AD-A158 359 INTERACTION OF UV-LASER RADIATION WITH MOLECULAR 1/1
SURFACE FILMS(U) COLUMBIA UNIV NEW YORK DEPT OF
ELECTRICAL ENGINEERING R M OSGOOD 01 JUL 85 CMSL-1
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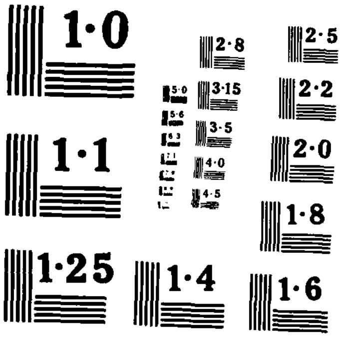

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MICROCOPY RESOLUTION TEST CHART

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The surface chemistry of Laser Photodeposition has been explored. The findings include the photodissociation physics of organometallics on surfaces and in the gas phase, and the first observation of surface enhanced chemistry.

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   Julian Chen, Graduate Student in Physics, M.S. in Physics. During this period Dr. Julian Chen received his Ph.D. in Physics with a thesis entitled "Physics of Photochemical Metallization." Note that most of the publications in this contract result from Dr. Chen's research.

   Heinz H. Gilgen, Associate Research Scientist, Postdoctoral (Optical Physics)

   R. M. Osgood, Professor of Electrical Engineering and Applied Physics

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Introduction

The general objective of this research project is to obtain a clear picture of the basic physics of laser-surface chemical interactions. In pursuit of this general objective, we examined the following specific tasks:

a) Demonstrate and understand laser-enhanced surface using both random and collective arrays of metal particles. The reaction will be by ultraviolet photodecomposition.

b) Measure and analyze the spectra of methylalkyls and ethylalkyls. Develop an understanding of the shift of the spectra when these molecules are absorbed on passive substrates.

c) Experimentally determine the mechanism for the ultraviolet-enhanced etching of semiconductors submerged in aqueous solution.

Application

There are two general applications of the research described here 1) laser-direct-writing of integrated semiconductor electronics and 2) development of heterogeneous catalysts for large-scale photochemical reations. Applications of laser direct writing are also being pursued at the Microelectronics Sciences Laboratories at Columbia under separate funding. In addition, extensive interchange regarding the work done on this contract is being done on almost a weekly basis with major industries in the New York area including IBM, Bell Telephone Laboratories, and Allied Corporation. In particular, the work on laser-direct writing is currently being pursued for applications in electrooptical devices, electronic packaging, and circuit repair at both Bell Laboratories and IBM. In addition, the work in this project on the basic photophysics of adsorbed metal alkyls has initiated a research project at Bell Laboratories on understanding these surface-bound layers for laser desorption and for standard CVD applications.

Laser Enhanced Surface Chemistry

A major accomplishment has been the first observation of laser-enhanced surface chemistry. In the experiments, described in more detail below, we have observed that submicrometer metal spheres can be used to enhance the surface photochemical decomposition rate of adsorbed molecules. In addition, by arranging such metal features in an organized pattern on the surface, we have shown that it is possible to further enhance the surface reaction rate. This technique may prove useful for producing catalytic surfaces for photochemical reactions and for making materials with novel optical properties.

A) Enhanced Surface Chemistry on Isolated Metal Particles.

The first phenomenon observed was the direct observation of an enhanced, photochemical-reaction rate at the surface of small metal features on a substrate. The experimental observations were motivated in part by the recent studies of enhanced Raman scattering on rough metal surfaces (SERS). The studies have shown that much of the enhancement results from the plasma resonance in the metal protrusions of the surface, which in turn greatly magnifies the local optical electric field. This explanation suggests that a similar enhancement should exist for photochemical phenomena occurring on shaped metal surfaces. The possibility of such surface-enhanced photochemistry has been discussed theoretically by others, such as Nitzan & Brus at Bell Labs. However, they emphasized that the rapid relaxation occurring on a metal surface could be expected to quench long-lived, photochemically active states. In the observation described here, the photodecomposition of a metal alkyl adlayer and its resultant metal deposit was used to show that enhanced photochemical reactions can occur in the vicinity of metal spheroids.

