

AD-A205 325

NAV FILE COPY

4

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0043

TECHNICAL REPORT No. 92

Photoabsorption of Molecules at Corrugated Thin Metal Films

by

P. T. Leung, Young Sik Kim and Thomas F. George

Prepared for Publication

in

Journal of Chemical Physics

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

February 1989

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

This document has been approved for public release and sale;
its distribution is unlimited.

DTIC
ELECTE
MAR 03 1988

X

H

82 0 03 051

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/89/TR-92		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260		7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Photoabsorption of Molecules at Corrugated Thin Metal Films			
12. PERSONAL AUTHOR(S) P. T. Leung, Young Sik Kim and Thomas F. George			
13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) February 1989	15. PAGE COUNT 25
16. SUPPLEMENTARY NOTATION Prepared for publication in the Journal of Chemical Physics			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	MOLECULAR PHOTOABSORPTION) INCIDENT PLANE WAVE) THIN METAL FILMS) MOLECULAR DIPOLE) CORRUGATED) ENHANCED SELECTIVE PHOTOCHEMISTRY	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A phenomenological study has been carried out for the photoabsorption of molecules in the vicinity of a corrugated thin metal film. In particular, perturbative results for a grating silver film have been obtained to first order in the corrugation parameter, where the effect of the incident field coupled with the long-range surface plasmon is observed. Based on the different coupling nature between the radiations from the incident plane wave and from the molecular dipole to the substrate film, it is proposed that, through control of the various parameters of the film, enhanced selective photoabsorption may be achieved.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL

Photoabsorption of molecules at corrugated thin metal films

P. T. Leung
Department of Physics
Portland State University
P. O. Box 751
Portland, Oregon 97201

Young Sik Kim* and Thomas F. George
Departments of Chemistry and Physics & Astronomy
239 Fronczak Hall
State University of New York at Buffalo
Buffalo, New York 14260

Abstract

A phenomenological study has been carried out for the photoabsorption of molecules in the vicinity of a corrugated thin metal film. In particular, perturbative results for a grating silver film have been obtained to first order in the corrugation parameter, where the effect of the incident field coupled with the long-range surface plasmon is observed. Based on the different coupling nature between the radiations from the incident plane wave and from the molecular dipole to the substate film, it is proposed that, through control of the various parameters of the film, enhanced selective photoabsorption may be achieved.

* Present address: Department of Chemistry, Princeton University
Princeton, New Jersey 08544

I. INTRODUCTION

Since the discovery of surface-enhanced Raman scattering,¹ there has been in the past ten years a large number of investigations on the possibility for enhancing other photochemical processes at rough surfaces.² In particular, processes such as photolysis and photochemical degradation have been studied in great detail, both experimentally and through theoretical models which include both the cases of localized³ and extended^{4,5} surface structures. By now, it has become clear that for a first-order process, such as photoabsorption which includes photodissociation (direct dissociation) and resonance fluorescence, the ultimate outcome for the enhancement of the process generally depends on two competing factors: the enhanced surface electromagnetic field and the surface-induced decay rates for the admolecules. Detailed reviews of this subject are available in the recent literature.^{2,6}

Still another substrate of great interest is the case of a corrugated thin metal film. Although the problem of light scattering from such a film has been intensively studied within the past few years,⁷⁻¹⁴ and to a less extent the problem of molecular decay,¹⁵⁻¹⁷ the possibility of new photochemical processes in the vicinity of such a film has not been addressed.

In this work, we present a phenomenological study of the photoabsorption of molecules located near a corrugated thin metal film. Specifically, we shall consider the photoabsorption of a two-level system (modeled as a point dipole) above a metallic (taken as Ag throughout) grating film, with an incident laser field at an angle θ and a molecular dipole assumed to be oriented normal to the film (see Fig. 1). Our formulation will be based on a generalization of our previous model for a single grating surface⁴ and an application of our recent work on the decay rates of molecules at such film systems.¹⁷ As pointed out before, the full dynamics of the problems must be

taken into account in order to treat the morphological induced effects.^{17,18} We shall see that due to the different coupling natures of the radiations from the molecular dipole and the incident plane wave with the surface plasmons of the film, there is a possibility of achieving enhanced selective photoabsorption for the admolecules.

II. ABSORPTION CROSS SECTION

The configuration of our problem is shown in Fig. 1, where the molecule of dipole moment $\vec{\mu}$ is located at $z = d$ above a thin metal (Ag) film bounded by two grating surfaces located at $z = 0$ and $z = -t$, respectively. Thus the profile functions take the forms

$$\zeta_1 = \zeta_{o1} e^{iQ_1 x}, \quad \zeta_2 = \zeta_{o2} e^{iQ_2 x}, \quad (1)$$

where we shall assume small corrugations ($\zeta_{o1} Q_1 \ll 1$) so that perturbation theory can be applied. The optical properties of the three media are described by their dielectric functions ϵ_1 , $\epsilon_2 = \epsilon'(\omega) + i\epsilon''(\omega)$ and ϵ_3 . Let us consider p-polarized laser light of the form

$$\begin{aligned} \vec{E}_{in} &= (E_{ox} \hat{e}_x + E_{oz} \hat{e}_z) e^{i(k_z^{(0)} z - \omega t)} e^{i\vec{k}_{\parallel}^{(0)} \cdot \vec{r}} \\ &= \vec{E}_o(\omega|z) e^{i\vec{k}_{\parallel}^{(0)} \cdot \vec{r}}, \end{aligned} \quad (2)$$

$$\vec{k}_{\parallel}^{(0)} = k_x^{(0)} \hat{e}_x, \quad \vec{r}_{\parallel} = (x, y), \quad (3)$$

A-1

which is incident on the system at an angle θ with respect to the normal direction. We want to calculate the absorption cross section of the molecule. For simplicity, we assume that $\vec{\mu}$ is oriented perpendicular ($\vec{\mu} = \mu \hat{e}_z$) to the film.

According to the phenomenological model,³⁻⁵ the absorption cross section for the free-molecule case (σ_o) can be obtained in Lorentzian form as

$$\sigma_o(\omega) = A |\vec{E}_{in}|^2 \sin^2 \theta \frac{\gamma_M^o}{(\omega - \omega_M^o)^2 + (\gamma_M^o/2)^2} \quad (4)$$

where A is a proportionality constant, and ω_M^o and γ_M^o denote the natural frequency and width, respectively, of the excited state of the free molecule.⁴ In the presence of the substrate film, Eq. (4) then becomes

$$\sigma(\omega) = A |E_z(d, \omega)|^2 \frac{\gamma_M}{(\omega - \omega_M)^2 + (\gamma_M/2)^2} \quad (5)$$

where $E_z(d, \omega)$ is now the total field driving the dipole, and ω_M and γ_M denote the dressed values for the frequency and width, respectively, due to the presence of the film substrate. Since these are usually dependent on the driving frequency ω , Eq. (5) is in general distorted from a Lorentzian shape.³⁻⁵ Moreover, it is known that the induced frequency shift can most of the time be neglected compared to the induced decay rate,¹⁹ and hence in the following we shall assume $\omega_M \approx \omega_M^o$ and take into account only the substrate-induced rate $\gamma(\omega)$. The remaining job then is to calculate $E_z(d, \omega)$ in Eq. (5). Following the perturbative approach of Maradudin and Mills,^{20,21} we obtain to first order of roughness

$$E_z(d, \omega) = (1 + R e^{2ik_1 d}) E_{in} \sin \theta + E_z^{(s)}(d, \omega) e^{ik_1 d}, \quad (6)$$

