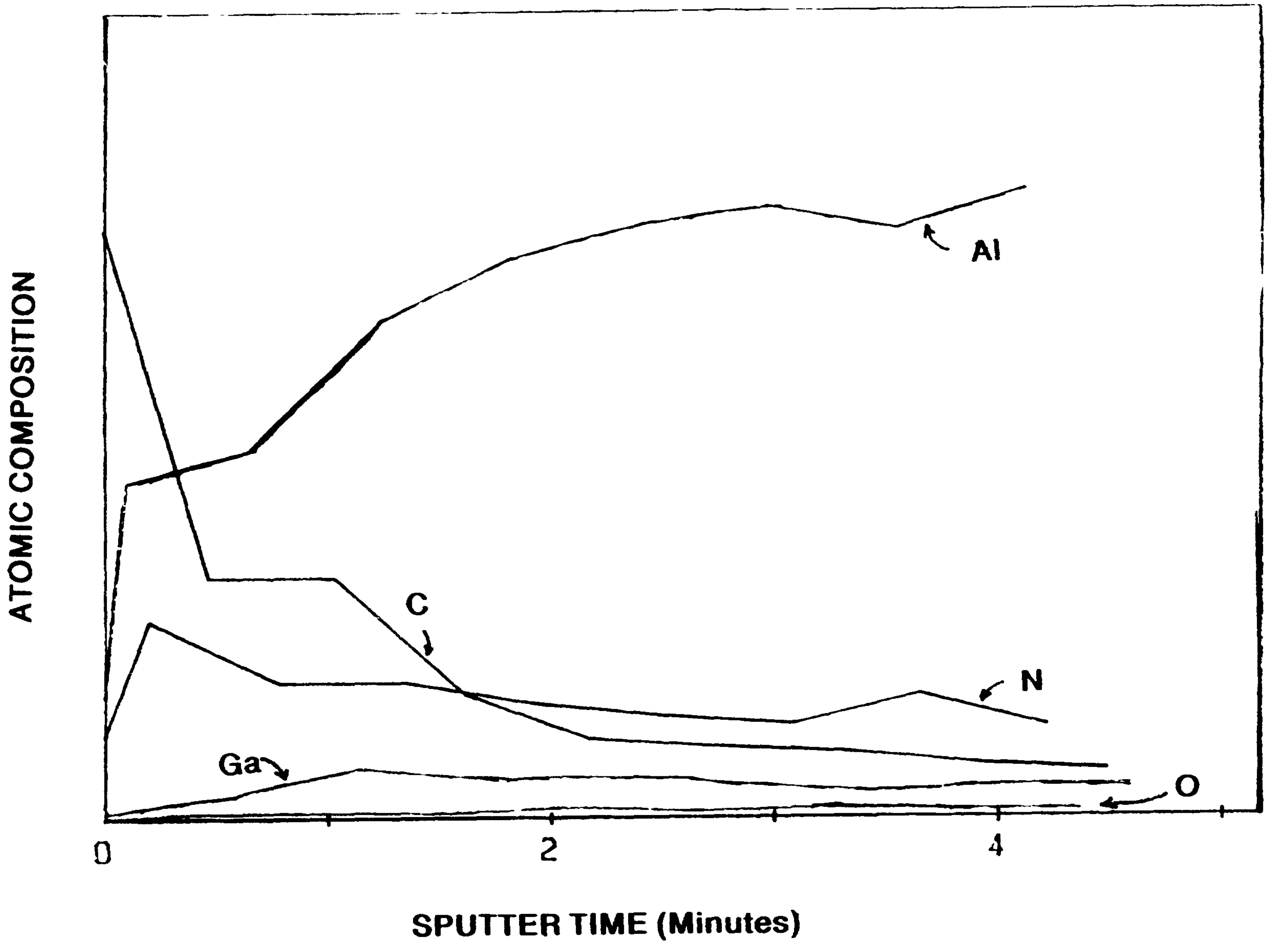


Figure A5: SEM of AlN film grown by photoablation. The scale is at the bottom of the photograph

Figure A5: SEM of AlN film at a slightly higher magnification. Note that the sharp features are AlN powder ejecta and that this film is itself fairly smooth.

FIGURE A6: AUGER DEPTH PROFILE



carbon containing molecules that diffused from the cell walls during the experiment. We had previously used the same cell for experiments on LI-CVD with alkylaluminum compounds. It is unlikely that carbon contamination would remain a serious problem because no carbon containing molecules are involved in the growth process Al and N are found throughout the sample. The cell can and will be cleaned by mechanical and chemical methods.

The Auger depth profiles for aluminum and nitrogen atoms in the film are relative measurements. The Auger spectrometer has not been calibrated between atomic signals.

At this time, in addition to growth optimization, thin film X-ray analysis is being planned. We are setting up a photoluminescence system for AlN. This requires photoexcitation at energies greater than 6.2 eV. We will use a pulsed 193 nm (6.4 eV) ArF laser with a fast 0.25 m monochromator/photomultiplier for dispersed detection and photon counting electronics for signal acquisition.

Growth rates can be extremely rapid with this method. One micron thick samples of 0.5 cm^2 area can be prepared in less than 20 minutes, using 10 Hz, 100 mJ pulses. Table I shows the results of a series of experiments that used 193 nm photoablation. The focus of the laser was about 0.1 cm^2 and the laser was operated at 10 Hz.

TABLE I

Ablation Film Growth Rates

Laser Energy (mJ/pulse)	10-20	35-45	110
Growth Time (minutes)	50	40	20
Thickness (microns)	0.29	0.44	1.45

We believe that, at a minimum, this method holds excellent promise for the development of amorphous AlN films for electronics. These are used as insulating layers, for heat sinks and for the fabrication of thin film resistors [3]. We are close to growing good films at room temperature. In the next year we will investigate whether conditions exist so that these films can be grown as single crystals. (We do not yet know the degree of organization of our films).

In the past year two groups have published on growth of AlN films for semiconductors by laser methods. Li and Tansey report LI-CVD from mixtures of TMAl and ammonia at substrate temperatures of about 200 ^{o}C and using a 193 nm ArF laser [4]. For reasons that are discussed in the attached preprint, we believe that 193 nm photolysis of TMAl is an inferior method of producing the aluminum precursor for growth of AlN. H. Mitsugu has grown AlN films using excimer laser photolysis of Me_2AlH and NH_3 [5].

B. LI-CVD DEPOSITION FROM TRIMETHYLALUMINUM

Attached is a manuscript describing a promising method for growth of Al films from TMAl using a KrF laser at 248 nm. This includes characterization of the mechanisms of Al atom production at 248 and 193 nm and a demonstration of the process. This manuscript will be submitted to the Journal of Applied Physics shortly.

Briefly, the method is based on our laboratory's discovery that TMAl dimers do not absorb at 248 nm, while the monomer does. TMAl is almost completely dimerized at room temperature and completely monomeric at 130 ^{o}C. Thus, the 248 nm laser will pass unimpeded through the reactor and only be absorbed by TMAl near the surface of a slightly heated substrate (100 - 130 ^{o}C). Therefore, expensive photons will only be absorbed where they can effectively deposit Al atoms on the substrate, and not in the middle of the cell where they will never encounter the substrate, nor, in the worst case, near the reactor window where they can form an obscuring film. Growth of films on reactor windows is an endemic problem in LI-CVD processes.

Moreover, as the manuscript shows, the photolysis process at 248 nm is several times more efficient in forming Al films than photolysis at 193 nm. The molecular basis for this is discussed in the manuscript.

This method was originally put forward as the Al atom source part of our original process design for LI-CVD of AlN. The work described in the manuscript validates the mechanism. In the next year growth of AlN will be attempted by combination of this Al atom source with various N atom sources and variation of substrate conditions (principally temperature). However, there is interest in better CVD methods for growth of Aluminum films for interconnects [6,7]. We believe that our method has several advantages over other CVD and LI-CVD methods that have been developed.

C. SYNTHESIS AND CHARACTERIZATION OF Al-N MOLECULAR ADDUCTS FOR CVD OF AlN.

The growth of thin films of AlN for semiconductors is a goal of much current research work. Part of this effort has been the development of new sources. In addition, new aluminum sources are sought for GaAlAs devices and Al film deposition. One particular part of this effort has been the testing of adducts formed between X_3Al and NY_3 molecules. Synthesis, characterization and growth of several of these adducts have been reported on in the literature as shown in Table I.

TABLE I

Adduct		Action	Method	Ref.
NH_3	$AlCl_3$	AlN	LICVD	8
Me_3N	AlH_3	GaAlAs	OMCVD	9,10
		Al	LPCVD	11
		Characterization	IR,UV	TW
Me_3N	$AlMe_3$	Al	OMCVD	9,10
		Characterization	IR,UV	TW
Me_3N	$AlMe_2H$	Al	OMCVD	10
$(Me_2N$	$AlMe_2)_2$	Al	OMCVD	9,10
NH_3	$AlMe_3$			
Me_3N	$AlEt_3$	Low vapor pressure. Easy to dissociate. Not well suited to CVD.		10,TW
Me_3N	$AlEt_2H$	Al	OMCVD	10

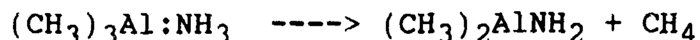
TW - This work

These adducts are interesting potential precursors for LI-CVD synthesis of AlN thin films because they have the proper stoichiometry. Their UV absorptions are red shifted from the component molecules, into regions accessible to more efficient lasers. Thermodynamic equilibrium favors the adduct at room temperatures and slightly above. However, they do not reduce the amount of carbon inclusion in the thin films that limits the use of TMAl as an aluminum atom source for OMCVD.