According to the above discussion, two conditions have to be fulfilled.

1. The reaction chosen must involve a short-lived dissociative state; that is, the chemical reaction should occur in $\sim 10^{-14}$ s.
2. The frequency of the incident light should be near a plasma resonance of the metal structure.

The resonant frequency of a metal ellipsoid depends sensitively on the dielectric constants of the metal and the shape of the metal feature. Near plasma resonance, the electric-field intensity on and near the cadmium spheres will be considerably greater than that of the incident field; consequently, the rate of photochemical reactions on and near the spheres should be correspondingly greater.

This effect was observed directly in an experiment in which a thin adlayer of DMCd was photodissociated on previously grown, small cadmium spheres of diameter 10-30 nm. Subsequent transmission-electronmicroscope photographs of the photodeposited cadmium near the cadmium spheres revealed that the small spheres grew into prolate spheroids of dimension ~ 0.1 μm, with the major axis oriented parallel to the electric field of the incident light. This growth pattern is consistent with an enhanced electric field in the vicinity of the metal spheres.

B) Coherent Surface-Enhanced Chemistry

As a result of our studies of laser-enhanced surface chemistry on isolated particles, we were led to consider enhancing of heterogeneous laser chemistry by using ordered arrays of metal features. Such an array can cause the laser electric field near the surface to be magnified due to coherent or "phased" scattering of the optical waves. Our first experiment to observe this phenomena was performed using submicrometer metal gratings which we fabricated by photodeposition as part of a separate DARPA/AFOSR program. As a result of the coherent ordering of metal strips, which are present in a grating structure, we anticipated seeing an angularly dependent rate of photodeposition on the metal grating. In fact, this variation was seen with a factor of 8 variation between the maximum and minimum growth rate (Fig.1). These results have immediate bearing on the fabrication of metal gratings using photodepositon. The results also show that ordered microfeatures on a solid surface may provide a powerful catalyst for heterogeneous photochemical reations.

In addition, we have developed a rigorous electromagnetic model for the surface-enhanced growth of submicrometer metal gratings. In the theory, we have modeled the grating maxima with a strip of small spherical conductors. We have then used Maxwell's equations, together with the appropriate boundary conditions to determine the total electromagnetic field at the surface of each metal strip. This expression has a maxima for grating spacings equal to an even number of half-wavelengths of the UV light in the substrate dielectric medium. The resonance spacing is broadened mainly due to nonuniformities in the microfabricated structure and the adsorption of the UV light in the metal and adsorbed molecular layers. The details of this theory were described in part in an article published in Optics Letters.

Gas and Surface Spectra of Metal Alkyls

A. Gas Phase Spectoscopy

The first set of molecules which were examined were dimethyl-metal alkyls. These molecules have been the "test bed" chemicals for laser direct writing; they are also commonly used for doping of compound semiconductors such as GaAs, and growing materials such as CdS. The experimental data collected provides the first detailed UV spectroscopy of these molecules and will, therefore, be helpful in developing light-aided growth and deposition of metals and possibly even compound semiconductors such as HgCdTe. The theory which has been developed for the absorption process, provides the first analytic, usable theory for predicting the shape and structure of the structured continuum seen in weakly bound molecules.

The electronic ground states of these three organometallics are well understood as a result of Raman and infrared studies. A careful analysis showed clearly that all of these organometallics have a quasilinear structure with the methyl groups undergoing free rotation.

There is only very limited knowledge of the excited electronic states of metal alkyls. The only previous measurements of the UV absorption spectra of dimethylzinc, dimethylcadmium, and dimethylmercury were two photographic studies reported in the 1930's by Thompson and Linnett, and Terenin and Prileshajewa. In the case of dimethylmercury, a structured continuum was observed, for dimethylcadmium and dimethylzinc, no structure was reported. Because of the paucity of experimental data, no theoretical analysis of the excited electronic states of these molecules has been made.

In this project, we have reported a new series of measurements of the UV absorption spectra of dimethylzinc, dimethylcadmium, and dimethylmercury. The spectra were measured from 30,000 to 57,000 cm^{-1} for various gas temperatures and pressures. For each of the above organometallics, we have observed structured continua with clear and regular progressions of vibrational peaks.

