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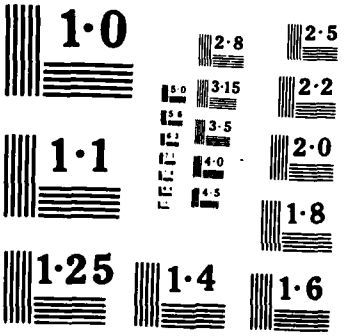
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Photodissociation of Molecules at Structured Metallic Surfaces

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P. T. Leung and Thomas F. George

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PHOTODISSOCIATION OF MOLECULES AT STRUCTURED METALLIC SURFACES

P. T. Leung and Thomas F. George
Departments of Chemistry and of Physics & Astronomy
State University of New York at Buffalo
Buffalo, New York 14260

Abstract

Direct photodissociation of molecules at structured metallic surfaces is considered, where the concepts of optimal and critical distances are introduced into the description of this phenomenon. Numerical results for the distortion of the line shape and the enhancement ratio are obtained for a shallow sinusoidal grating.

I. Introduction

Ever since the first observation of surface-enhanced Raman scattering (SERS),[1] possible surface enhancement of other optical processes such as resonance fluorescence and photon trapping has been a subject of much interest.[2-6] The related dynamical process of the photodissociation of gas molecules near or physisorbed on a rough metallic surface is also of great interest for the following reasons. From a practical viewpoint, it is the first step that one must study in order to understand and control the various phenomena ranging from the deposition of molecules[7] to heterogeneous catalysis[8] on a rough surface. It is also of great theoretical interest, for although it is now clear that the surface definitely plays a role in enhancing the Raman scattering signal via its plasmon field set up by the laser under resonance conditions,[9] it is not so clear in the case of dissociation. The reason for this is that while the surface plasmon field still enhances the absorption process, line-broadening effects[10] due to transitions to final continuum states play a competing role to suppress the dissociation. These two competing mechanisms, namely, the enhanced local field and the increased decay rate near a structured surface, have also been noticed in the literature.[4,11]

The excitement of this subject is further aroused when we consider that while a model calculation[4] for a molecular dipole adsorbed on a silver sphere shows enhancement effects (although to a much less extent as compared to SERS), a recent experiment[11] on the photochemical degradation of rhodamine 6G adsorbed on a silver-island surface shows no enhancement effect whatsoever, and in some cases even diminution effects are observed. On the other hand, enhanced photodissociation of surface-supported organometallic molecules has been reported.[12] Furthermore, the observation of different

gas/adlayer dissociation ratios for different metal-alkyl compound induced by UV laser radiation[13] suggests the possible existence of an optimal molecule-surface distance (to be determined by the aforementioned competing mechanisms) at which the dissociation rate is the largest. Based on all the observations mentioned above, we recognize that there are various issues in the photodissociation of molecules at a surface which are still not fully resolved.

In this paper, we present a systematic study of such processes within a simple model. We shall assume our surface to be a shallow sinusoidal grating, bearing in mind that a general structured surface can be viewed as a superposition of many different sinusoidal structures via Fourier analysis. The surface fields for this case are well known,[14,15] and we shall derive an expression for the molecular decay rate on such a surface. We shall see that, with the introduction of such concepts as critical and optimal distances, many of the experimental observations mentioned above[11-13] can be understood (at least qualitatively) from this simple approach.

II. Cross Section

Within first-order time-dependent perturbation theory, the quantum-mechanical cross section for a dipole transition can be expressed in proportion to the line-shape function $I(\omega)$ as[16]

$$\sigma(\omega) = A_0 \, I(\omega) \quad , \tag{1}$$

where A_0 is the proportionality constant, and $I(\omega)$ is given by the Fourier transform of the autocorrelation function