We have synthesized trimethylaluminum-ammonia, and triethylaluminum-trimethylamine and purchased trimethylamine alane commercially. The triethylaluminum-trimethylamine adduct has a low vapor pressure, is not useful for CVD [10], and we were not able to obtain spectra obtained UV and IR spectra for this molecule.

The trimethylaluminum ammonia adduct is a white powder that forms on mixing. Figure C1 is the IR spectrum of this molecule and Figure C2 is the UV spectrum. The structure in the UV spectrum is from an ammonia impurity. For reference, Figure C3 is the UV absorption spectrum of TMAl and Figure C4 shows the UV absorption spectra of a variety of amines, including ammonia. Figure C5 is the IR spectrum of trimethylaluminum, and Figure C6 shows the IR spectra of trimethyl- and triethylamine.

Comparing Figures C3 with C5 and C6, we see that the room temperature absorption of the adduct extends to longer wavelength than that of ammonia or TMAl. The absorption at 248 nm should be sufficient for photolysis. Heating the adduct to 100 ^{o}C resulted in a sharp pressure rise. IR spectra of the heated adducts showed the presence of methane, therefore



$$(CH_3)_3Al:NH_3 \longrightarrow (CH_3)_2AlNH_2 + CH_4$$

Irradiation at 193 nm leads to the formation of a white deposit which we have not further identified.