The overall features of the absorption spectra of these three molecules between 36,000 and 57,000 cm^{-1} are shown in Fig.2. Each spectrum consists of a relatively weak continuum at the long wavelength side and, at short wavelengths, a stong, structured continuum with clear vibrational structure, Fig.3. The spacing of the vibrational peaks is a factor of about 20 larger than the instrument resolution.

These spectra have enabled us to develop a model which clarifies the photodissociation process of these organometallics in their lower-two-excited electronic states. In this model, the vibrational peaks result from direct but asymmetric photodissociation, an effect previously discussed Pack for symmetric triatomic molecules. The vibrational structure on the continuum provides insight into the dynamics of the unstable excited states. Using an analytic version of the Pack theory, which we have recently developed, we have made a quantitative comparison of the calculated envelope with the observed spectra. Identification of the excited electronic states from the observed spectra shows that the electronic structure of these dimethylated metal alkyls is similar to the calculated electronic structure of the metal dihydrides with four valence electrons. These dihydrides, which are the simplest species of polyatomic molecules, have been frequently discussed in theoretical papers, but have not been observed in the gas phase.

In addition, we have measured and analyzed the spectra of the trimethyl- and dimethylmetalalkyls. These materials are used both for direct laser writing and in many areas of conventional and advanced metallorganic materials growth. For example, diethylzinc is used as a common dopant molecule in VPE; and trimethylindium is a major chemical reactant in MOCVD. The UV spectra of these molecules is important, therefore, for both the diagnostics of the conventional growth of semiconductor materials and for photon-assisted processing. Our measurements have shown that additional of progressively more complex ligands to the metallorganic molecules shifts the molecular continuum spectra into closer coincidence with existing medium-UV laser sources. In addition, the spectra of the molecules becomes generally less structured as the number and complexity of ligands increases. We recently presented a paper describing our results at the American Chemical Society Meeting in Philadelphia.

B. Surface Spectoscopy

A major result of the research was the first measurement of the spectra of the weakly bound or physisorbed molecule layers of metal alkyls on solid substrates.

Physisorbed molecular layers constitute an ubiquitous phase on chemically passive surfaces immersed in a relatively dense gas atmosphere. Because the surface binding energy of these molecules is small, typically $\sim$0.01-0.1eV, at room temperature, a gas ambient is necessary to maintain the dynamic equilibrium between evaporation and condensation for these liquid-like physisorbed films. The spectroscopy of the adsorbed layers, measured as a function of coverage, can provide insight into the transition of a two-dimensional molecular layer to a near-liquid state. However, spectral studies using photon or charged particle probes are hindered by the interference from the ambient gas. As a result, several techniques have been devised to obtain the spectra of only the physisorbed layers. One important approach is to use a high-surface-area substitute such as ultra-fine powder or silica gel. This technique leaves considerable uncertainty as to the structural details and cleanliness of the surface. In the ultraviolet, increased scattering from such dispersed-area surfaces requres such a high source intensity to obtain an adequate signal-to-noise ratio that unacceptable photochemcial degradation will occur. Another approach is to use either spatial or polarization modulation of the light source. In this case, a particular surface selective phenomenon, e.g. reflectivity, is used to isolate the response of the adsorbed phase.

We have now demonstrated an alternative technique which is based upon careful subtraction of the obscuring gas-phase absorption by means of an online computer. To demonstrate this technique, we have measured the spectra of dimethylcadmium, physisorbed layers on fused-silica substrates under a wide range of gas pressures, 0 $\sim$ 10 torr, and temperatures, -20°C 30°C. The spectra can be interpreted by comparison with recent measurements of the gas-phase spectrum of dimethylcadmium. These spectra are shown in Fig.4.

Knowledge of the spectra will eventually allow us to develop an accurate model of the photodeposition.

Laser-Induced Liquid Interface Reactions

Thus far, our emphasis in this research project has been on understanding gas-phase laser chemical interactions with surfaces. Recently, we have found that ultraviolet etching of GaAs can be obtained by shining a very low level of ultraviolet light on an acid-based, solution-solid interface. This technique uncertainty as to the structural details and cleanliness of the surface. In the ultraviolet, increased scattering from such dispersed-area surfaces requres such a high source intensity to obtain an adequate signal-to-noise ratio that unacceptable photochemcial degradation will occur. Another approach is to use either spatial or polarization modulation of the light source. In this case, a particular surface selective phenomenon, e.g. reflectivity, is used to isolate the response of the adsorbed phase.