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \langle \vec{\mu}^*(0) . \vec{\mu}(t) \rangle \, e^{-i\omega t} \quad , \tag{2}$$

where $\vec{\mu}(t)$ is the Heisenberg time-dependent operator for the induced dipole moment of the molecule. Instead of solving the problem in a fully quantum-mechanical way, we adopt a semiclassical approach by describing $\vec{\mu}(t)$ in the context of the classical mechanical model for a damped harmonic oscillator. Corrections of higher order in Planck's constant can in principle be sought by following the formalism of Ref. 16. Thus we have[4]

$$\ddot{\vec{\mu}}(t) + (\omega_M^0)^2 \vec{\mu}(t) + \gamma_M^0 \dot{\vec{\mu}}(t) = (\omega_M^0)^2 \alpha_M \vec{E} \quad , \tag{3}$$

where ω_M^0 and γ_M^0 are respectively the molecular frequency and decay rate in the bulk, α_M is the molecular polarizability, and $\vec{E}$ is the external field at the site of the molecule.

For a molecule sitting on a metallic surface, the total external field can be written in the form

$$\vec{E} = \vec{E}_0 + \vec{E}_r + \vec{E}_{sp} + \vec{E}_{im} \quad , \tag{4}$$

which represents the sum of the incident, reflected, surface plasmon and image fields. If we Fourier analyze Eq. (3) and assume that $\vec{E}(\omega)$ can be written in the form[4]

$$\vec{E}(\omega) = [1 + A(\omega)].\vec{E}_0(\omega) + G(\omega).\vec{\mu}(\omega) \tag{5}$$

where all the coefficients are in general tensors, we can write the solution of Eq. (3) in the form[4]

$$\mu(t) = \mu(\omega)e^{-i\omega t} \tag{6}$$

with

$$\mu(\omega) = \frac{\alpha_M(\omega_M^0)^2}{\omega_M^2 - \omega^2 - i\omega\gamma_M} \hat{n}_\mu.[1 + A].\vec{\mathcal{E}}_0 \quad . \tag{7}$$

Here $\hat{n}_\mu$ is the unit vector of the direction of the molecular dipole, ω_M and γ_M are respectively the "surface modified" molecular frequency and decay rate which are to be determined by the image field $G(\omega).\vec{\mu}(\omega)$ in Eq. (5),[4] and we have assumed a monochromatic incident field of the form $\vec{E}_0 = \vec{\mathcal{E}}_0 e^{-i\omega t}$. By substituting Eqs. (6) and (7) into Eqs. (1) and (2), we obtain the cross section in the form

$$\sigma(\omega) = 2\pi c\alpha^2 a_0 |\hat{n}_\mu.[1 + A].\hat{n}_0|^2 \frac{\gamma_M}{(\omega-\omega_M)^2 + (\frac{\gamma_M}{2})^2} , \tag{8}$$

where $\hat{n}_0 = \vec{\mathcal{E}}_0/\mathcal{E}_0$, c is the speed of light, α the fine structure constant and a_0 the Bohr radius. It turns out that this semiclassical approach leads to the same result as the one obtained from a complete classical treatment by calculating the Poynting fluxes of the incident beam and of that adsorbed by the molecular system.[4] We also note that Eq. (8) exhibits the general Lorentzian form which is appropriate for adsorption as well as for fast (direct) dissociation processes,[16] for the latter takes place on a time scale on the order of 10^{-14} s following the absorption, which leads to a yield of almost unity for such reactive processes.[17]

III. Surface Field

It is clear from Eq. (8) that the effects of the surface enter into the process through the terms A, γ_M and ω_M. Since under most circumstances, the change of the molecular frequency due to the presence of the image field is almost completely negligible,[10] we shall assume $\omega_M \cong \omega_M^0$ in all our calculations below. To investigate the surface effects on A and γ_M, we shall consider a simple geometrical setting of the problem. Specifically, we shall consider dissociation on a shallow sinusoidal metallic grating with

the molecular dipole oriented perpendicular to it along the z-axis and located at (0,0,d). Furthermore, we shall consider monochromatic P-polarized incident laser light at an angle of incidence equal to θ (see Fig. 1). The surface fields are well known for this case, and following the notations of Ref. 15 (except that we have light incident from the $z > 0$ region), we can write A in the form[14,15]