where R is the Fresnel reflectance for a flat film,²² $k_1 = \sqrt{\epsilon_1} \omega/c$ is the wave number in the first medium, and $E_z^{(s)}$ is the contribution from the roughness to the scattered field, whose μ -th component is given by^{20,21}

$$\begin{aligned} E_\mu^{(s)}(\vec{r}; \omega) = & - \frac{k^2}{16\pi^3} \int d^2 k_\parallel e^{i\vec{k}_\parallel \cdot \vec{r}_\parallel} \int dz' d_{\mu\nu}(\vec{k}_\parallel | \omega | zz') \{ [\epsilon_2 \Theta(z'+t) \\ & - \epsilon_1] \delta(z') \hat{\xi}_1(\vec{k}_\parallel - \vec{k}_\parallel^{(0)}) + [\epsilon_3 - \epsilon_2 \Theta(-z')] \delta(z'+t) \\ & \times [\hat{\xi}_2(\vec{k}_\parallel - \vec{k}_\parallel^{(0)}) + t] \} E_\nu^{(0)}(\vec{k}_\parallel^{(0)} | \omega | z'), \end{aligned} \quad (7)$$

where $k = \omega/c$, $d_{\mu\nu}$ and $\hat{\xi}_i$ are the Fourier transform of the "flat" propagators and profile functions, respectively, $E_\nu^{(0)}$ is the total field in the various media in the case of a flat film, and Θ is the Heaviside step function. The integrals involving the δ -functions must be carefully performed since $E_\nu^{(0)}$ is in general discontinuous across the various boundaries.

We have recently developed a method²³ of handling these integrals by applying the formalism of Agarwal,²⁴ from which we have obtained results which are a modified version of those in the original work of Maradudin and Mills²⁰ and are in agreement with those obtained from other approaches, including Mills',²⁵ subsequent modifications by applying the work of Juranek.²⁶ It is straightforward to show that such modifications for a single interface can be extended to the case of a multilayer structure. For the simplest case of a replicating grating film where we have

$$\zeta_1(\vec{r}_\parallel) = \zeta_2(\vec{r}_\parallel) + \tau = \zeta_0 e^{i\vec{Q} \cdot \hat{e}_x}, \quad (8)$$

we obtain from Eq. (7)

$$\begin{aligned} E_z^{(s)}(d, \omega) = & -\frac{k^2}{4\pi} \zeta_0 \left\{ (\epsilon_2 - \epsilon_1) [d_{zx}(\vec{k}_\parallel \omega | d, 0_-) E_x^{(0)}(\omega | 0_+) \right. \\ & + d_{zz}(\vec{k}_\parallel \omega | d, 0_-) E_z^{(0)}(\omega | 0_+)] \\ & + (\epsilon_3 - \epsilon_2) [d_{zx}(\vec{k}_\parallel \omega | d, -\tau_+) E_x^{(0)}(\omega | -\tau_-) + d_{zz}(\vec{k}_\parallel \omega | d, -\tau_+) \\ & \left. \times E_z^{(0)}(\omega | -\tau_-)] \right\}, \quad (9) \end{aligned}$$

$$\vec{k}_\parallel = \vec{Q} + \vec{k}_\parallel^{(0)},$$

$$k_\parallel = Q + k_1 \sin \theta. \quad (10)$$

The expressions for the propagators $d_{\mu\nu}$ can be found in Ref. 21, and the results for various $E^{(0)}$'s for a flat film are also available in the literature.^{22,24} Using these available results, we can finally compute $E_z(d, \omega)$ in Eq. (6) in terms of E_{in} (see the Appendix), and together with the relation between γ_M and γ_M^0 which we have obtained in a previous work,¹⁷ we can finally calculate the absorption cross section $\sigma(\omega)$ in Eq. (5) in the presence of the substrate film in comparison to a given free-molecule absorption profile $\sigma_0(\omega)$.

III. POSSIBILITY OF ENHANCED SELECTIVE PHOTOABSORPTION

Instead of showing some straightforward model calculation based on Eqs. (4) and (5), here we shall pay attention to a very interesting feature of the problem which may lead to the realization of a mechanism for enhanced selective photoabsorption for adsorbed molecules. In a recent study of the decay rate spectrum for admolecules near such a grating film,¹⁷ we pointed out that the coupling of the molecular fluorescence radiation to the two thin film surface plasmons is governed by a very different dispersion relation as compared to those in the case of plane wave light scattering experiments.^{15,16} The difference arises from the dipole nature of the molecular emission which consists of a superposition of all the plane wave harmonics. Hence the resonance peaks due to the cross-coupling of the plasmons on the two film surfaces into the long-(and short-)range surface plasmons in the decay-rate spectrum are in general at different positions as compared to those in the light scattering spectrum.¹⁷ Since these peak positions (in both spectrums) are very sensitive to the geometrical (roughness, thickness,...) and dielectric properties of the film, for a given absorption level one can then try to adjust these parameters so that the cross-coupling peak of the scattered field lies close to the natural frequency ω_M^0 of the system, and that of the induced decay rate stays away from ω_M^0 . Under optimal conditions enhanced selective photoabsorption of this particular level (ω_M^0) may be achieved, since the other levels close to ω_M^0 would now be strongly damped due to the fact that they can experience large induced decay rates. We shall illustrate this below through a numerical model calculation.

IV. NUMERICAL ILLUSTRATIONS

To illustrate the sensitivity of the cross-coupling peaks to the film parameters, let us first study the intensity of the total field at the molecule site ($z = d$). Defining $I(\omega) = |E_z(d, \omega)|^2$ with E_z given in Eq. (6), Fig. 2 shows the spectrum of $I(\omega)$ at $d = 150 \text{ \AA}$ for different grating periods Q for a supported (asymmetrically-bound) film. It shows, aside from the well-known "dip" at $\omega \sim 3.6 \text{ eV}$ for Ag due to the excitation of the non-radiative surface plasmon mode, that the long-range evanescent surface plasmon (LRSP) mode due to the cross-coupling is manifested clearly in the spectrum, where its peak moves as Q is varied. At such a distance, the short-range cross-coupling mode almost vanishes completely. Figure 3 shows similar variation of this LRSP peak with the thickness (t) of the film for a fixed value of Q , where the peak is seen to disappear as t tends to infinity. Figure 4 shows similar effects as in Fig. 2, except that we now have a free-standing (symmetrically-bound) film, which is known to be a very efficient system for cross-coupling between the two film surface plasmons.^{16,17} Figure 5 shows similar effects as in Fig. 3 for the free-standing film in Fig. 4. To illustrate the possible selective enhanced mechanism as discussed in Sec. III, we consider a hypothetical molecular system with Lorentzian absorption lines $\sigma_o(\omega)$ as illustrated in Fig. 6. Let us consider the photoabsorption spectrum of this system when being located at $d = 150 \text{ \AA}$ from a supported grating film as that in Figs. 2 and 3, and with $Q = 1.5 \times 10^{-3} \text{ \AA}^{-1}$. Using the results for the decay rate worked out previously,¹⁷ the decay rate spectrum for the same grating film system is plotted in Fig. 7, from which the peak due to cross-coupling into LRSP located at $\omega \sim 1.1 \text{ eV}$ is clearly seen to be located at a different position than that for light scattering in Fig. 1 where the spectrum peaks at $\omega \sim 1.6 \text{ eV}$. Figure 8 shows the distorted absorption line shape $\sigma(\omega)$

for the molecular system in Fig. 6 located in the vicinity of the above grating film. It can be seen that one of the absorption lines is suppressed while only the one with $\omega_M^0 = 1.5$ eV is excited. Moreover, there is not much enhancement for this line since the corrugation amplitude $\zeta_0 \approx 40$ Å used in this calculation is too small. We have tried to increase this to go beyond 100 Å where we do have enhancement, but then the result is not very meaningful due to the limitation of the present perturbative approach. Nevertheless, the present results do give very strong indications that such selective enhanced photoabsorption may indeed be possible for deeper grating films, in which case a non-perturbative treatment must be adopted. We plan to reformulate this problem using a non-perturbative approach to calculate the fields and decay rates in the future.