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At present, we believe the rapid reaction rate occurs for ultraviolet radiation because of the creation of hot carriers via photoabsorption at the surface of the semiconductors. Recently, we have found that this hot-carrier enhancement of the reaction rate is apparently also present for Si, InP, and CdS. This observation is reinforced by the fact that the optical properties for these semiconductors in the UV are very similar.

List of Manuscript Submitted or Published
During the Total Contract Peroid
Under ARO Contract #DAAG-29-82-K-0089

C.J. Chen and R.M. Osgood, "Direct Observation of the Local-Field-Enhanced Surface Photochemical Reactions," Phys. Rev. Lett, 50, 1705 (1983)

C.J. Chen and R.M. Osgood, "Measurements of the Electronic Spectra of Physisorbed Molecular Layers," Chem. Phys. Lett, 50, 1705 (1983).

C.J. Chen and R.M. Osgood, "Surface-Catalyzed Photochemical Reactions of Physisorbed Molecular Layers," Appl. Phys. B., 31, 171 (1983)

R.M. Osgood, Jr., D.J. Ehrlich, T.F. Deutsch, D.J. Silversmith, and A. Sanchez, "Laser Microchemistry for Direct Writing of Microstructurers," SPIE, 385, 112 (1983)

H.H. Gilgen, D. Podlesnik, C.J. Chen and R.M. Osgood, Jr., "Direct Holographic Processing Using Laser Chemistry," edited by A.W. Johnson and D.J. Ehrlich, Elsevier, (North-Holland, Amsterdam, 1984). p. 70.

C.J. Chen and R.M. Osgood, "Theory of Photodissociation of Linear Symmetric Polyatomic Molecules," presented at the Annual Meeting of the American Chemical Society.

C.J. Chen and R.M. Osgood, "Photodissociation Spectra of Nine Metal-Alkyls," presented at the Annual Meeting of the American Chemical Society.

C.J. Chen, H.H. Gilgen, and R.M. Osgood, "Resonant, Optical Growth of Submicrometer Metal-Gratings," Optics Letters., 10, 173 (1985)

H.H. Gilgen, C.J. Chen, R.R. Krchnavek, R.M. Osgood, Jr., "The Physics of Ultraviolet Photodeposition," presented at the Laser Processing and Diagnostics Applications in Electronic Materials, Linz, D. Bauerle, ed, (Springer, Berlin, 1984)

R.M. Osgood, Jr., H.H. Gilgen, and Peter Brewer, "Low-temperature Deposition and Removal of Material Using Laser-Induced Chemistry," Summary Abstract, J. Vac. Science Technol. A (2), April-June 1984.

C.J. Chen and R.M. Osgood, "A Spectroscopic Study of The Excited States of Dimethylzinc, Dimethycadmium, and Dimethylmercury," J. Chem. Phys., 81, 327, July 1, 1984.

C.J. Chen and R.M. Osgood, "An Analytic Theory of Photodissociation of Linear Symmetric Polyatomic Molecules," J. Chem. Phys., 81, 318, July 1, 1984.

List of Manuscripts Submitted or Published (continued)

C.J. Chen and R.M. Osgood, "Ultraviolet Absorption Spectra of Trimethylaluminium, Trimethylgallium, and Trimethylindium," In preparation.

R.M. Osgood and T.F. Deutsch, "Laser-Induced Chemistry for Microelectronics," Science, Vol.277, pp. 709-714, 1985.

R.M. Osgood and H.H. Gilgen, "Laser Direct Writing of Materials," Ann. Rev. Materials Sci. 1985.