$$A(\omega) = \begin{pmatrix} 0 & -\frac{k_z}{k_t} R e^{2iK_z d} + \frac{i\Gamma_g}{k_g} S e^{(ik_z - \Gamma_g)d} \\ 0 & R e^{2ik_z d} + S e^{(ik_z - \Gamma_g)d} \end{pmatrix}, \quad (9)$$

where $K_g = \frac{\omega}{c}\sin\theta + g$, $g = 2\pi/\lambda_g$ with λ_g being the spatial period of the grating, $\Gamma_g = (K_g^2 - \omega^2/c^2)^{1/2}$, $k_z = \frac{\omega}{c}\cos\theta$, $k_t = \frac{\omega}{c}\sin\theta$, and θ is the angle of incidence. The quantities R and S in Eq. (9), originating respectively from the reflected and surface plasmon fields, are given as

$$R = \frac{\varepsilon k_z - i\beta}{\varepsilon k_z + i\beta} \quad (10)$$

$$S = \frac{2(\xi_g K_g) k_z \beta_g (1-\varepsilon)}{k_t(\varepsilon\Gamma_g + \beta_g)} \cdot \frac{\beta\beta_g + \varepsilon k_t K_g}{\beta_g(\varepsilon k_z + i\beta)} , \quad (11)$$

where $\beta^2 = k_t^2 - \frac{\omega^2}{c^2}\varepsilon$, $\beta_g^2 = K_g^2 - \frac{\omega^2}{c^2}\varepsilon$, ξ_g is the amplitude of the sinusoidal grating, and $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is the frequency-dependent complex dielectric constant of the metallic grating. The plasmon resonance condition is achieved when

$$\frac{\omega^2}{c^2}\varepsilon_1(\omega) - K_g^2[\varepsilon_1(\omega) + 1] = 0 \quad . \quad (12)$$

In writing A(ω) as in Eq. (9), we have assumed a column-vector notation for

any field $\vec{E}$ in the form $\begin{pmatrix} E_{\parallel} \\ E_z \end{pmatrix}$, where $E_{\parallel}$ is the component on the xy-plane and E_z is the z-component. Thus, for the perpendicular dipole at (0,0,d), $\hat{n}_\mu = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ in Eq. (8) and hence we have

$$|\hat{n}_\mu \cdot [1 + A] \cdot \hat{n}_0|^2 = |1 + Re^{2ik_z d} + Se^{(ik_z - \Gamma_g)d}|^2 \sin^2\theta \quad . \tag{13}$$

IV. Decay Rate

In order to see completely how the effects of the surface enter into Eq. (8), we now derive an expression for γ_M for a molecule sitting on a shallow sinusoidal grating. For the case of a randomly rough surface, the molecular decay rate has been derived[18] by application of the Rahman-Maradudin formalism[19] for the image potential due to a point charge (e) resting on such a surface. Furthermore, the image potential for a shallow sinusoidal grating has also been worked out by Rahman and Mills[20] following the Rahman-Maradudin formalism. To first order in ξ_g/λ_g, the result can be expressed as

$$\phi(z) = -\frac{e}{8}\frac{(\varepsilon-1)}{(\varepsilon+1)^2}\xi_g g\{(\varepsilon-1)[gK_0(gz) + \frac{2}{z}K_1(g,z)] + \frac{4K_1(gz)}{z}\} \quad , \tag{14}$$

where K_0 and K_1 are the modified Bessel functions. From this, it is straightforward to calculate the image field,

$$E(z) = -\frac{e}{8}\frac{(\varepsilon-1)}{(\varepsilon+1)^2}\xi_g g\{(\varepsilon-1)[(g^2 + \frac{4}{z^2})K_1(gz) + \frac{2g}{z}K_0(gz)]$$
$$+ 4[\frac{g}{z}K_0(gz) + \frac{2}{z^2}K_1(gz)]\} \quad . \tag{15}$$