V. CONCLUSION

In this paper, we have studied phenomenologically the photoabsorption of a molecule in the vicinity of a grating film. Our main result here is the speculation of the possibility of enhanced selective photoabsorption. It is well known that due to its monochromaticity and tunability, the laser has found great applications in various selective photochemical processes. Nevertheless, to have the selective absorption enhanced, one requires a highly-intense laser source, which may then lead to multiphoton processes and hence weakens the selectivity in the photoprocess. In this present mechanism which we are proposing, however, we have made use of the fact that the induced decay rate and the enhanced LRSP field have very different resonance structures, and hence the excitation of other levels may be suppressed by the enhanced decay rates at their natural frequencies. Hence, we conclude that it is worth pursuing the problem further using a non-perturbative approach to

allow large grating amplitudes for the film and to recalculate $\sigma(\omega)$ for such a system, so that a realistic enhanced selective photoabsorption may be exhibited.

ACKNOWLEDGMENTS

The authors would like to thank the referee for informing them of the work of Mills in Ref. 25. This research was supported by the Office of Naval Research, the National Science Foundation under Grant CHE-8620274 and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.

APPENDIX

Here we give a brief account on how the final expression for $E_z^{(s)}(d, \omega)$ may be obtained from Refs. 21 and 22. From Ref. 22 it is straightforward to show that

$$E_x^{(0)}(\omega|0_+) = (1-R) E_{in} \cos\theta \quad ; \quad E_z^{(0)}(\omega|0_+) = (1+R) E_{in} \sin\theta \quad (A1)$$

$$E_x^{(0)}(\omega|-t_-) = T E_{in} \cos\beta \quad ; \quad E_z^{(0)}(\omega|-t_-) = T E_{in} \sin\beta \quad ,$$

where

$$R = \frac{(1-\Delta_1)(1+\Delta_2) e^{-ik_2 t \cos\alpha} - (1+\Delta_1)(1-\Delta_2) e^{ik_2 t \cos\alpha}}{(1+\Delta_1)(1+\Delta_2) e^{-ik_2 t \cos\alpha} - (1-\Delta_1)(1-\Delta_2) e^{ik_2 t \cos\alpha}} \quad , \quad (A2)$$

and

$$T = \frac{\Delta_2 e^{-ik_3 t \cos\beta}}{(1+\Delta_1)(1+\Delta_2) e^{-ik_2 t \cos\alpha} - (1-\Delta_1)(1-\Delta_2) e^{ik_2 t \cos\alpha}} \quad , \quad (A3)$$

$$\Delta_1 = \frac{k_1 \cos\alpha}{k_2 \cos\theta} \quad , \quad \Delta_2 = \frac{k_3 \cos\alpha}{k_2 \cos\beta} \quad , \quad k_i = \sqrt{\epsilon_i} \frac{\omega}{c} \quad , \quad (A4)$$

and θ , α and β are the angles made by the light rays with respect to the normal direction in media 1, 2 and 3, respectively. By using the Green dyadics worked out in Ref. 21, we obtain

$$E_z^{(s)}(d, \omega) = -\frac{k^2}{4\pi} \epsilon_0 \{ (\epsilon_2 - \epsilon_1) [C_1 C_2 E_x^{(0)}(\omega|0_+) + C_4 E_z^{(0)}(\omega|0_+)] \\ + (\epsilon_3 - \epsilon_2) [C_1 C_3 E_x^{(0)}(\omega|-t_-) + C_5 E_z^{(0)}(\omega|-t_-)] \} e^{i\alpha_1 d}, \quad (A5)$$

where the coefficients C_i are given by:

$$C_1 = \frac{k_1 \sin \theta}{Q + k_1 \sin \theta}, \quad (A6)$$

$$C_2 = \frac{2\alpha_2 \epsilon_2 \rho (1 + \frac{\alpha_3 \epsilon_2 - \alpha_2 \epsilon_3}{\alpha_3 \epsilon_2 + \alpha_2 \epsilon_3} e^{-2i\alpha_2 t})}{2\alpha_2 \epsilon_1 - (\alpha_2 \epsilon_1 + \alpha_1 \epsilon_2) (1 - \frac{\alpha_3 \epsilon_2 - \alpha_2 \epsilon_3}{\alpha_3 \epsilon_2 + \alpha_2 \epsilon_3} e^{-2i\alpha_2 t})}, \quad (A7)$$

$$C_3 = \frac{2\alpha_2 \epsilon_2 \rho e^{-i\alpha_2 t} (1 + \frac{\alpha_3 \epsilon_2 - \alpha_2 \epsilon_3}{\alpha_3 \epsilon_2 + \alpha_2 \epsilon_3})}{2\alpha_2 \epsilon_1 - (\alpha_2 \epsilon_1 + \alpha_1 \epsilon_2) (1 - \frac{\alpha_3 \epsilon_2 - \alpha_2 \epsilon_3}{\alpha_3 \epsilon_2 + \alpha_2 \epsilon_3} e^{-2i\alpha_2 t})}, \quad (A8)$$

$$C_4 = \frac{4\pi}{i\alpha_1} (\frac{c^2}{\epsilon_2 \omega^2} \alpha_2^2 - 1) (\frac{\epsilon_2}{\epsilon_1}) \frac{(\frac{\epsilon_2}{\epsilon_3} + \frac{\alpha_2}{\alpha_3}) e^{i\alpha_2 t} - (\frac{\epsilon_2}{\epsilon_3} - \frac{\alpha_2}{\alpha_3}) e^{-i\alpha_2 t}}{(\frac{\alpha_2}{\alpha_1} - \frac{\epsilon_2}{\epsilon_1}) (\frac{\alpha_2}{\alpha_3} + \frac{\epsilon_2}{\epsilon_3}) e^{i\alpha_2 t} - (\frac{\alpha_2}{\alpha_1} + \frac{\epsilon_2}{\epsilon_1}) (\frac{\alpha_2}{\alpha_3} - \frac{\epsilon_2}{\epsilon_3}) e^{-i\alpha_2 t}}, \quad (A9)$$

$$C_5 = \frac{4\pi}{i\alpha_1} (\frac{c^2}{\epsilon_2 \omega^2} \alpha_2^2 - 1) (\frac{\epsilon_2}{\epsilon_1}) \frac{2 \frac{\alpha_2}{\alpha_3}}{(\frac{\alpha_2}{\alpha_1} - \frac{\epsilon_2}{\epsilon_1}) (\frac{\alpha_2}{\alpha_3} + \frac{\epsilon_2}{\epsilon_3}) e^{i\alpha_2 t} - (\frac{\alpha_2}{\alpha_1} + \frac{\epsilon_2}{\epsilon_1}) (\frac{\alpha_2}{\alpha_3} - \frac{\epsilon_2}{\epsilon_3}) e^{-i\alpha_2 t}}, \quad (A10)$$

where

$$\rho = \frac{2\pi ic^2}{\epsilon_2 \omega^2} (Q + k_1 \sin \theta) \quad , \quad (A11)$$

and $\alpha_i^2 = \epsilon_i \frac{\omega^2}{c^2} - (Q + k_1 \sin \theta)^2$, with the sign of α_i being carefully taken to meet various boundary conditions at infinity.