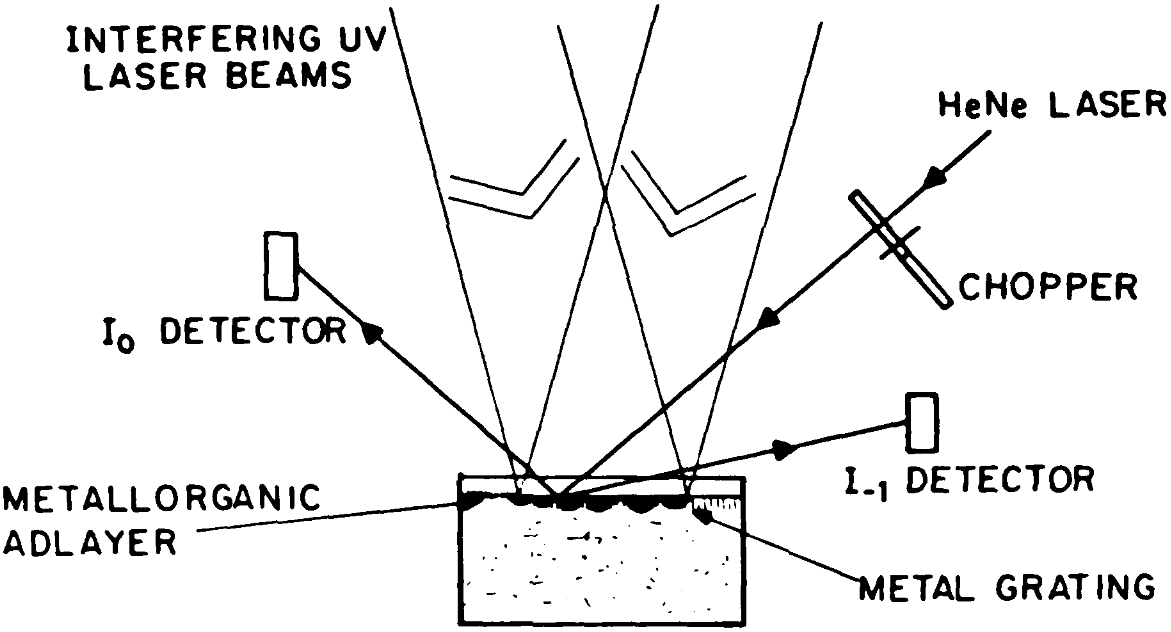
FIGURE CAPTIONS

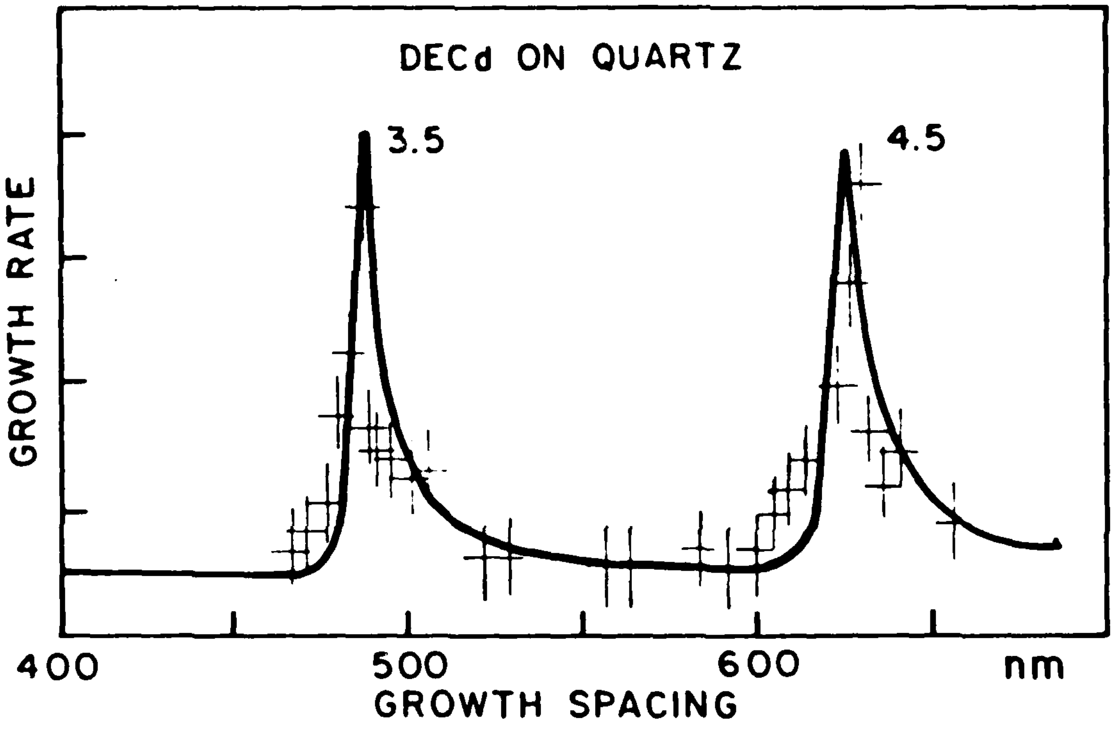
Fig.1 - Experimental setup for observing surface-enhanced growth (top), growth rate of metal grating versus grating spacing.