From Eq. (15) and by making use of the properties of K_0 and K_1, it is not difficult to derive the image field due to a dipole (E_μ) on a surface. For a perpendicular dipole located at (0,0,d), we obtain

$$G^R(\omega) \equiv \frac{E_\mu}{\mu} = \frac{1}{8}\frac{(\varepsilon-1)}{(\varepsilon+1)^2}\xi_g g\{g[(\varepsilon-1)(g+\frac{2}{d}) + \frac{4}{d}](gK_1 + \frac{K_0}{d})$$

$$+ \frac{4}{d^2}(\varepsilon+1)(gK_0 + \frac{3K_1}{d})\} \quad , \tag{16}$$

where μ is the dipole moment. Note that this result is first order in $\xi_g g$, in contrast to that for a randomly rough surface which has a lowest-order result in $(\xi_g g)^2$.[18] Following similar procedures as in Refs. 10 and 18, we obtain

$$\frac{\gamma_M}{\gamma_M^0} = 1 + \frac{3}{2}\frac{q}{k^3}\,\mathrm{Im}G^F(1 + \frac{\mathrm{Im}G^R}{\mathrm{Im}G^F}) \quad , \tag{17}$$

where q is the quantum yield of emitting state and $G^F(\omega)$ is the corresponding function as in Eq. (16) for a flat surface. According to the classical model of Sommerfeld for a perpendicular dipole at (0,0,d), G^F is given by[10]

$$G^F(\omega) = -k^3\int_0^\infty du\, \mathcal{R}\, e^{-2\ell_1 \partial}\frac{u^3}{\ell_1} \quad . \tag{18}$$

where $\partial = kd$, $\mathcal{R} = \frac{\ell_2 - \varepsilon\ell_1}{\ell_2 + \varepsilon\ell_1}$, $\ell_1 = -i(1-u^2)^{1/2}$ and $\ell_2 = -i(\varepsilon - u^2)^{1/2}$. Substituting Eqs. (16) and (18) into Eq. (17) and assuming a quantum yield of approximate unity,[10] we can have an accurate estimate of γ_M, and together with the result in Eq. (13), we can investigate the complete surface effects on molecular dissociations via Eq. (8).

V. Numerical Results and Discussion

To illustrate the surface effects, we consider here the direct dissociation of I_2 molecules at 4500 Å on a silver (Ag) grating. We assume a grating period (λ_g) of 8000 Å and the ratio $\xi_g/\lambda_g \sim 8 \times 10^{-3}$.

Furthermore, the angle of incidence (θ) is fixed at 34.4° and the components of the complex dielectric constant for Ag are taken from the data compiled by Johnson and Christy.[21] In order to have a more fine adjustment within the neighborhood of resonance frequencies (for both molecular and plasmon resonances), we have numerically fitted the data to obtain the following empirical formulas for ε_1 and ε_2:

$$\varepsilon_1 = -79.80/E_\gamma^2 - 6.888/E_\gamma + 6.084, \quad E_\gamma < 3.12 \text{ eV} \tag{19}$$

$$\varepsilon_2 = \begin{cases} (1 - 3.704)\ \ln E_\gamma)(2.466/E_\gamma^2 + 0.220/E_\gamma - 0.192)^{1/2}, & E_\gamma < 1.14 \text{ eV} \\ 0.1(79.70/E_\gamma^2 + 7.123/E_\gamma - 6.194)^{1/2}, & 1.14 \text{ eV} < E_\gamma < 3.12 \text{ eV} \end{cases} \tag{20}$$

where E_γ is the energy of the incident photon. With all these data fixed, we find from Eq. (12) that the plasmon resonance occurs at a frequency with $E_\gamma \cong 2.895$ eV.

Figure 2 shows how the Lorentzian line shape for a free molecule is distorted due to the surface effects. It is of interest to compare these results with those obtained for a molecular dipole located on top of a silver sphere.[4] Since we have adjusted the two resonance frequencies to be almost the same, the "double peak" feature is not observed in our result. We notice further that enhanced dissociation is obtained as long as the molecule is not too close to the surface. We also find that the line shape becomes highly asymmetric because of surface effects. There seems to exist a window for the plasmon resonance effects at the steep edge of the profile, which is also a property possessed by the famous asymmetric Fano profile.[22] When one goes off resonance to the right, the plasmon field becomes so small that only the incident and reflected fields will predominate the process giving rise to interference phenomenon. Furthermore, if the molecule is too close to the surface (e.g., d = 10 Å), complete diminution will occur. This

gives hint to the existence of a critical distance (d_{cr}) below which one does not have any enhancement. In Fig. 3, we plot the enhancement ratio σ/σ_0 where σ_0 is the cross section for a free molecule versus the molecule-surface distance for different fixed laser frequencies. The graphs indeed show the existence of the critical distances as well as the optimal distances (d_{op}, at which dissociation is a maximum) for each case. More precise numerical results are listed in Table 1.