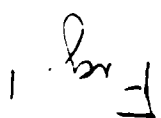
REFERENCES

1. M. Fleischmann, P. J. Handra and A. J. McQuillan, Chem. Phys. Lett. 26, 163 (1974).
2. For reviews, see, e.g., G. M. Goncher, C. A. Parsons and C. B. Harris, J. Phys. Chem. 88, 4200 (1984); D. A. Jelski, P. T. Leung and T. F. George, Int. Rev. Phys. Chem. 7, 179 (1988).
3. J. I. Gersten and A. Nitzan, Surf. Sci. 158, 165 (1985), and references therein.
4. P. T. Leung and T. F. George, J. Chem. Phys. 85, 4729 (1986).
5. P. T. Leung and T. F. George, Chem. Phys. Lett. 134, 375 (1987).
6. See also, P. T. Leung and T. F. George, Spectroscopy 4, 35 (1989).
7. I. Pockrand, Opt. Commun. 13, 311 (1975); I. Pockrand and H. Raether, Appl. Opt. 16, 1784 (1977).
8. D. Sarid, Phys. Rev. Lett. 47, 1927 (1981).
9. G. S. Agarwal, Phys. Rev. B 31, 3534 (1985); S. D. Gupta, G. V. Varada and G. S. Agarwal, Phys. Rev. B 36, 6331 (1987).
10. M. G. Weber and D. L. Mills, Phys. Rev. B 32, 5057 (1985).
11. T. Inagaki, M. Motosuga, E. T. Arakawa and J. P. Goudonnet, Phys. Rev. B 31, 2548 (1985); 32, 6238 (1985).
12. I. A. Avrutskii, A. S. Svarhin and V. A. Sychugov, Opt. Spectrosc. (USSR) 63, 198 (1987).
13. M. G. Cavalcante, G. A. Farias and A. A. Maradudin, J. Opt. Soc. Am. B 4, 1372 (1987).
14. Z. Chen and H. J. Simon, J. Opt. Soc. Am. B 5, 1396 (1988).
15. R. W. Gruhlke, W. R. Holland and D. G. Hall, Phys. Rev. Lett. 56, 2838 (1986); Opt. Lett. 12, 364 (1987).
16. R. W. Gruhlke and D. G. Hall, Appl. Phys. Lett. 53, 1041 (1988).
17. . . T. Leung, Y. S. Kim and T. F. George, Phys. Rev. B, submitted.
18. P. T. Leung, Y. S. Kim and T. F. George, Phys. Rev. B 38, 10032 (1988); Y. S. Kim, P. T. Leung and T. F. George, Chem. Phys. Lett. 152, 453 (1988).
19. See, e.g., R. R. Chance, A. Prock and R. Silbey, Adv. Chem. Phys. 37, 1 (1978).
20. A. A. Maradudin and D. L. Mills, Phys. Rev. B 11, 1392 (1975).

21. D. L. Mills and A. A. Maradudin, Phys. Rev. B 12, 2943 (1975).
22. See, e.g., L. N. Hadley and D. M. Dennison, J. Opt. Soc. Am. 37, 451 (1947).
23. P. T. Leung and T. F. George, Phys. Rev. 36, 4664 (1987).
24. G. S. Agarwal, Phys. Rev. B 14, 846 (1976).
25. D. L. Mills, Phys. Rev. B 12, 4036 (1975).
26. E. Juranek, Z. Phys. 233, 324 (1970).
27. See also, M. Born and E. Wolf, Principles of Optics, 6th Ed. (Pergamon, New York, 1980).

FIGURE CAPTIONS

1. Configuration of the photoabsorption problem at a corrugated thin film.
2. Intensity of the electric field at $z = d = 150 \text{ \AA}$ from a supported grating film ($\epsilon_1 = 1.0$, $\epsilon_3 = 3.6$) as a function of frequency at fixed film thickness $t = 100 \text{ \AA}$ and grating amplitude $\zeta_0 = 40 \text{ \AA}$. The angle of incidence θ is set at 1 radian, and the grating wave number is varied as: $Q = 1.0 \times 10^{-3} \text{ \AA}^{-1}$ (solid line); $Q = 1.5 \times 10^{-3} \text{ \AA}^{-1}$ (dotted line); and $Q = 2.0 \times 10^{-3} \text{ \AA}^{-1}$ (dashed line). The y-axis on each graph is in arbitrary units.
3. Same as Fig. 2, except that Q is fixed at $2.0 \times 10^{-3} \text{ \AA}^{-1}$ and t is varied: dotted line 2 ($t = 50 \text{ \AA}$); dashed line ($t = 100 \text{ \AA}$); dotted line 1 ($t = 200 \text{ \AA}$); solid line ($t \rightarrow \infty$).
4. Same as in Fig. 2, except that the results are for a free-standing film, $\epsilon_1 = \epsilon_3 = 1.0$.
5. Same as Fig. 3, except that the results are for a free-standing film, $\epsilon_1 = \epsilon_3 = 1.0$.
6. Hypothetical molecular system with two Lorentzian absorption lines.
7. Decay rate spectrum for the system as in Figs. 2 and 3 with $Q = 1.5 \times 10^{-3} \text{ \AA}^{-1}$ and $t = 100 \text{ \AA}$.
8. Distorted photoabsorption line shape for the molecular system in Fig. 6 in the presence of the grating film as described in Fig. 7.