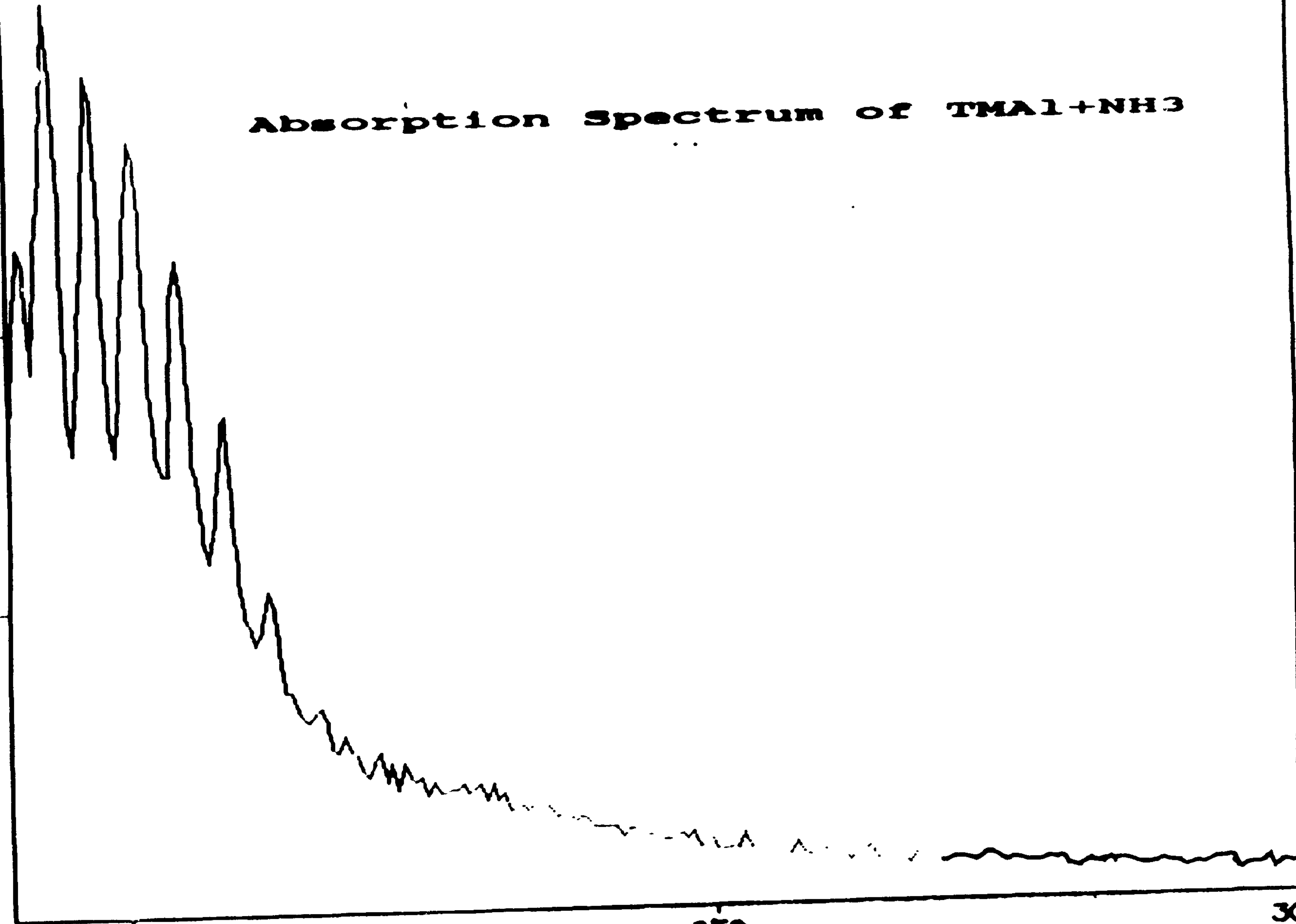

Absorption Spectrum of TMA1+NH3
0.03
0
200
250
300
Nanometers

FIGURE C2

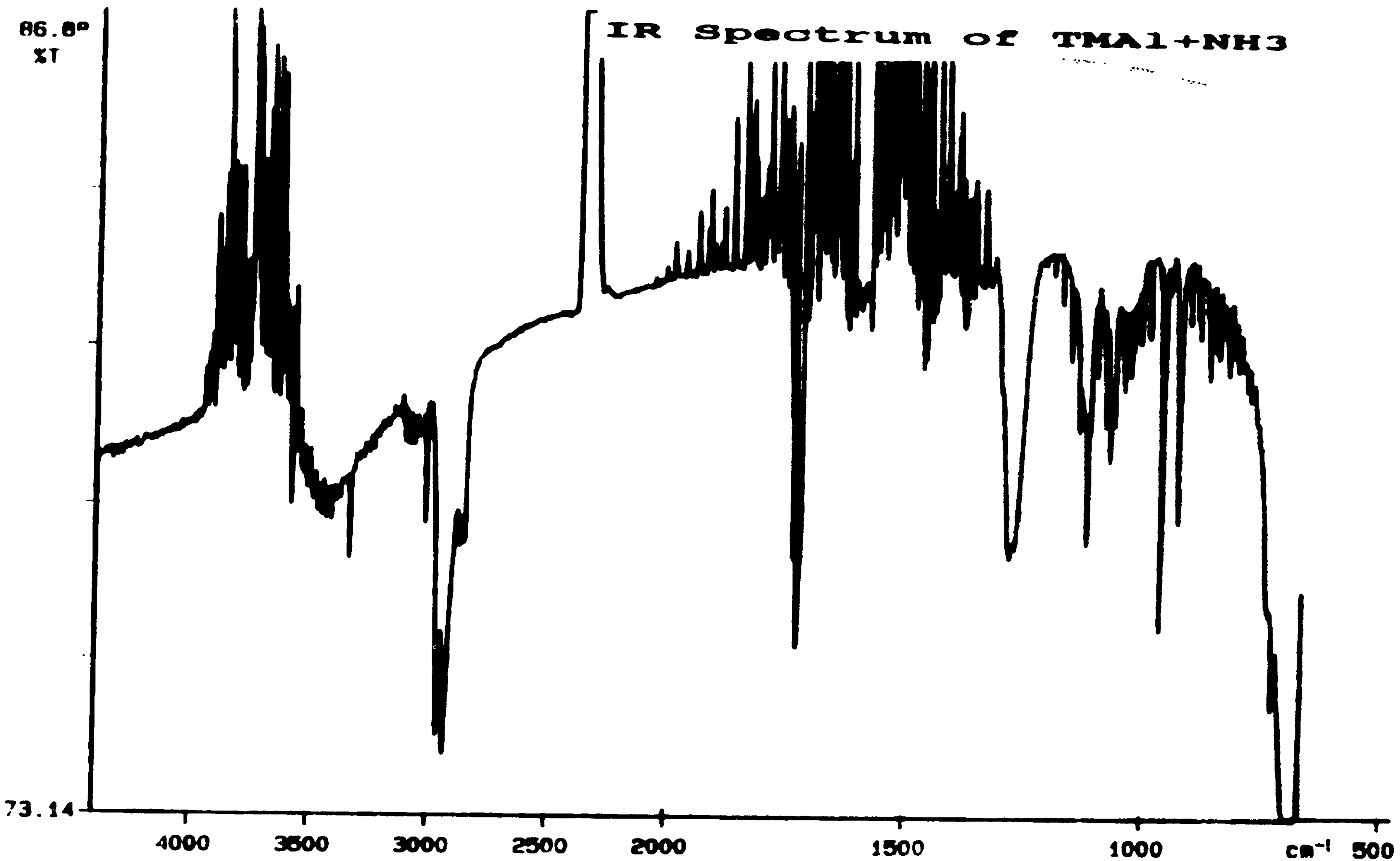
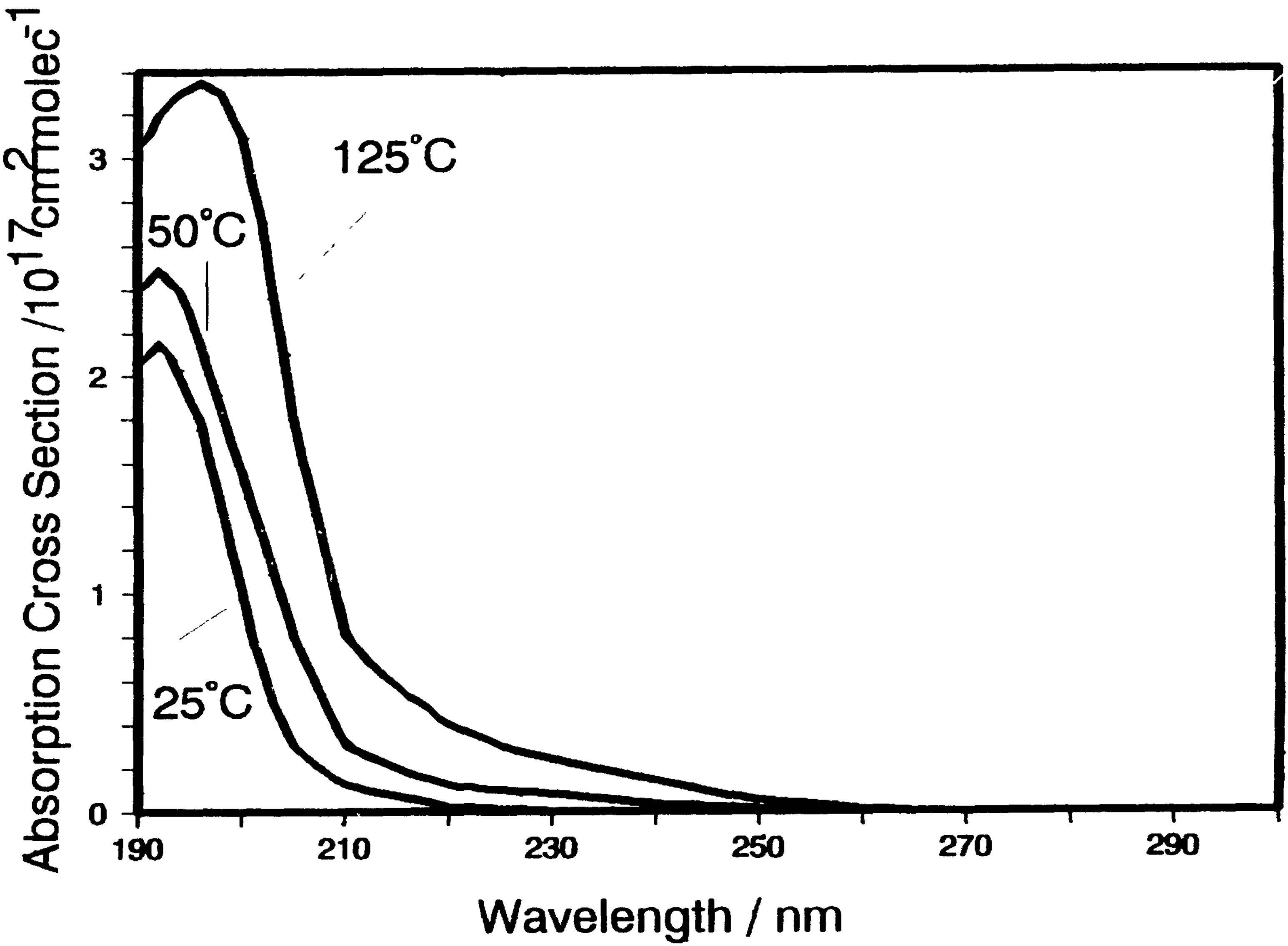


FIGURE C3: UV Absorption of trimethylluminum



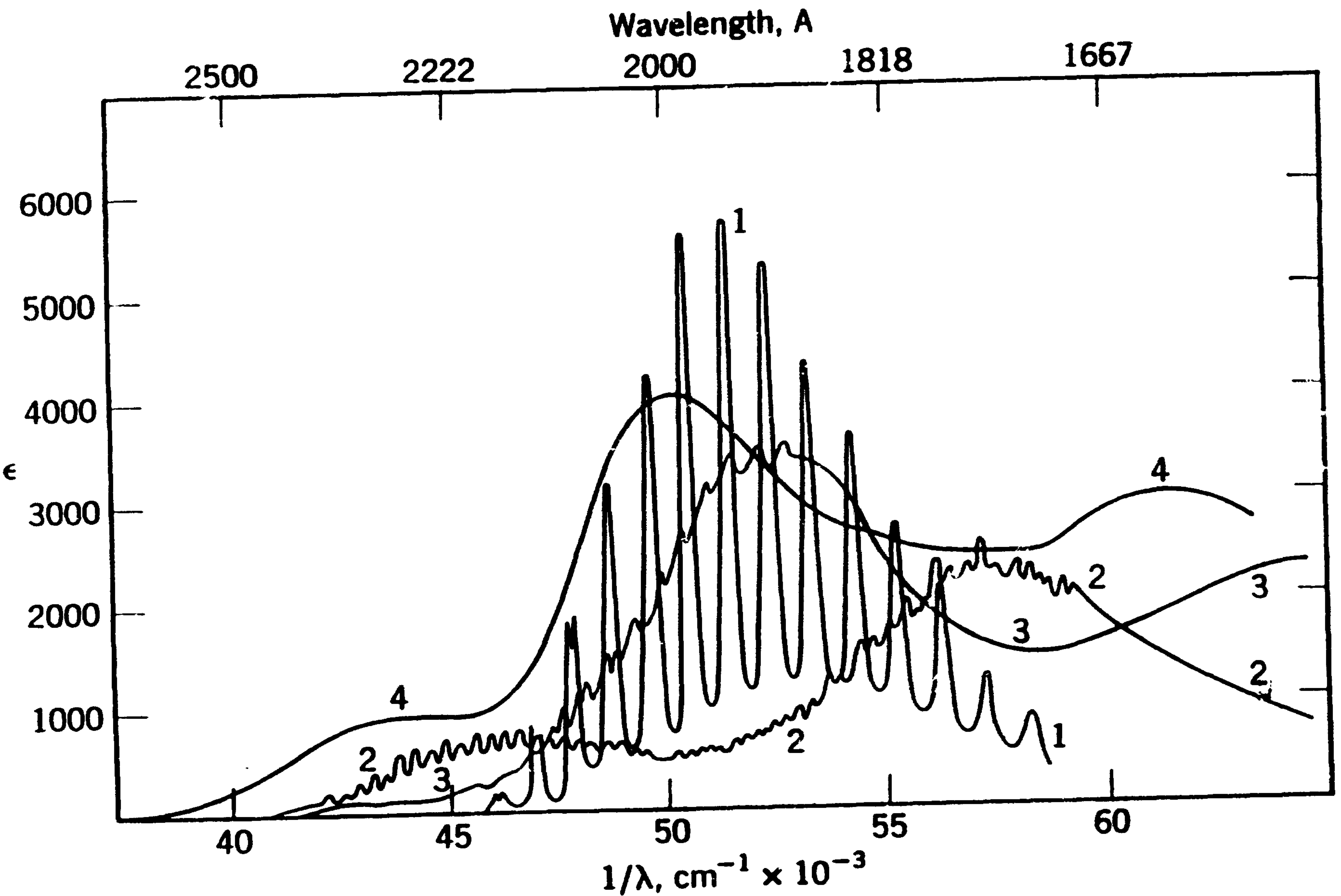


Fig. C4 Absorption spectra of (1) ammonia [$NH_3(g)$]; (2) methylamine [$CH_3NH_2(g)$]; (3) dimethylamine [$(CH_3)_2NH(g)$]; (4) trimethylamine [$(CH_3)_3N(g)$]. From Tannenbaum, Coffin, and Harrison.[427]