With the existence of these distances, the experimental observations by Garoff et al[11] and Ehrich and Osgood[13] can at least be understood qualitatively. In particular, we observe from graph (a) in Fig. 3 that at the plasmon resonance one can still have a large enhancement in the cross section even at distances far from the surface. This might be the crucial justification for the observation of Ehrlich and Osgood,[13] who found that an appreciable amount of molecular dissociation occurs already in the gas phase far above the substrate for $Cd(CH_3)_2$ but not for $Al_2(CH_3)_6$. For the latter, which is not on plasmon resonance under their experimental conditions, dissociation occurs mostly inside the adlayers.

As a final comment, although we have assumed a perpendicular dipole in our model calculation, we expect that the qualitative features of the results obtained here will prevail if one assumes a parallel or even randomly-oriented dipole. Especially at small molecule-surface distances, the induced decay rate for both the perpendicular and the parallel orientations will be very similar.[10]

IV. Conclusions

Within a simple model, we have seen how various experimental observations of photodissociation of molecules on a surface can be understood qualitatively. Furthermore, the concept of critical distance may lead to practical applications. As an example, we suggest that if one could coat the metallic surface by means of the "fatty acid monolayer assembly technique",[23] one could then guarantee that surface-assisted dissociation is maintained and thus achieve a more efficient heterogeneous catalysis process on the surface.[8] To acquire more realistic values for both d_{cr} and d_{op}, one can extend the present calculations to cases with deeper gratings. The surface fields in this case have been established in the literature.[24-26] Furthermore, larger roughness requires a reformulation of the treatment of the molecular decay rate, which is possible by incorporating terms of higher order in $\xi_g g$ in Eq. (14) within the Rahman-Maradudin formalism.[19] Work in this direction is in progress in our laboratory.

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Table 1. Numerical Results From Figure 3

Graph	Energy of incident photon (E_γ)	Critical distance (d_{cr})	Optimal Distance (d_{op})
(a)	2.895 eV	33 Å	340 Å
(b)	2.5 eV	70 Å	210 Å
(c)	2.755 eV	120 Å	280 Å

Figure Captions

1. Geometrical arrangement of the photodissociation process.
2. Distortion of the Lorentzian line profile for various molecule-surface distances for a perpendicular molecular dipole. The system consists of an I_2 molecule on a silver sinusoidal grating. Refer to the text for numerical data.
3. Enhancement factor vs. molecule-surface distance for various incident laser frequencies. (a) E_γ = 2.895 eV (at plasmon resonance), (b) E_γ = 2.5 eV and (c) E_γ = 2.755 eV (at molecular resonance). Other parameters are the same as in Fig. 1.