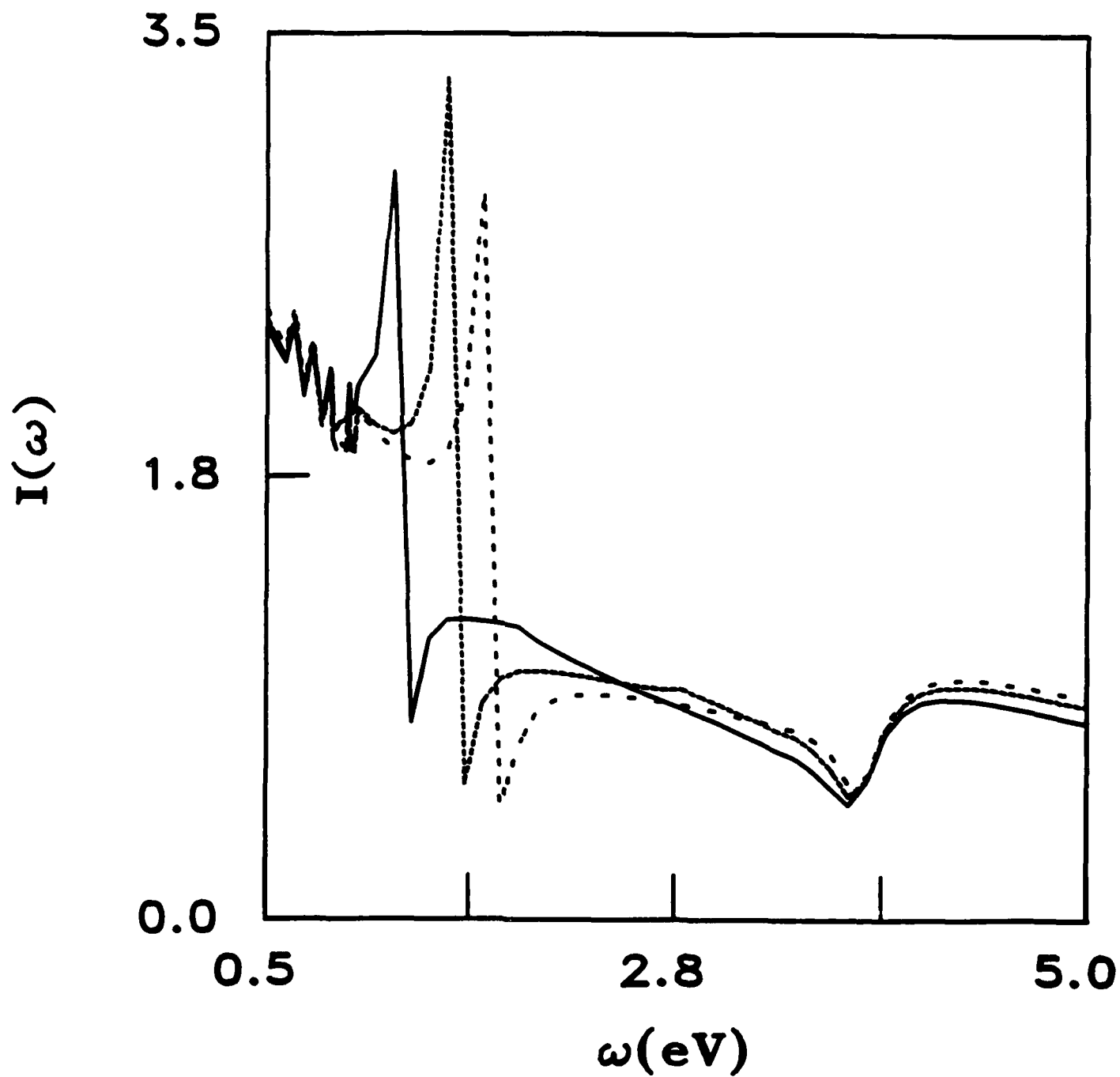


Fig. 3

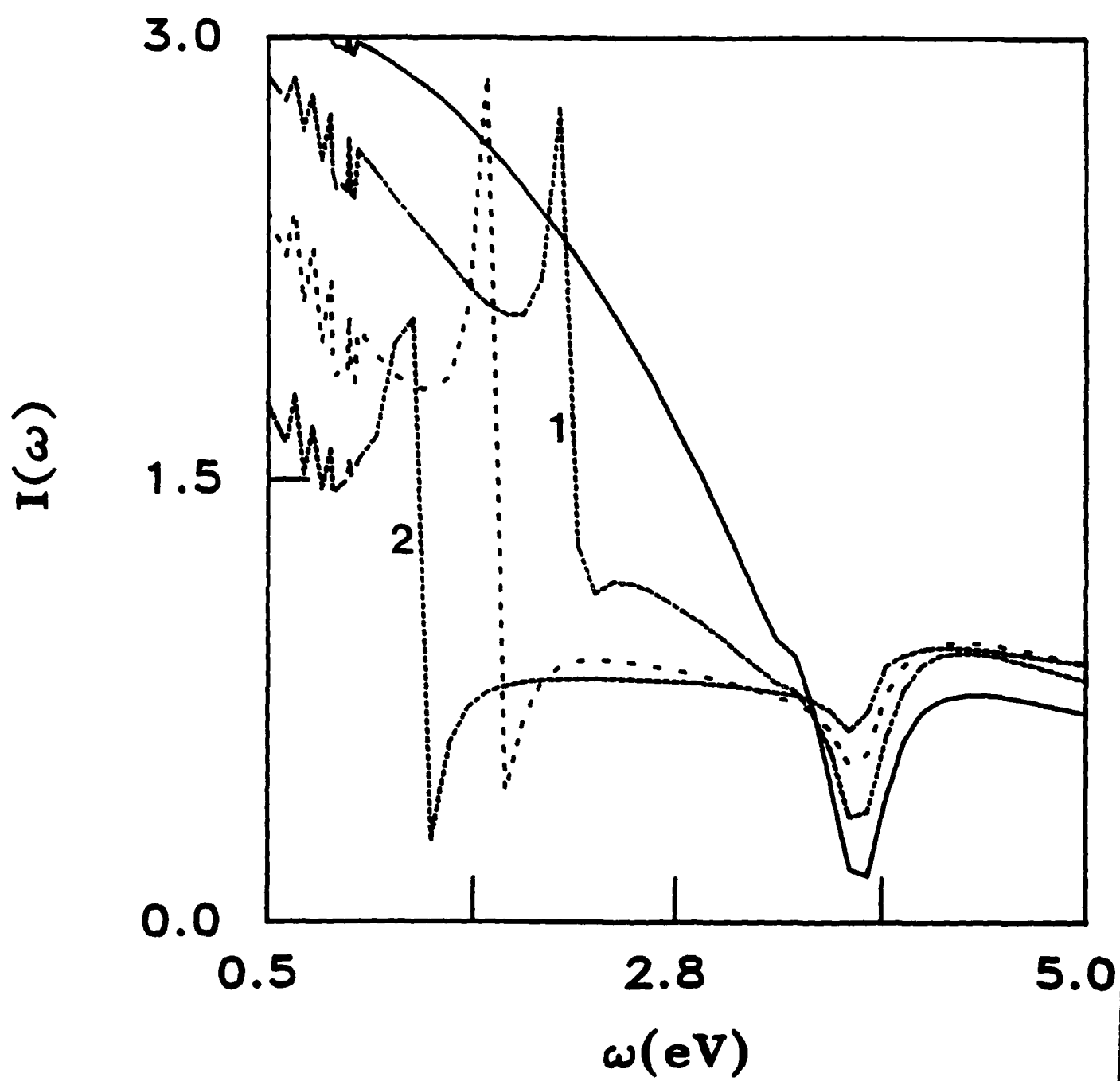


Fig. 4