From Calvert and Pitts, PHOTOCHEMISTRY

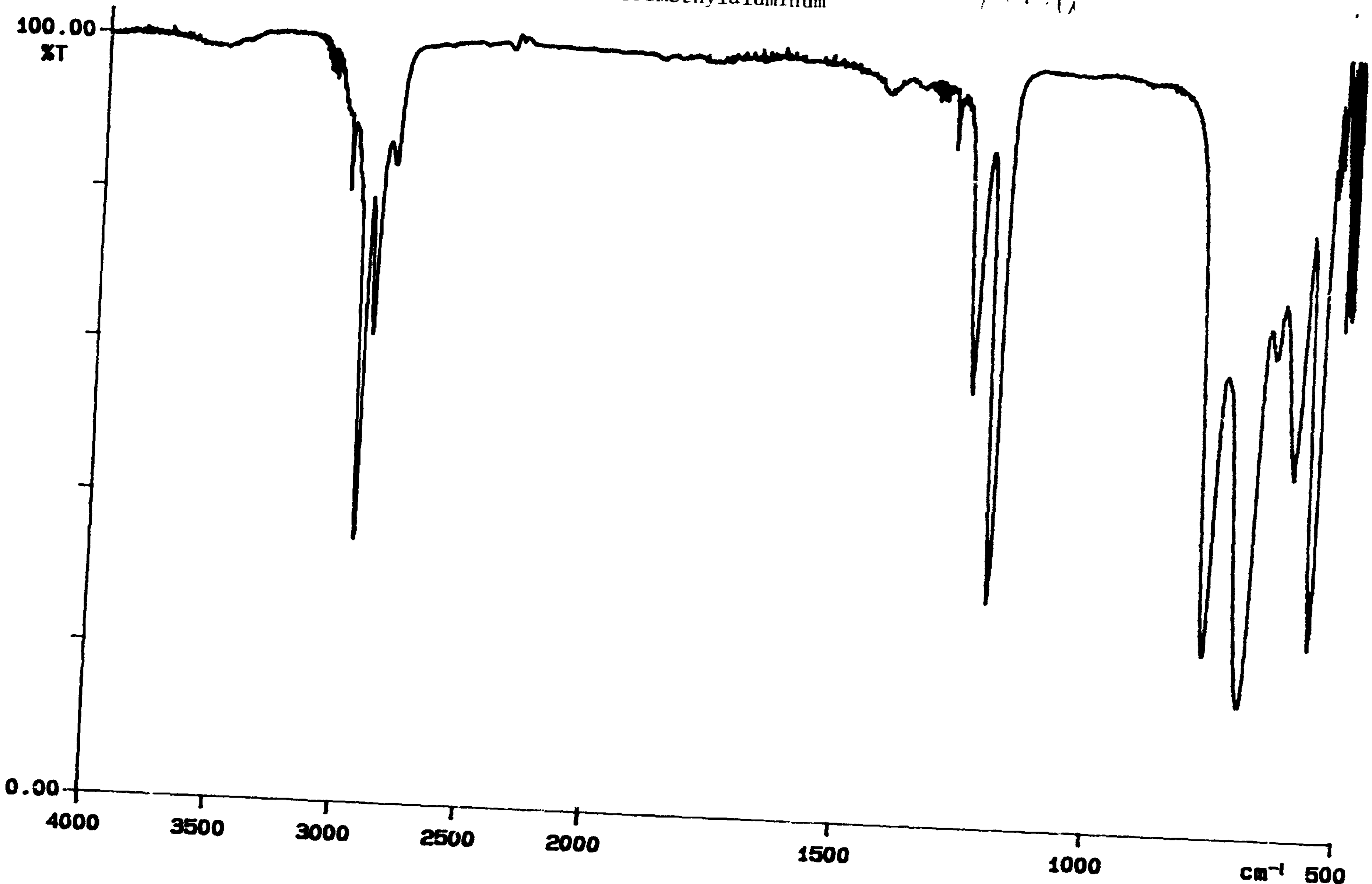


FIGURE C5: IR absorption of trimethylaluminum

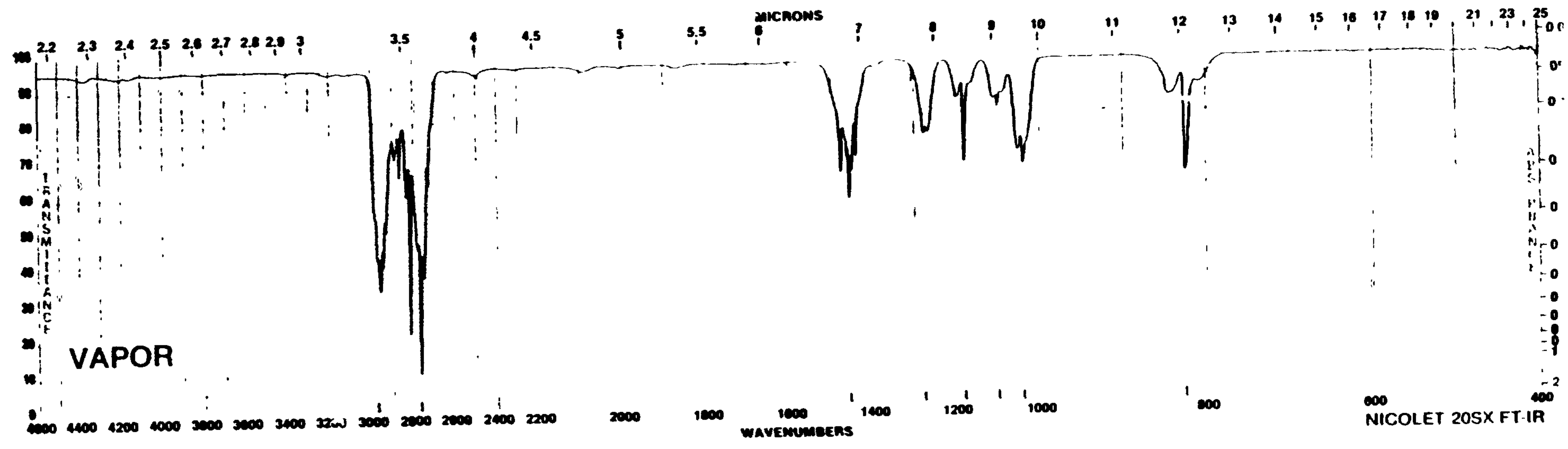
24320-5 *CAS [75-50-3]*
Trimethylamine, anhydrous, 99%

FW 59.11
mp -117°C
d 0.636

Fp 20°F

NMR II, 1,257B
Merck 10,9517

2979.6	1279.7	1043 2
2774 5	1184.1	826.5
1458 9	1103.0	



13206-3 *CAS [121-44-8]*
Triethylamine, 99%

FW 101.19
mp -7°C
bp 88.8°C

d 0.726
Fp 20°F
n_D^{20} 1.4000

IR III, 175G
NMR II, 1,258B
Merck 10,9477

2970.4	1382.2	1137 1
2754.1	1293.0	1070 9
1467.6	1204 7	736.4

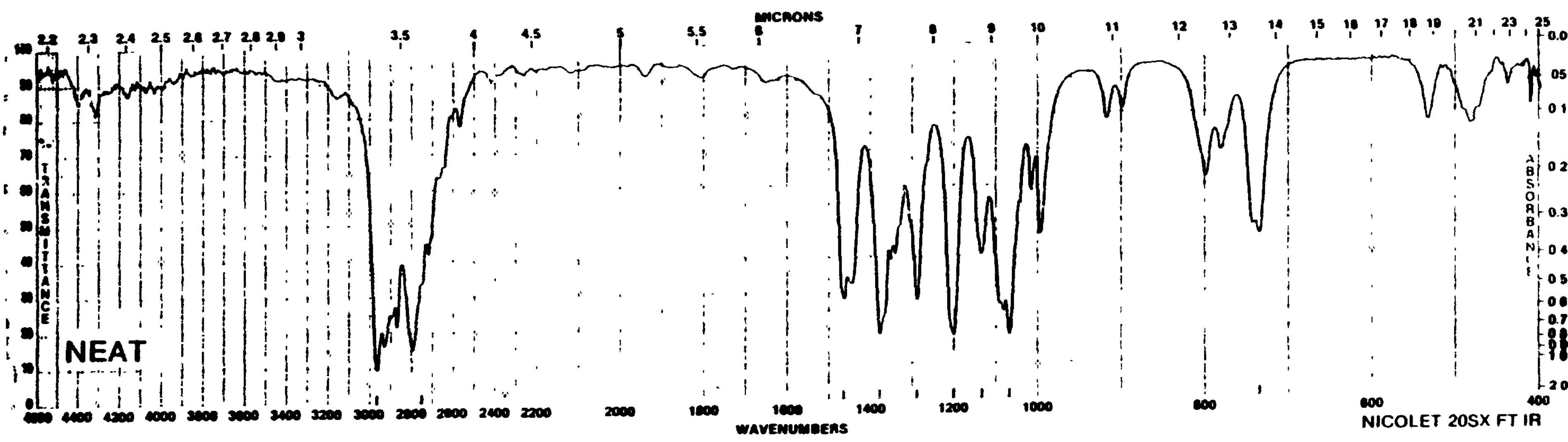


FIGURE C6: IR absorption spectra of amines

Figure C7 shows the IR absorption spectrum of the trimethylaluminum-alane adduct. Figure C8 is a series of UV absorption spectra of this adduct at various temperatures between 20 and 210 ^{o}C. The latter temperature is typical of those used for OMCVD experiments done with these adducts. Note that the absorption at 248 nm (KrF) and 266 nm (quadrupled Nd-YAG) increase several fold at 210 ^{o}C as opposed to those at room temperature.