Figure 1

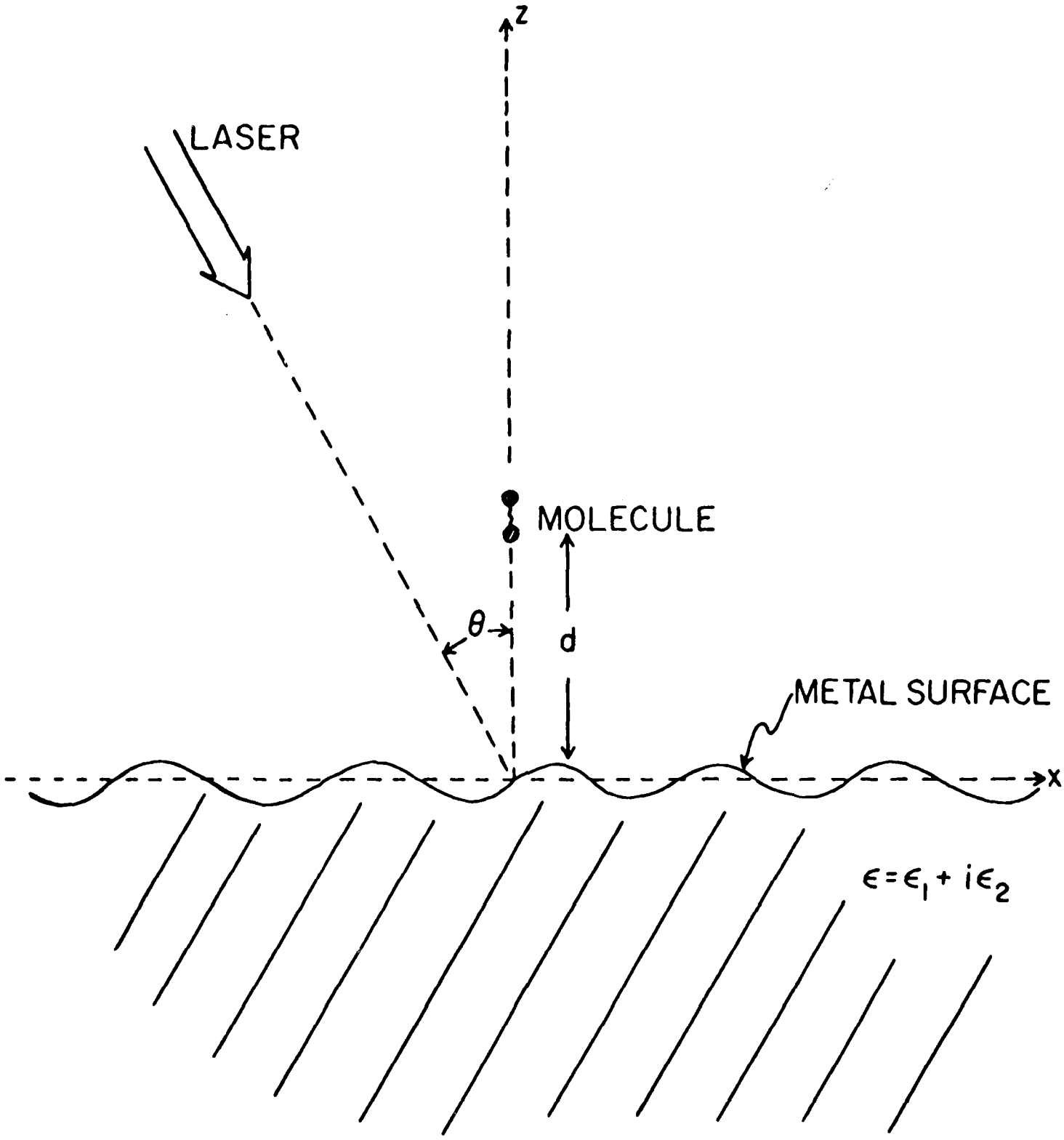