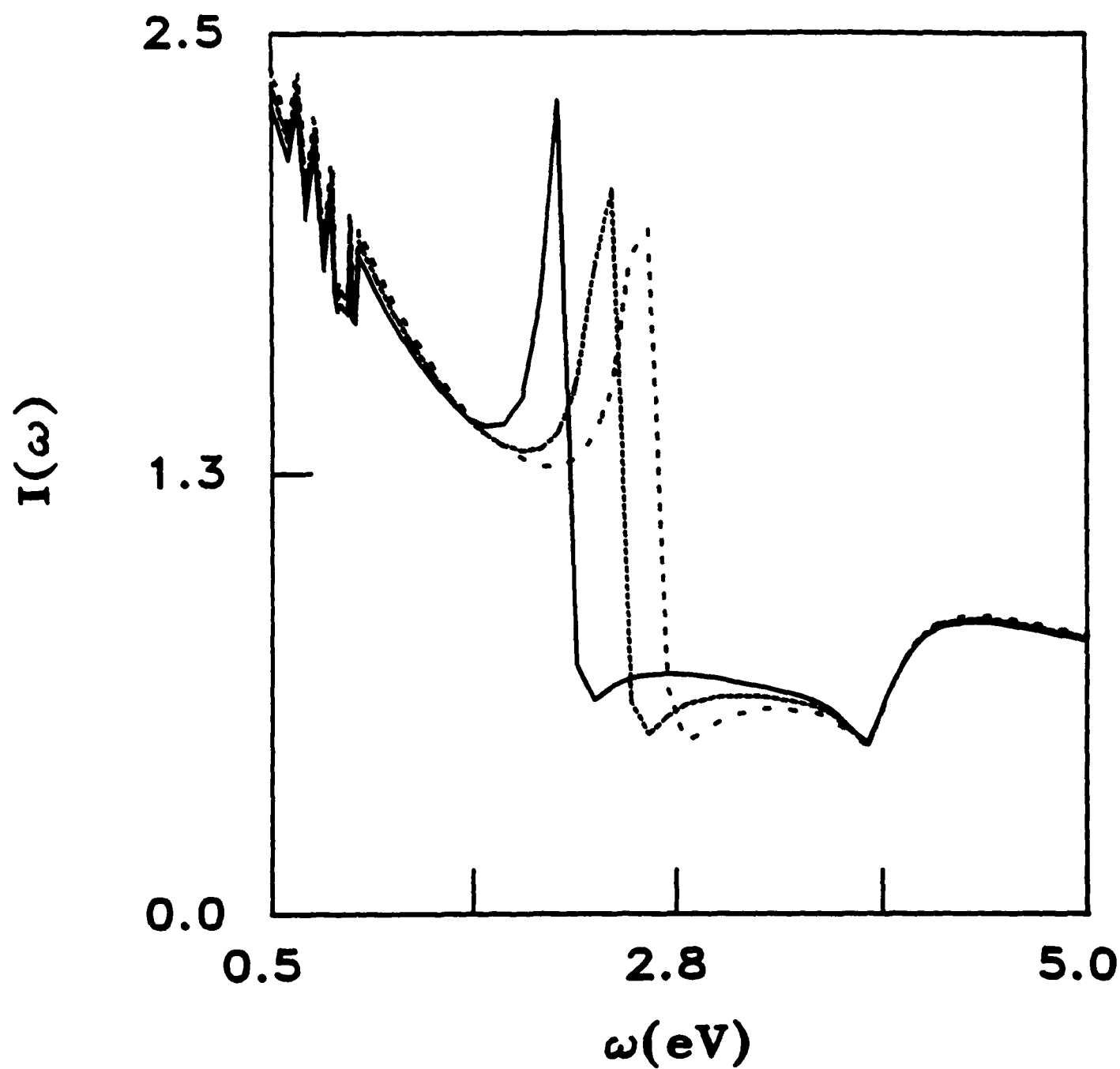


Fig. 5

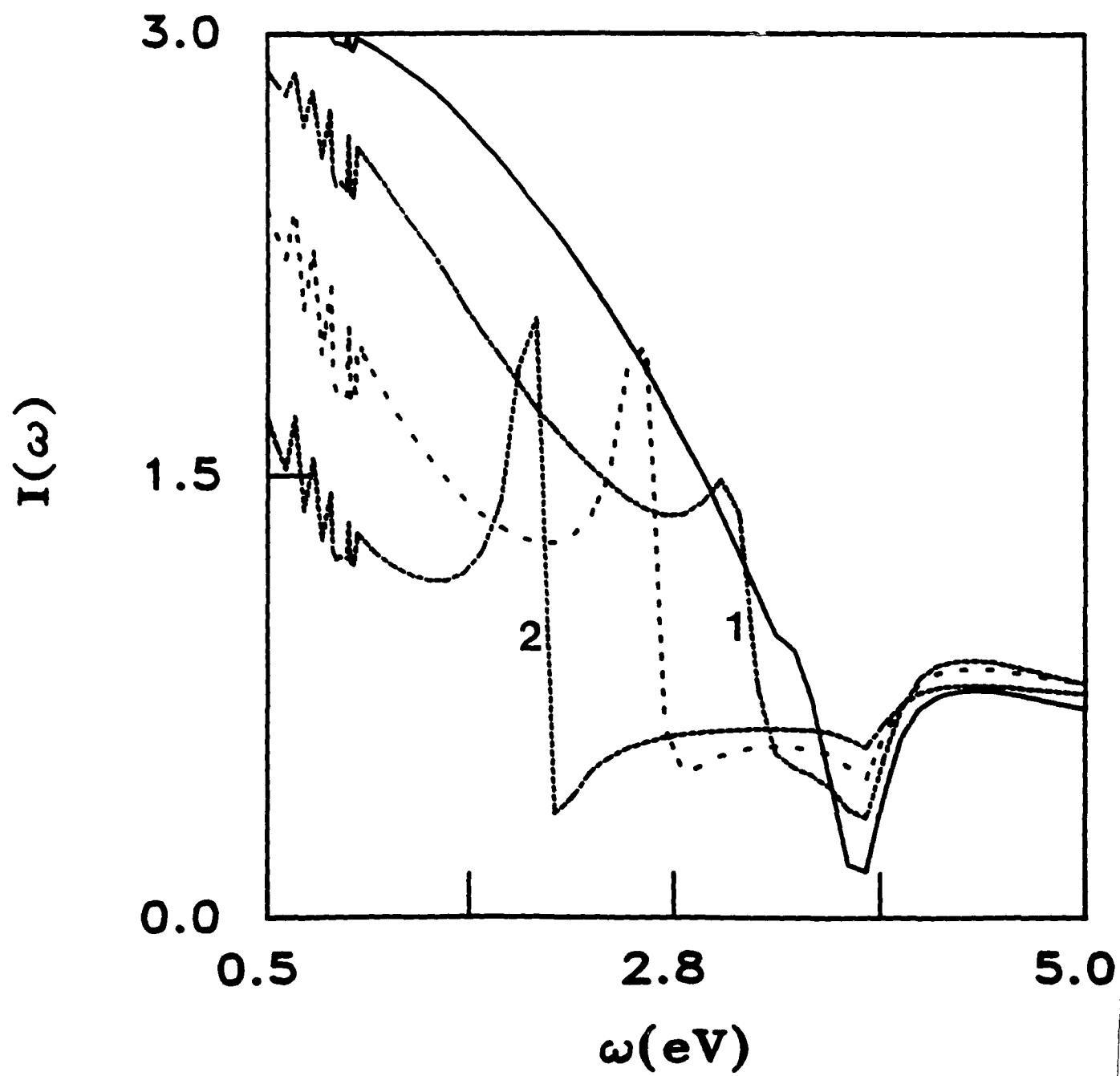


Fig. 8

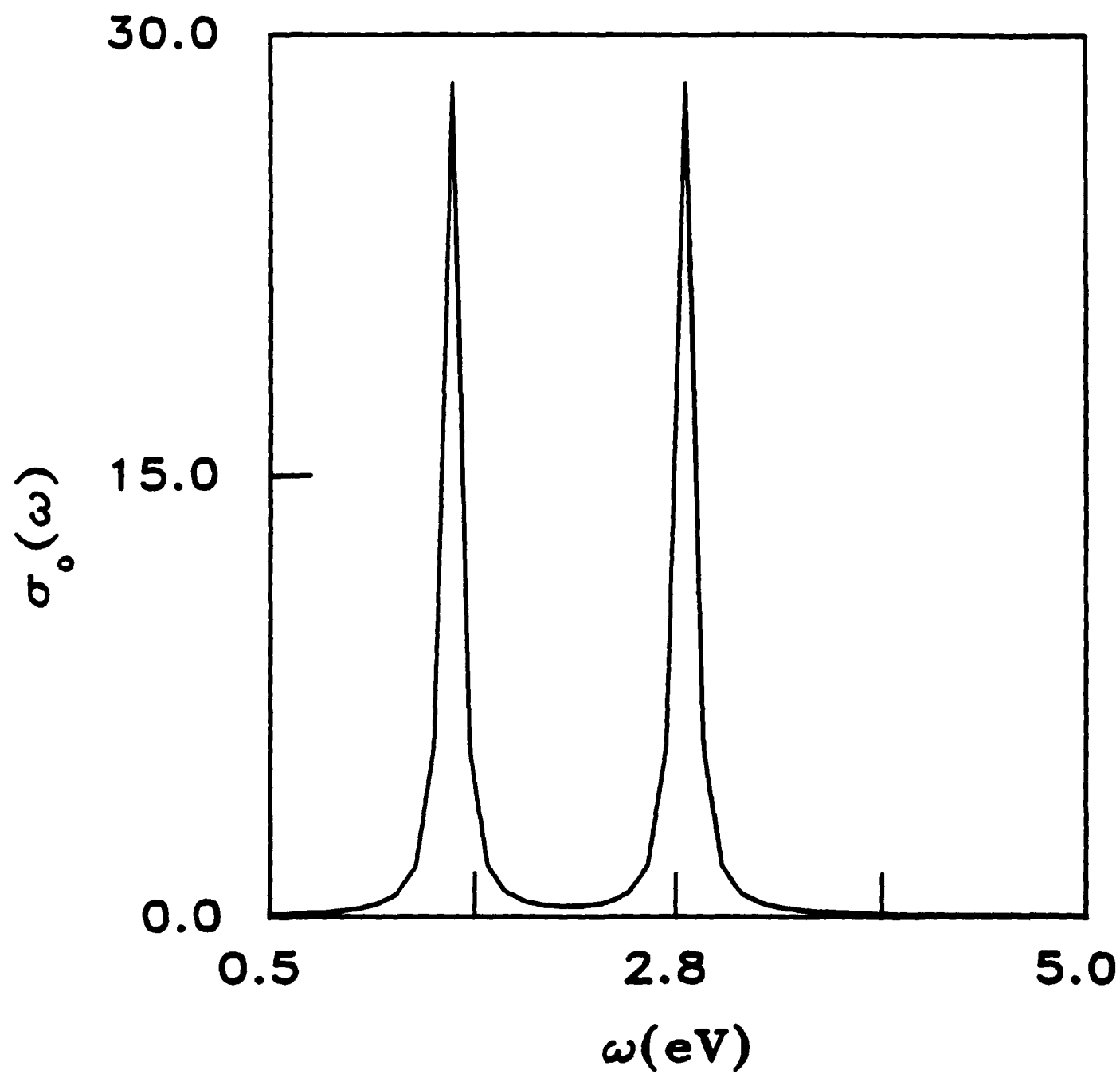