FIGURE C7: IR absorption spectrum of TMA1-Allane

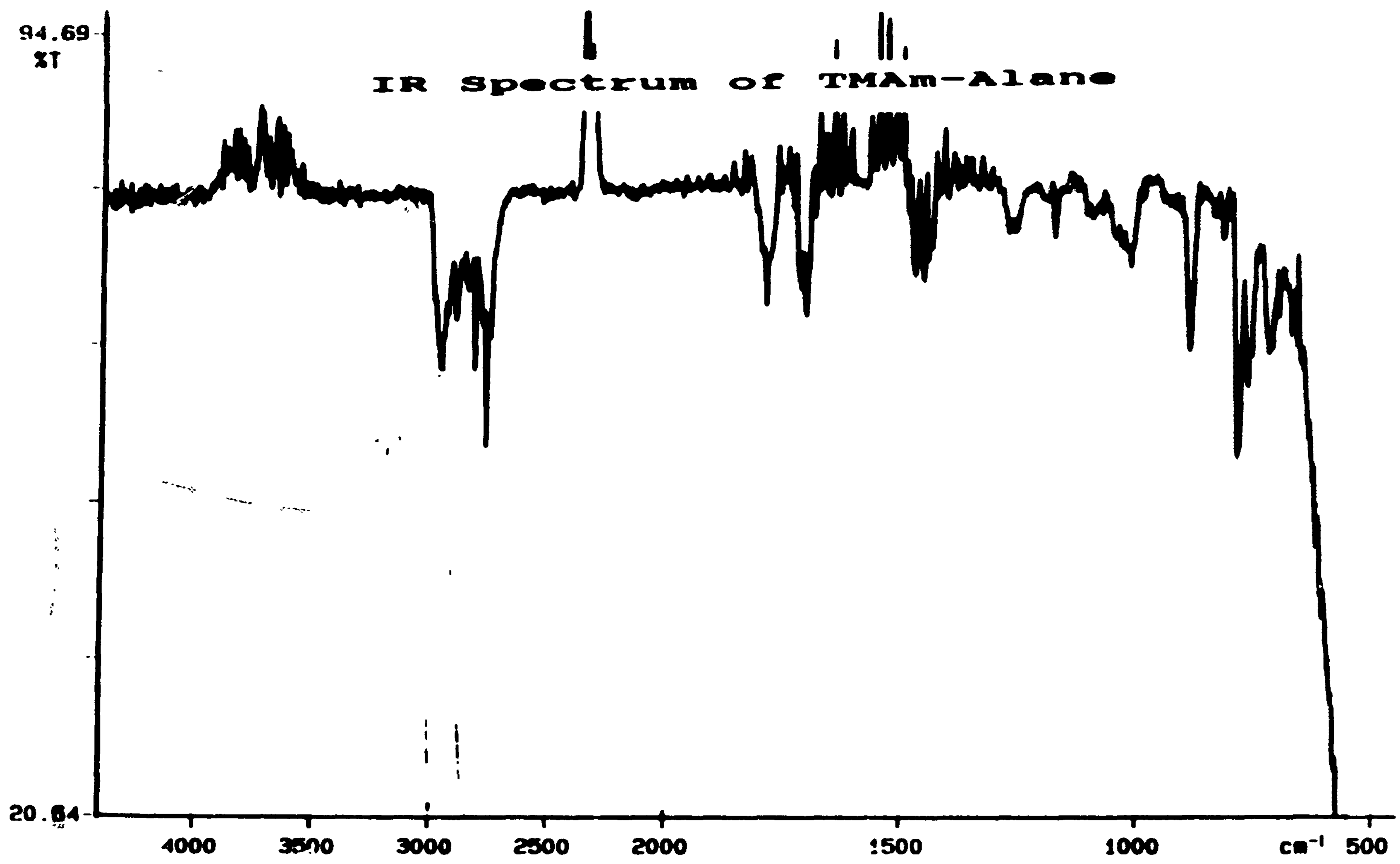
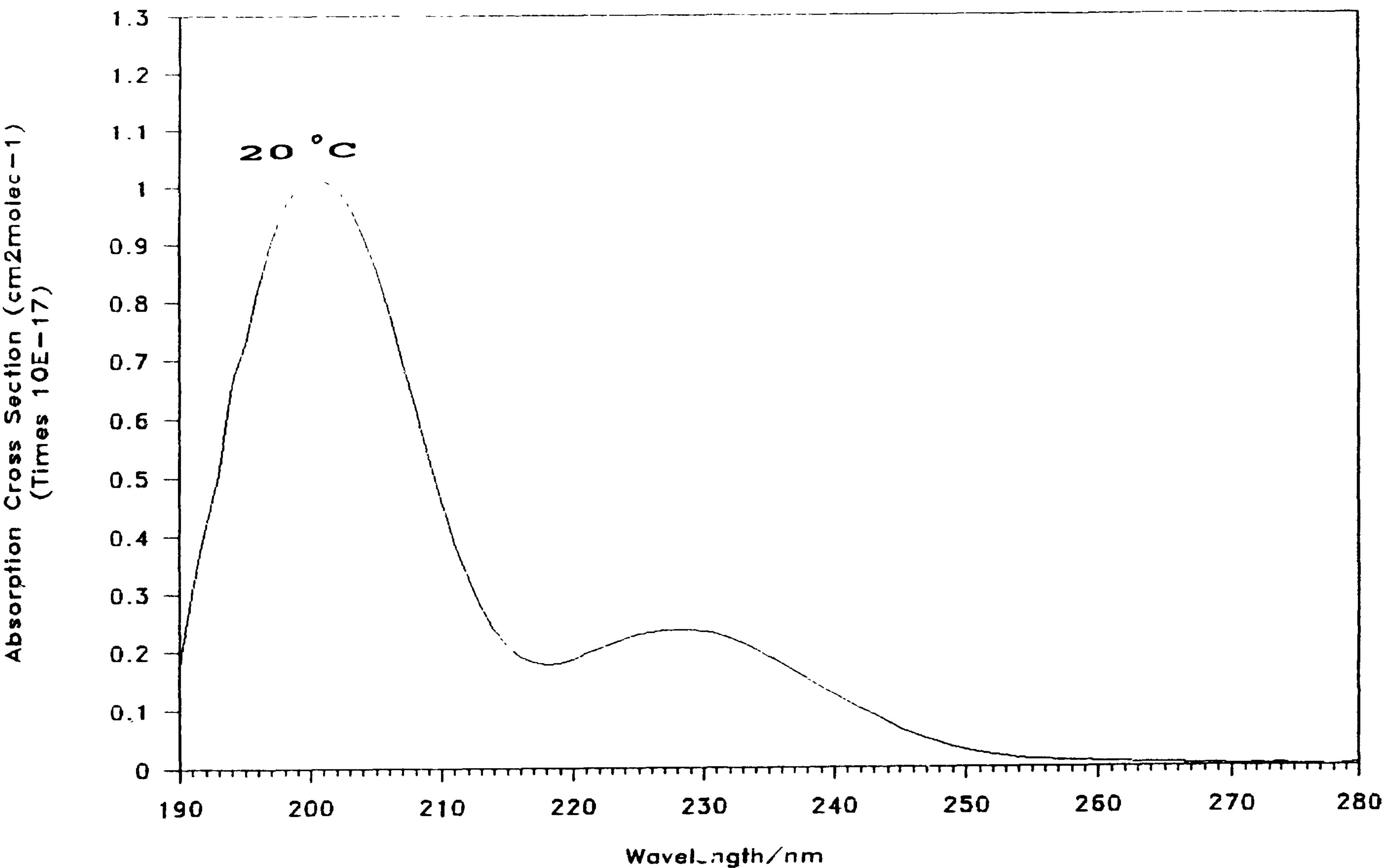