Fig.2 - The UV absorption spectra of dimethylzinc, dimethylcadmium, and dimethylmercury.

Fig.3 - The $\chi'\Sigma_g \rightarrow B'\,\Pi_u$ transition of dimethylmercury, showing the double series of vibrational progressions.

SURFACE-CATALYZED PHOTOGROWTH OF SUBMICROMETER STRUCTURES





GRATING GROWTH RATE IS ENHANCED AT CERTAIN GROOVE SPACINGS DUE TO "COHERENT" ELECTROMAGNETIC INTERRACTIONS FROM METAL GROOVE ARRAY

Fig. 2

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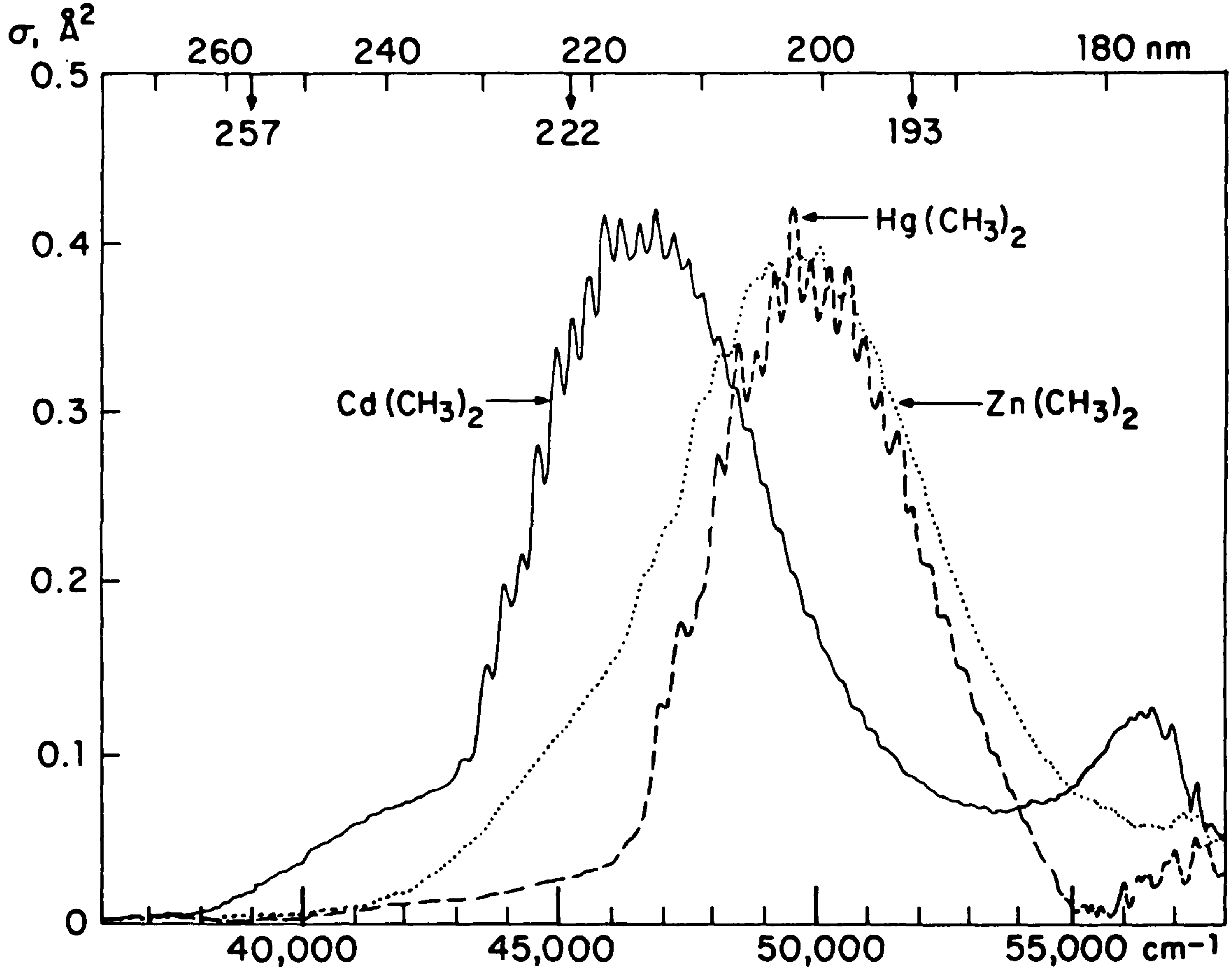