Fig. 7

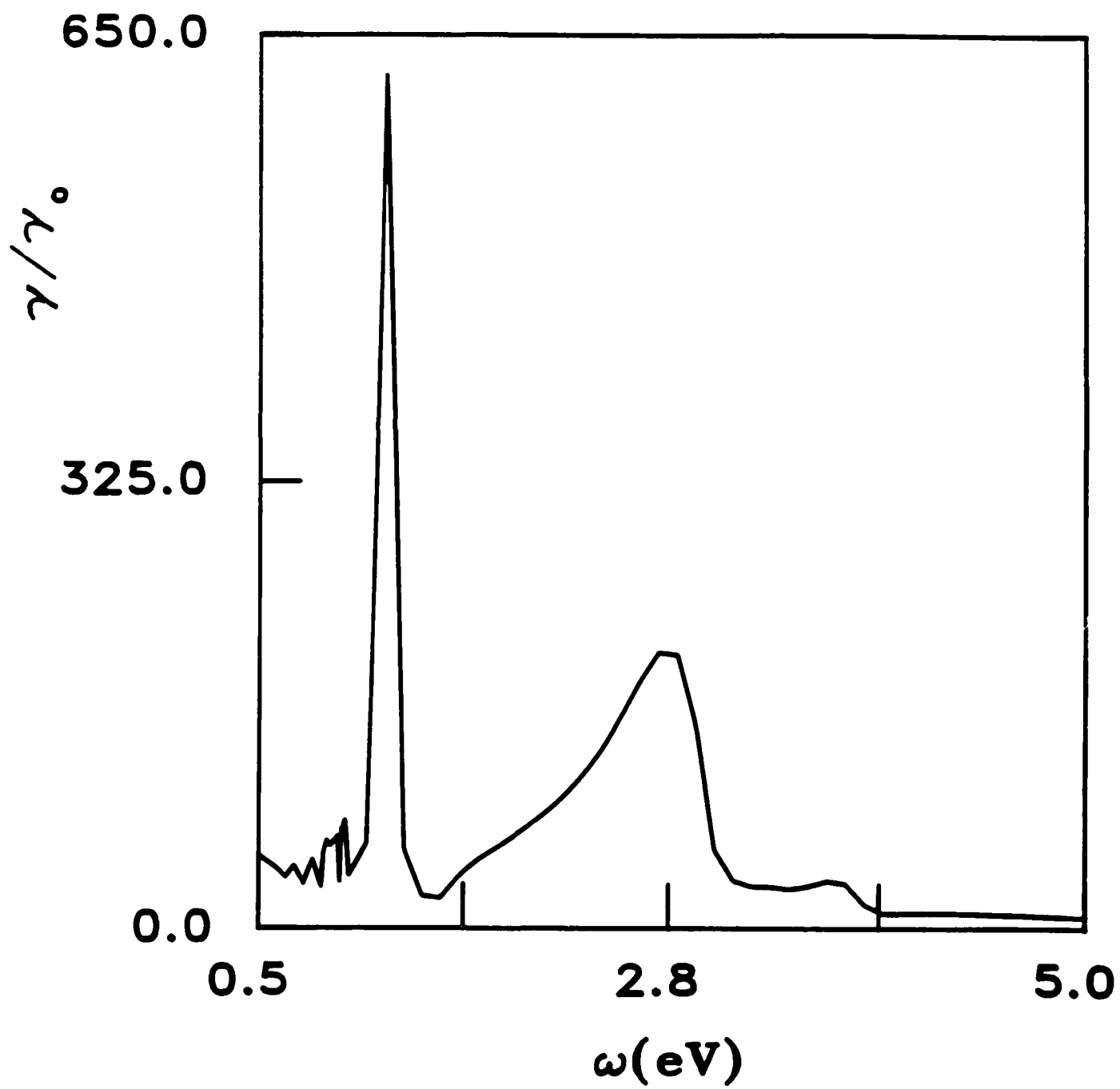
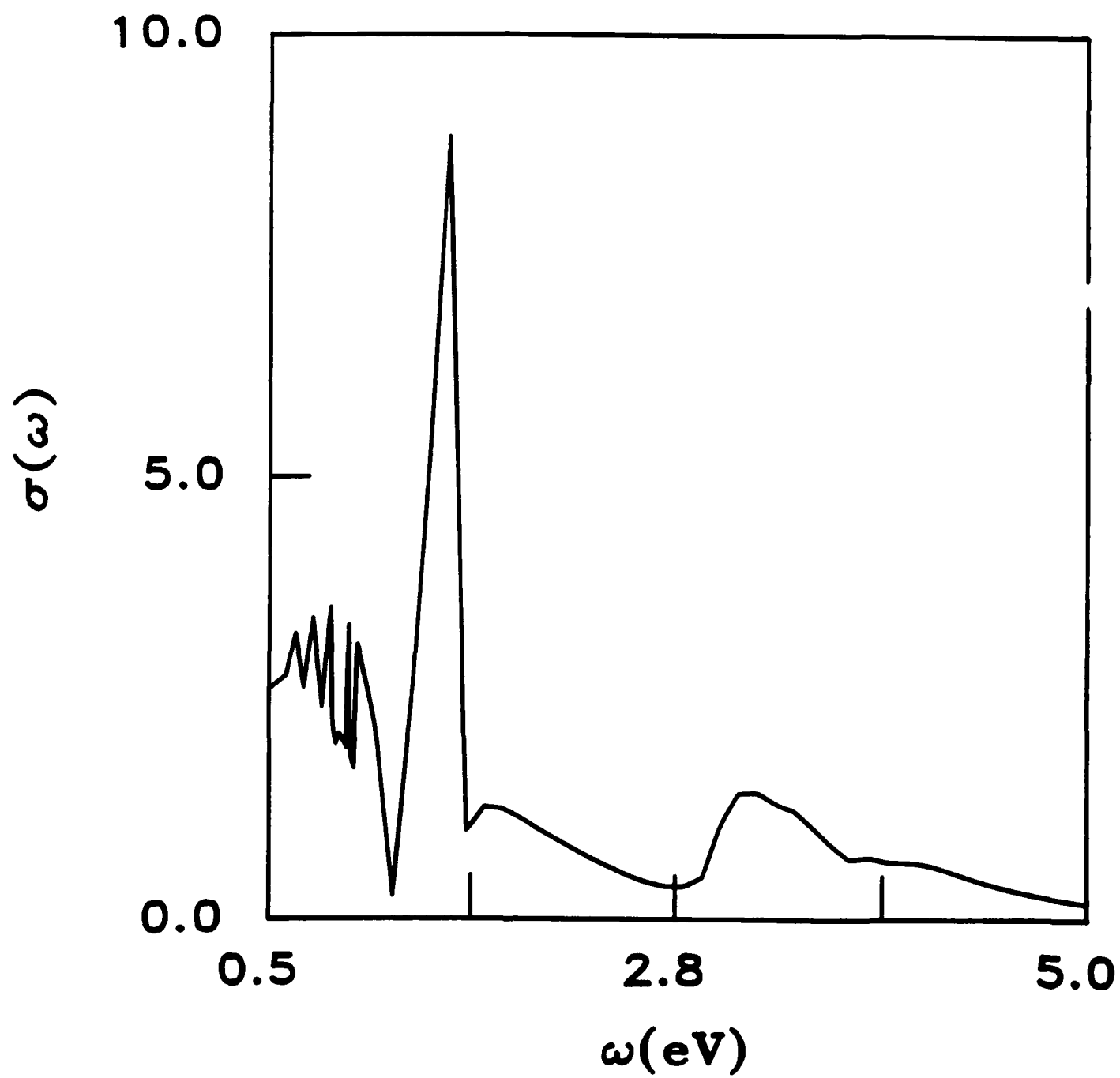