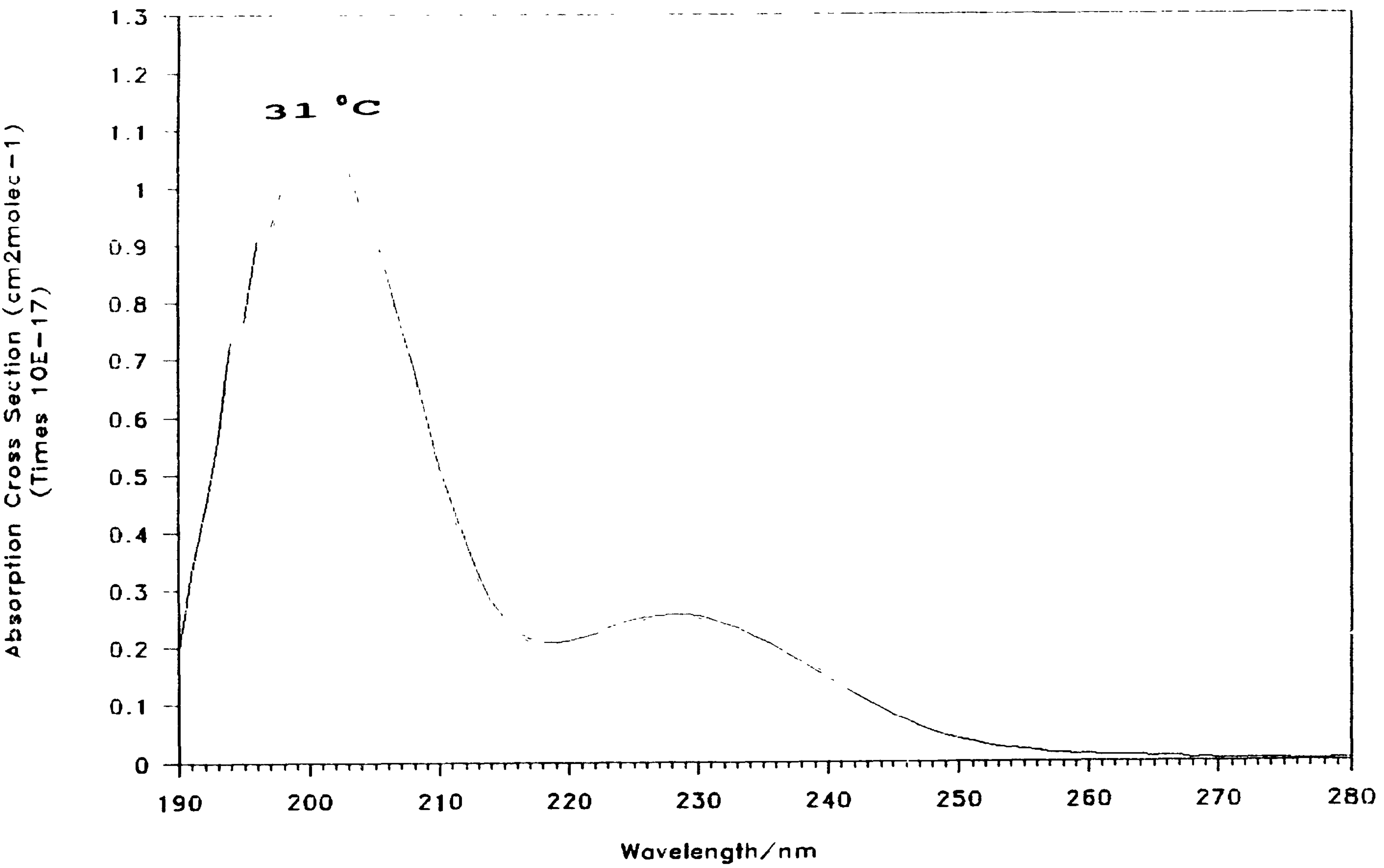
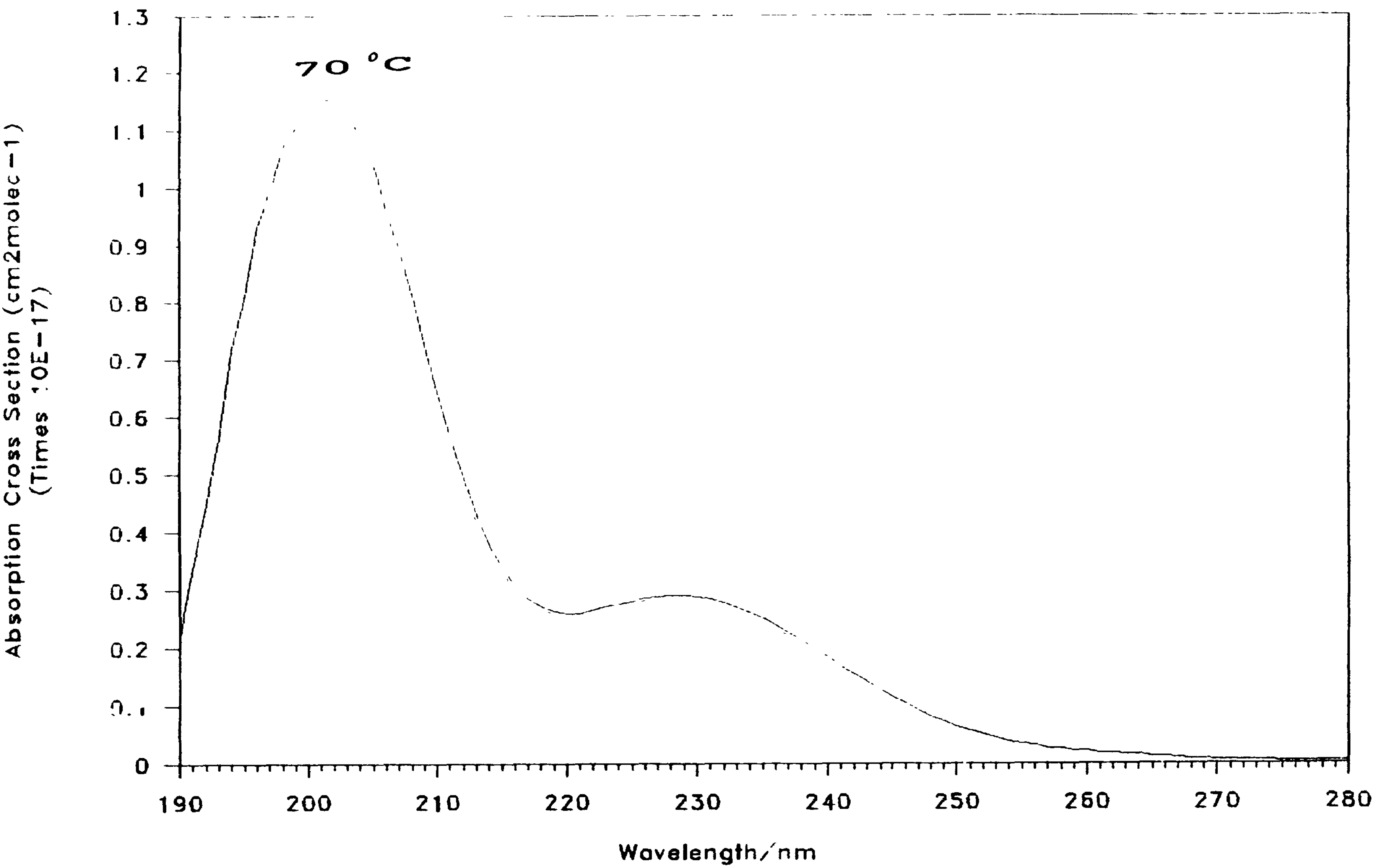
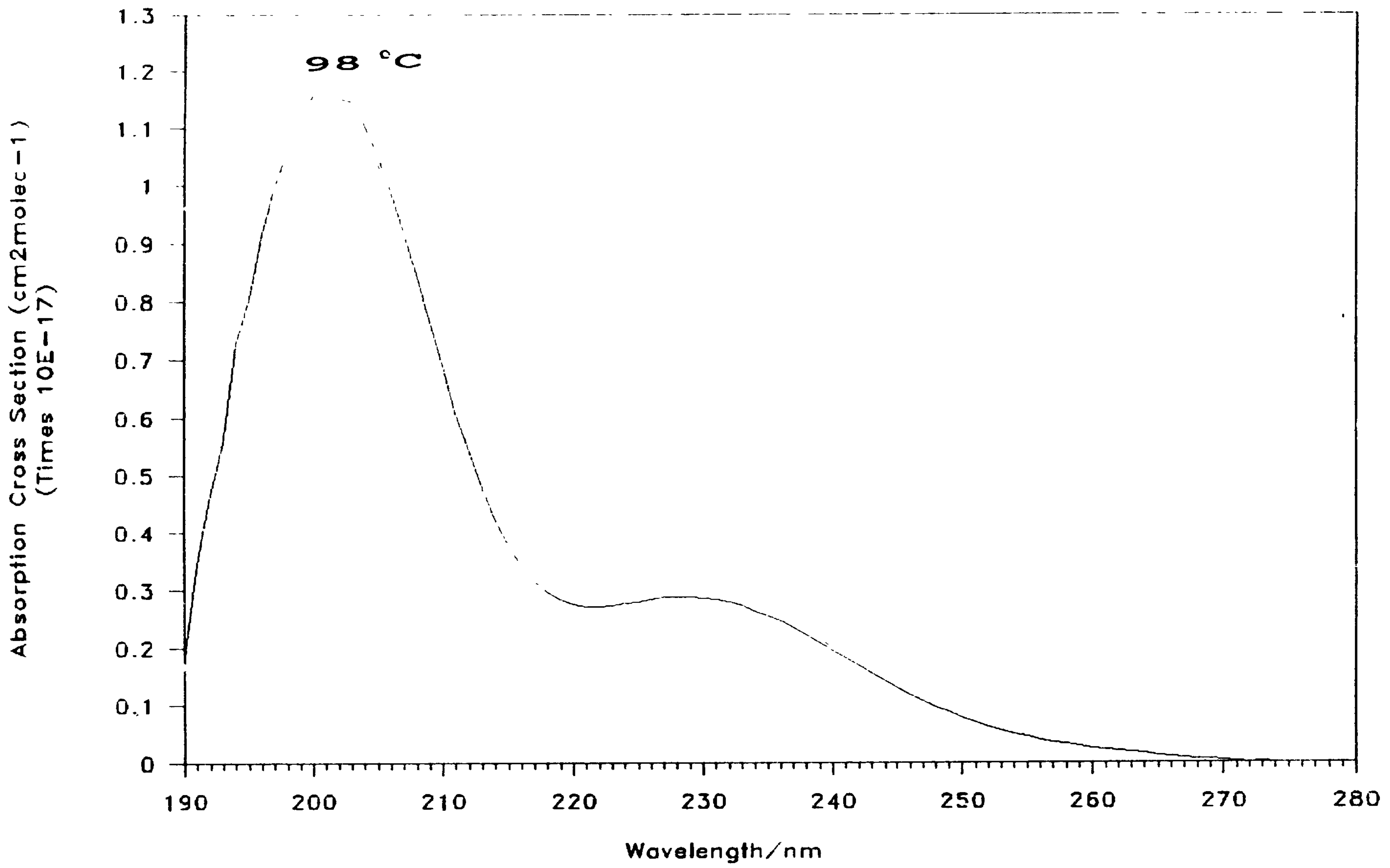