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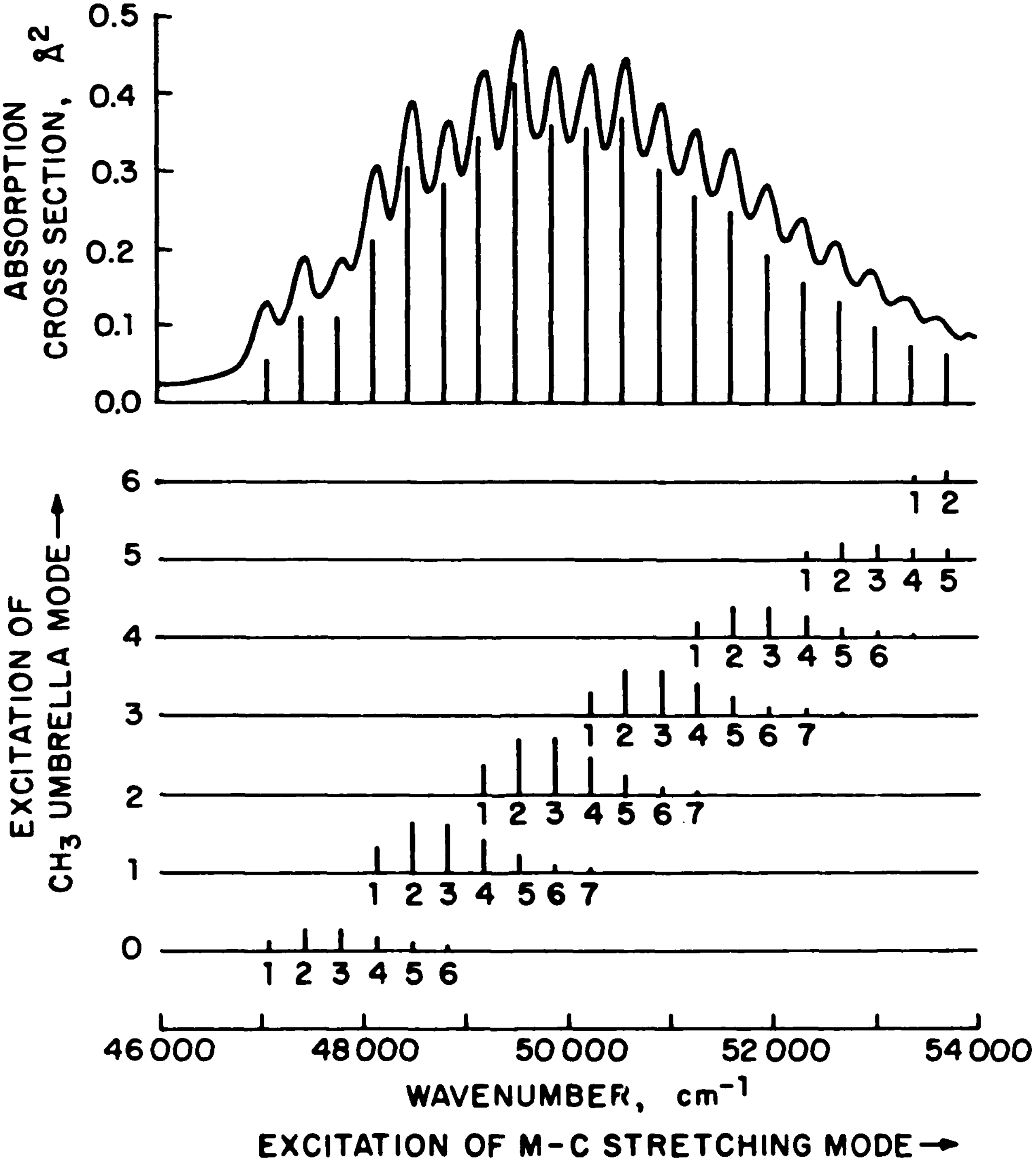
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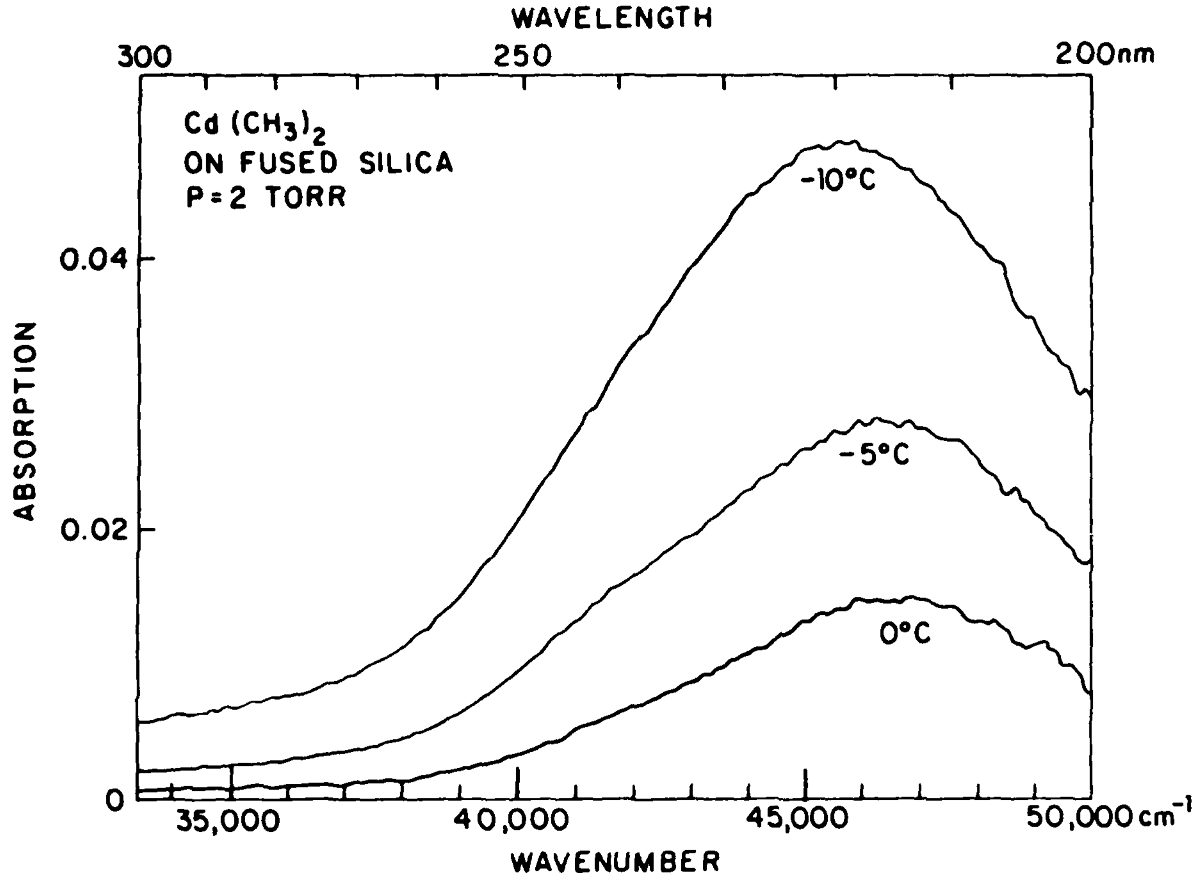
Fig 4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