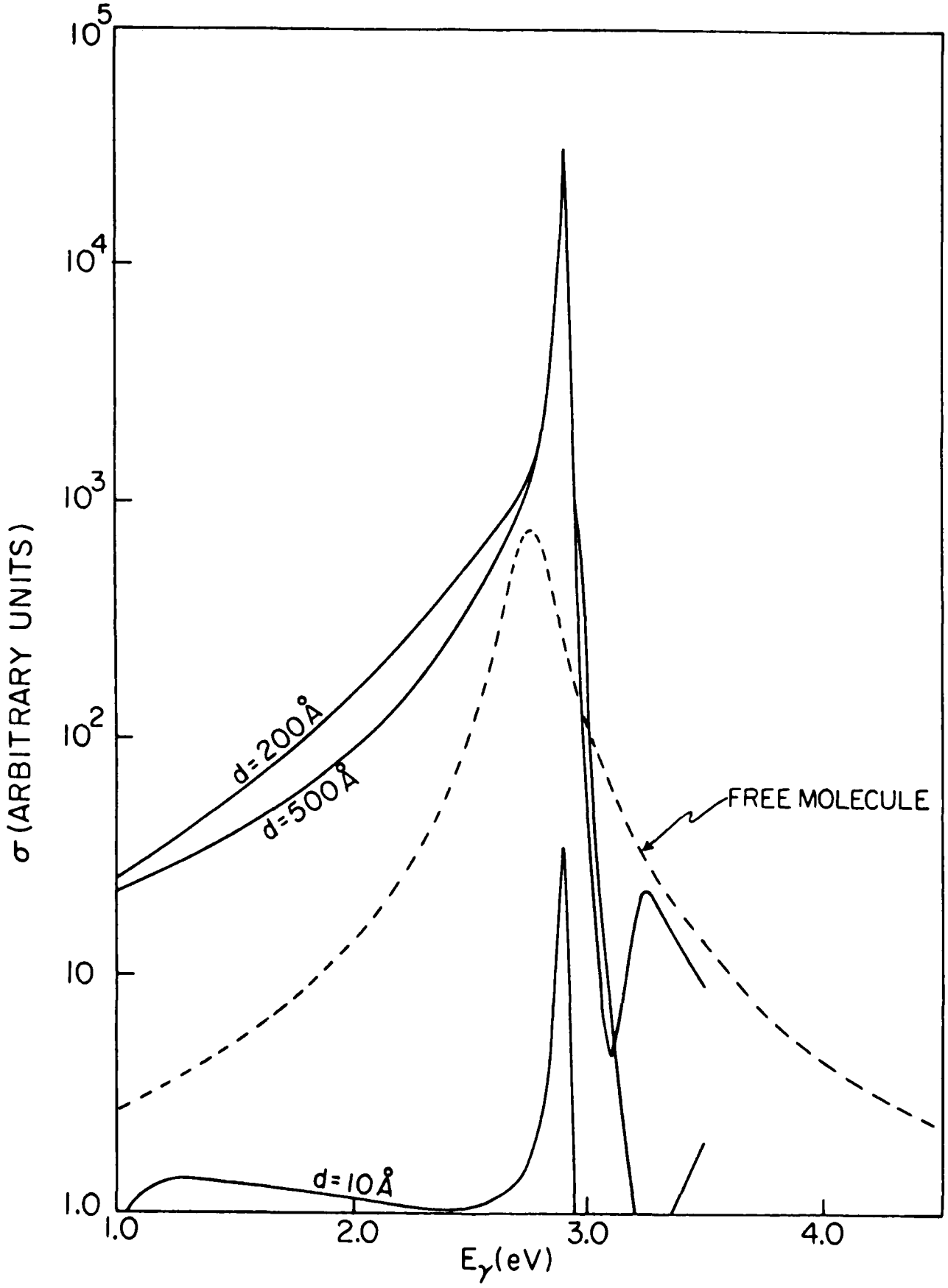