FIGURE C8




31 °C
Absorption Cross Section (cm2molec-1)
(Times 10E-17)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190
200
210
220
230
240
250
260
270
280
Wavelength/nm


70 °C
Absorption Cross Section (cm2molec-1)
(Times 10E-17)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
190
200
210
220
230
240
250
260
270
280
Wavelength/nm


98 °C
Absorption Cross Section (cm2molec−1)
(Times 10E−17)
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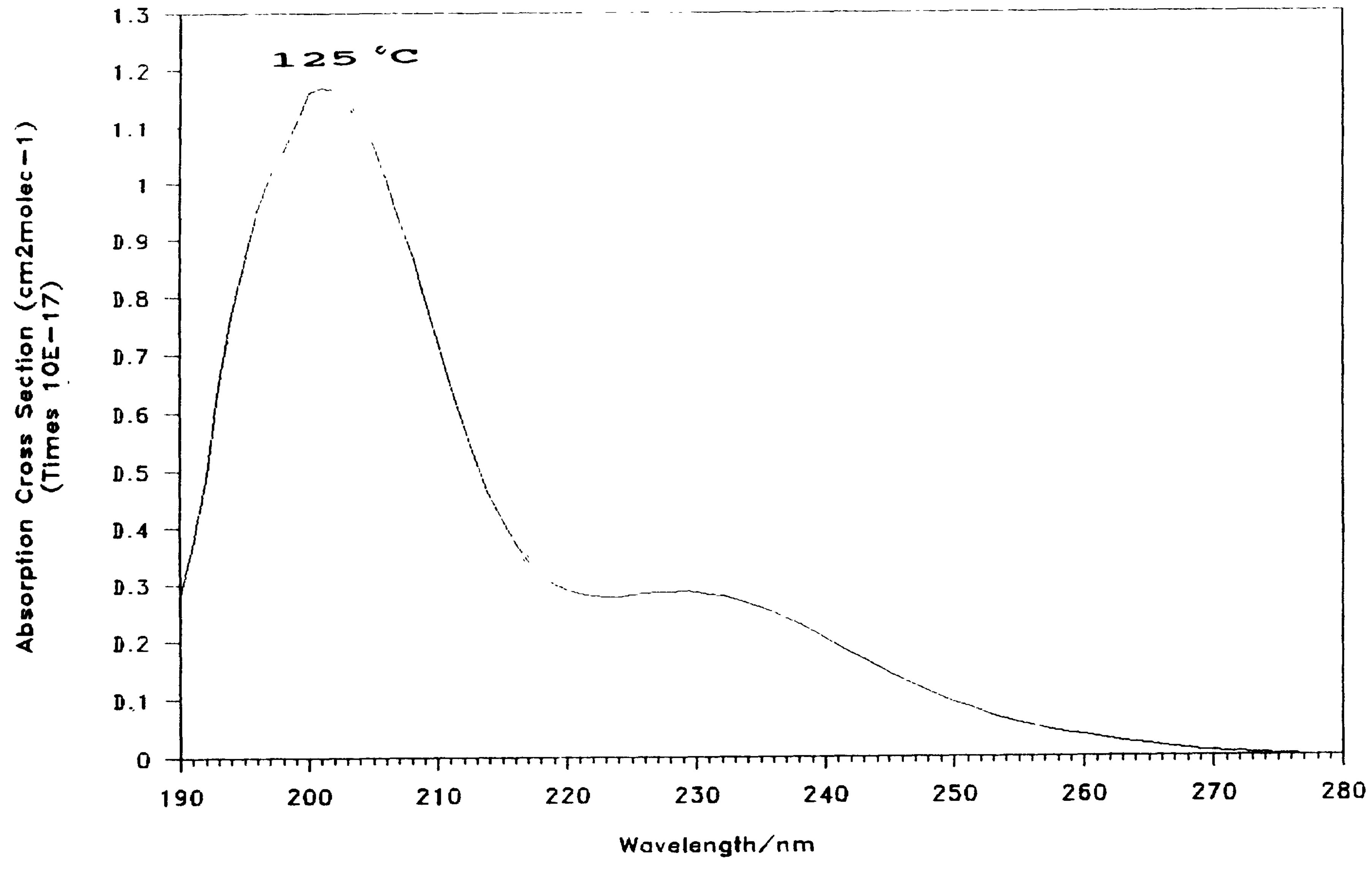
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190
200
210
220
230
240
250
260
270
280
Wavelength/nm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Absorption Cross Section (cm2molec-1)
(Times 10E-17)
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1.1
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0.8
0.7
0.6
0.5
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0
190
200
210
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230
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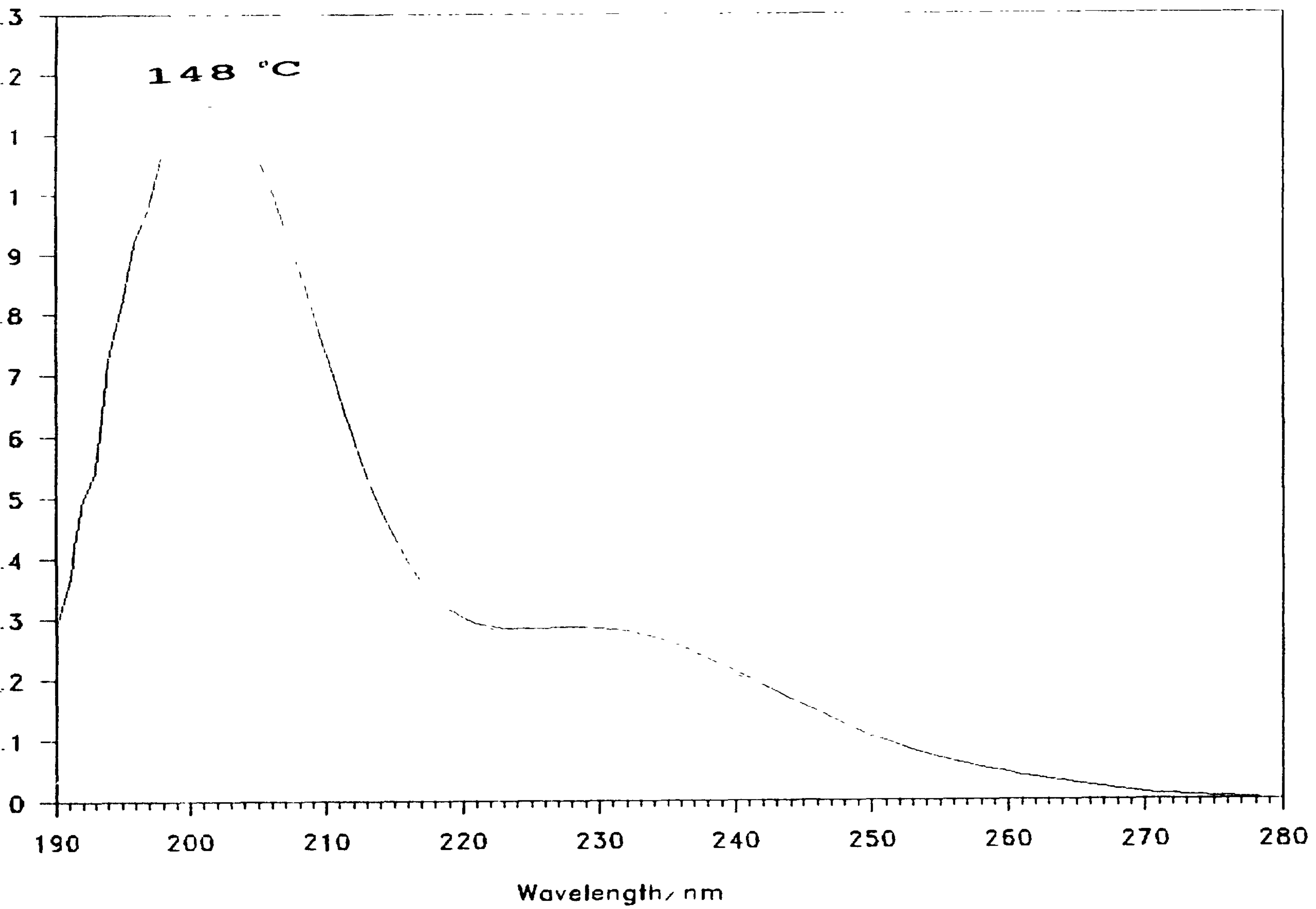
250
260
270
280
Wavelength/nm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Wavelength, nm
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200
210
220
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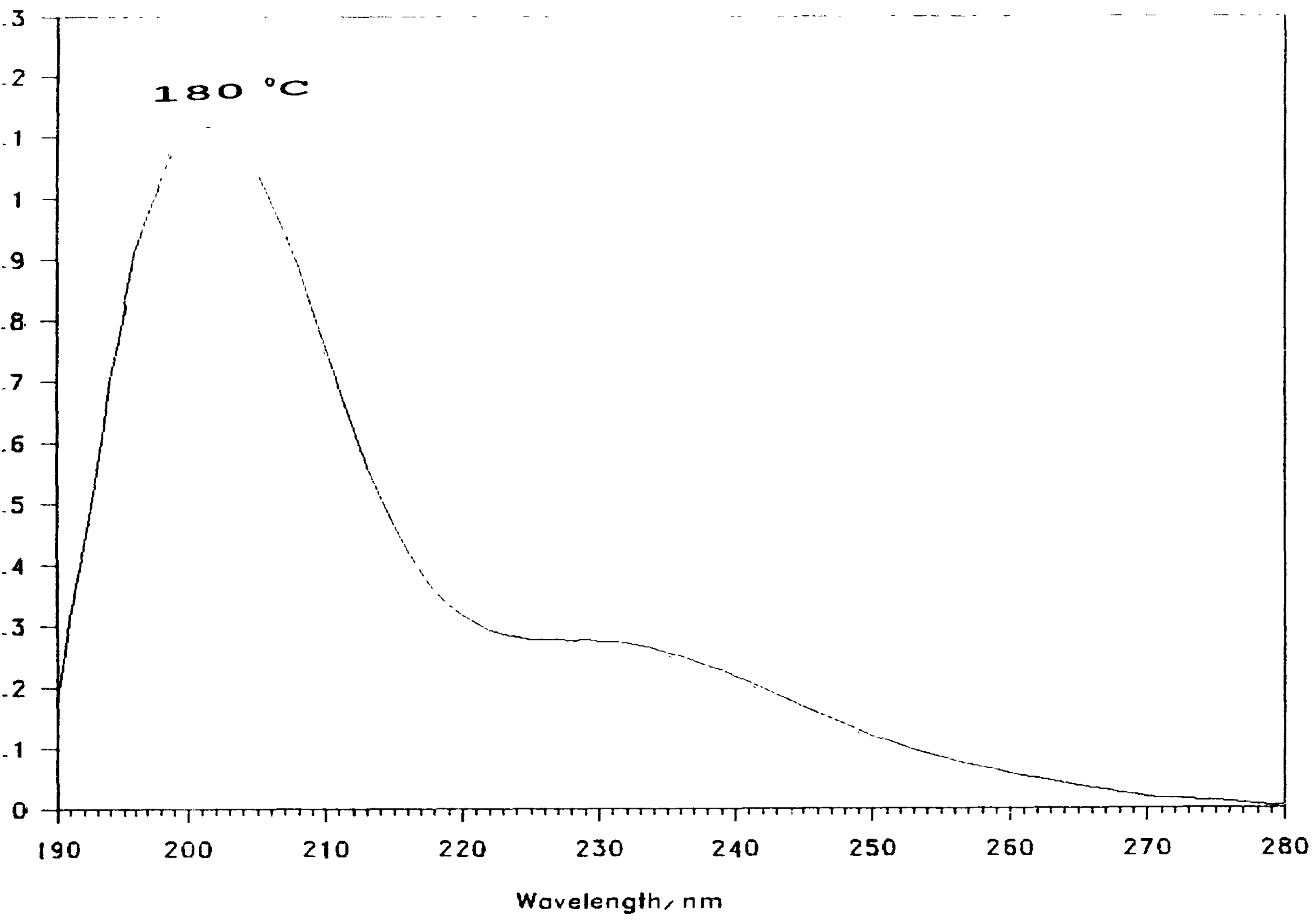
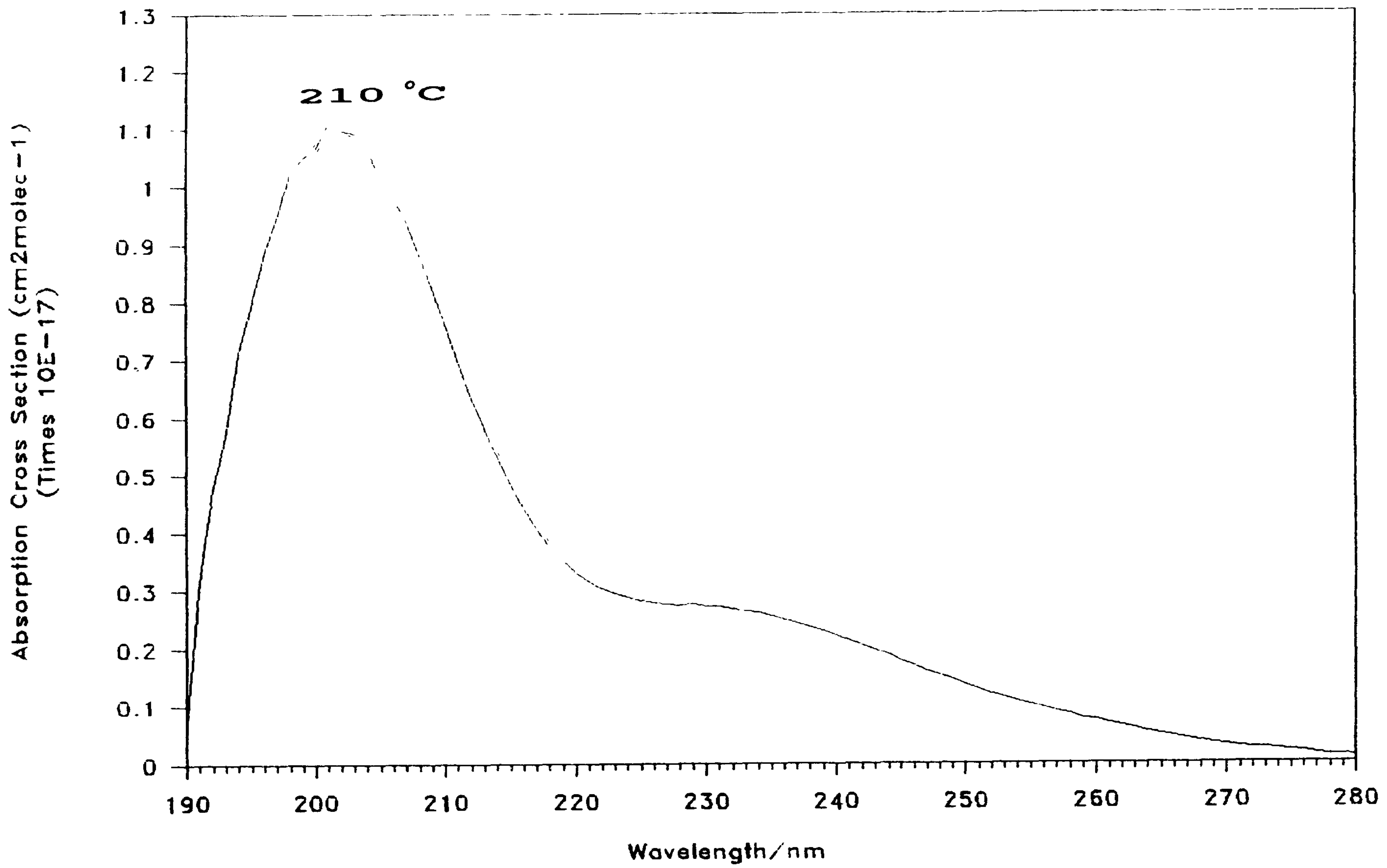
240
250
260
270
280