Fig. 8



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi: 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
		Dr. David L. Nelson Chemistry Division Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217	1

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. J. E. Jensen
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, California 90265

Dr. C. B. Harris
Department of Chemistry
University of California
Berkeley, California 94720

Dr. J. H. Weaver
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. F. Kutzler
Department of Chemistry
Box 5055
Tennessee Technological University
Cookeville, Tennessee 38501

Dr. A. Reisman
Microelectronics Center of North Carolina
Research Triangle Park, North Carolina
27709

Dr. D. DiLella
Chemistry Department
George Washington University
Washington D.C. 20052

Dr. M. Grunze
Laboratory for Surface Science and
Technology
University of Maine
Orono, Maine 04469

Dr. R. Reeves
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. J. Butler
Naval Research Laboratory
Code 6115
Washington D.C. 20375-5000

Dr. Steven M. George
Stanford University
Department of Chemistry
Stanford, CA 94305

Dr. L. Interante
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Mark Johnson
Yale University
Department of Chemistry
New Haven, CT 06511-8118

Dr. Irvin Heard
Chemistry and Physics Department
Lincoln University
Lincoln University, Pennsylvania 19352

Dr. W. Knauer
Hughes Research Laboratory
3011 Malibu Canyon Road
Malibu, California 90265

Dr. K.J. Klaubunde
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. G. A. Somorjai
Department of Chemistry
University of California
Berkeley, California 94720

Dr. J. Murday
Naval Research Laboratory
Code 6170
Washington, D.C. 20375-5000

Dr. J. B. Hudson
Materials Division
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Theodore E. Madey
Surface Chemistry Section
Department of Commerce
National Bureau of Standards
Washington, D.C. 20234

Dr. J. E. Demuth
IBM Corporation
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. M. G. Lagally
Department of Metallurgical
and Mining Engineering
University of Wisconsin
Madison, Wisconsin 53706

Dr. R. P. Van Duyne
Chemistry Department
Northwestern University
Evanston, Illinois 60637

Dr. J. M. White
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. D. E. Harrison
Department of Physics
Naval Postgraduate School
Monterey, California 93940

Dr. R. L. Park
Director, Center of Materials
Research
University of Maryland
College Park, Maryland 20742

Dr. W. T. Peria
Electrical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Keith H. Johnson
Department of Metallurgy and
Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. S. Sibener
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Arnold Green
Quantum Surface Dynamics Branch
Code 3817
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. S. L. Bernasek
Department of Chemistry
Princeton University
Princeton, New Jersey 08544

Dr. W. Kohn
Department of Physics
University of California, San Diego
La Jolla, California 92037

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. F. Carter
Code 6170
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Richard Colton
Code 6170
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Dan Pierce
National Bureau of Standards
Optical Physics Division
Washington, D.C. 20234

Dr. R. Stanley Williams
Department of Chemistry
University of California
Los Angeles, California 90024

Dr. R. P. Messmer
Materials Characterization Lab.
General Electric Company
Schenectady, New York 22217

Dr. Robert Gomer
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Ronald Lee
R301
Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910

Dr. Paul Schoen
Code 6190
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. John T. Yates
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Dr. Richard Greene
Code 5230
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. L. Kesmodel
Department of Physics
Indiana University
Bloomington, Indiana 47403

Dr. K. C. Janda
University of Pittsburgh
Chemistry Building
Pittsburg, PA 15260

Dr. E. A. Irene
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Adam Heller
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH
UNITED KINGDOM

Dr. H. Tachikawa
Chemistry Department
Jackson State University
Jackson, Mississippi 39217

Dr. John W. Wilkins
Cornell University
Laboratory of Atomic and
Solid State Physics
Ithaca, New York 14853

ABSTRACTS DISTRIBUTION LIST, 056/625/629

Dr. R. G. Wallis
Department of Physics
University of California
Irvine, California 92664

Dr. D. Ramaker
Chemistry Department
George Washington University
Washington, D.C. 20052

Dr. J. C. Hemminger
Chemistry Department
University of California
Irvine, California 92717

Dr. T. F. George
Chemistry Department
University of Rochester
Rochester, New York 14627

Dr. G. Rubloff
IBM
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. Horia Metiu
Chemistry Department
University of California
Santa Barbara, California 93106

Dr. W. Goddard
Department of Chemistry and Chemical
Engineering
California Institute of Technology
Pasadena, California 91125

Dr. P. Hansma
Department of Physics
University of California
Santa Barbara, California 93106

Dr. J. Baldeschwieler
Department of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Dr. J. T. Keiser
Department of Chemistry
University of Richmond
Richmond, Virginia 23173

Dr. R. W. Plummer
Department of Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 41106

Dr. N. Winograd
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802

Dr. Roald Hoffmann
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. Steckl
Department of Electrical and
Systems Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. G.H. Morrison
Department of Chemistry
Cornell University
Ithaca, New York 14853