Figure 2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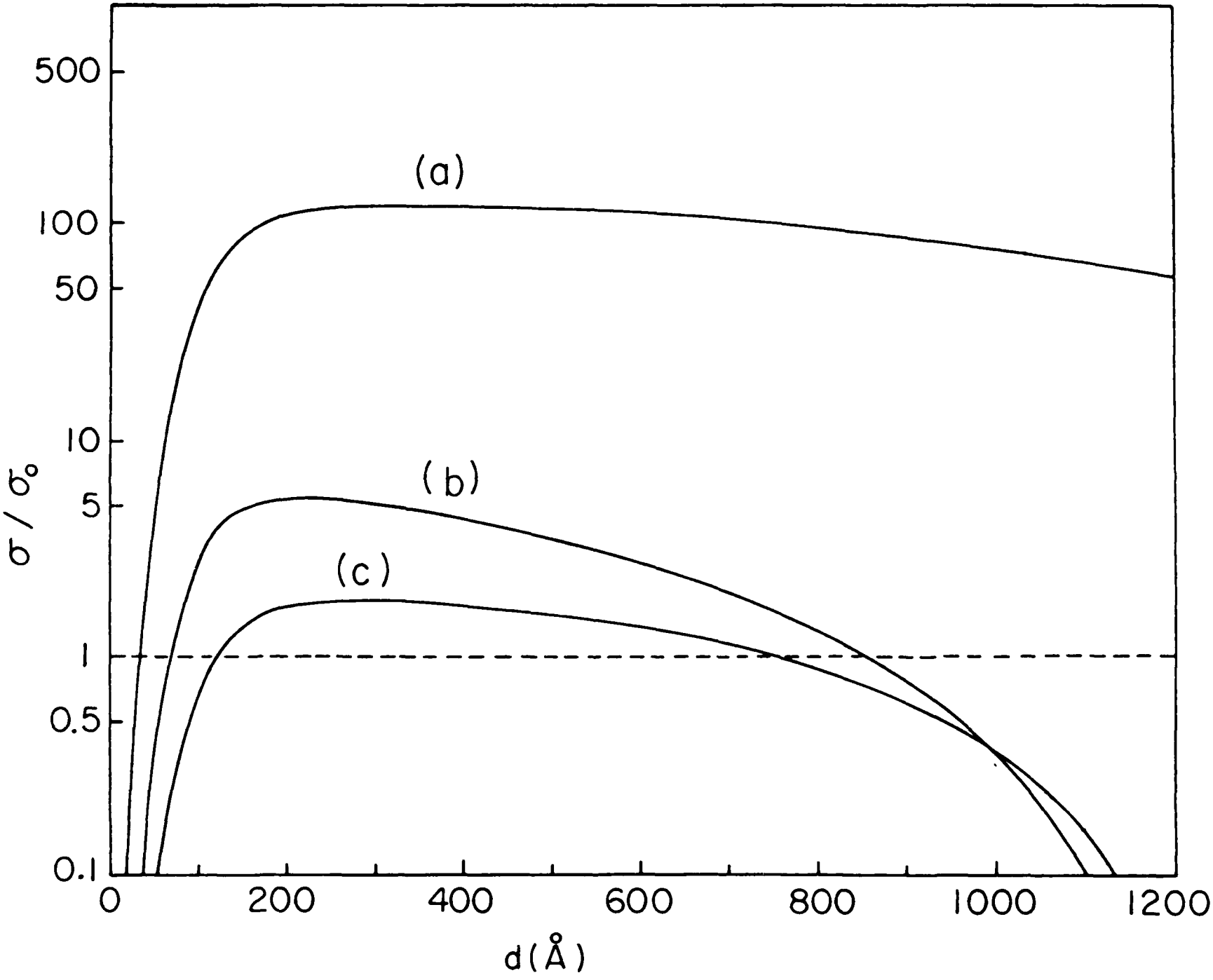

Figure 3

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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
Surface Chemistry Division (6170)
455 Overlook Avenue, S.W.
Washington, D.C. 20375

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

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. P. Lund
Department of Chemistry
Howard University
Washington, D.C. 20059

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Dr. F. Carter
Code 6132
Naval Research Laboratory
Washington, D.C. 20375

Dr. Richard Colton
Code 6112
Naval Research Laboratory
Washington, D.C. 20375

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 5570
Naval Research Laboratory
Washington, D.C. 20375

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

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

Dr. K. C. Janda
California Institute of Technology
Division of Chemistry and Chemical Engineering
Pasadena, California 91125

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

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

Dr. Martin Fleischmann
Department of Chemistry
Southampton University
Southampton S09 5NH
Hampshire, England

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

Dr. Richard Smardzewski
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

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

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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
Division of Chemistry
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, NewYork 12181

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

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

Dr. J. Baldeschwieler
California Institute of Technology
Division of Chemistry
Pasadena, California 91125

ABSTRACTS DISTRIBUTION LIST, 056/625/629

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

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

Dr. W. Goddard
Division of Chemistry
California Institute of Technology
Pasadena, California 91125

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

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

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

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

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

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

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

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

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

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

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

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