180 °C
.3
.2
.1
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
190
200
210
220
230
240
250
260
270
280
Wavelength, nm
Absorption Cross Section (cm2molec−1)
(Times 10E−17)


210 °C
Absorption Cross Section (cm2molec−1)
(Times 10E−17)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
190
200
210
220
230
240
250
260
270
280
Wavelength/nm

REFERENCES

1. E.I. Meletis and S. Yan. J. Vac. Sci. Technol. **A9**, 2279 (1991).

2. K. Kubata, Y. Kabayashi and K. Fujimoto. J. Appl. Phys. **66**, 2984 (1989).

3. Y. Kurihara, et al. IEEE Trans. on Comp., Hybrids and Manufac. Tech., **14**, 204 (1991).

4. X. Li and T.L. Tansley. J. Appl. Phys., **68**, 5369 (1990).

5. H. Mitsugu. Seramikkusu, **25**, 950 (1990).

6. G.S. Higashi. Appl Sur. Sci., **43**, 6 (1989).

7. G.S. Higashi. Chemtronics, **4**, 123 (1989).

8. T. Watari. Nikkan Kogyo Shimbun, 10/12/90, p.5.

9. A.C. Jones, J.S. Roberts, P.E. Oliver and B. Cockayne, Chemtronics 3, 152 (1988).

10. J.S. Roberts, et al. J. Cryst. Growth, 104, 857 (1990).

11. W.L. Gladfelter, D.C. Boyd and K.F. Jensen. Chem. of Mat. 1, 339 (1989).

3. Written publications

* Laser Induced Vapor Deposition from Trimethlaluminum and its efficiency of deposition depending on dimer-monomer equilibrium

Authors: Dr. Kanekazu Seki
Dr. Joan M. Frye
Dr. Hideo Okabe
Dr. Joshua B. Halpern

Paper to be submitted to **The Journal of Applied Physics.**

* Photo ablation of AlN powders for AlN film growth

Authors: Dr. Kanekazu Seki
Dr. Joshua B. Halpern
Dr. Joan M. Frye

Paper in preparation for submission to **Applied Physics Letter.**

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5. NONE

6. New discoveries, inventions

1. Photoablative growth of Ablative growth of AlN filds from AlN powders.

2. Improved efficiency of LICVD processes from truthful aluminum by thermal manipulations of the monomer dimer equilibrium a 248 nm (KrF) in radiation

See text for details.