

AD-A185 754

CLASSICAL DECAY RATES FOR MOLECULES IN THE PRESENCE OF
A SPHERICAL SURFAC. (U) STATE UNIV OF NEW YORK AT
BUFFALO DEPT OF CHEMISTRY Y S KIM ET AL. OCT 87

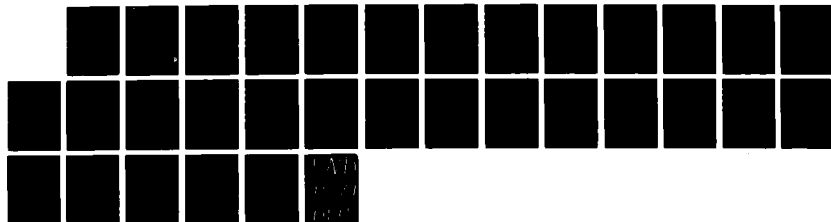
1/1

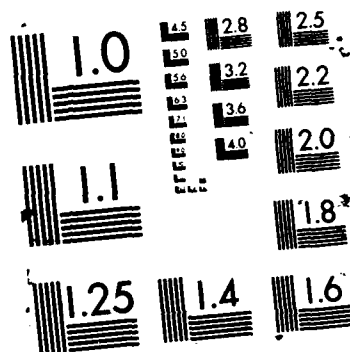
UNCLASSIFIED

UBUFFALO/DC/87/TR-55 N00014-86-K-0043

F/G 7/4

NL





(2)

AD-A185 754

Classical Decay Rates for Molecules in the Presence of a Spherical Surface:A Complete Treatment

Young Sik Kim*
Department of Chemistry
University of Rochester
Rochester, New York 14629

P. T. Leung 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 comprehensive treatment of the classical decay rates for a molecule in the vicinity of a spherical surface is presented through the application of the work of van del Pol and Bremmer and that of Fock. This theory takes full advantage of the Hertz vector formalism, which is mathematically simpler than the widely-adapted Lorenz-Mie approach which uses the complicated vector harmonic expansions. Results are obtained for both radiative and nonradiative transfer when the molecule is located outside or inside the surface. Numerical results are given for the cases of a surface, cavity and "aerosol", and comparison with other works are made.

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

NOV 12 1987

*Present address: Departments of Chemistry and Physics & Astronomy
239 Fronczak Hall
State University of New York at Buffalo
Buffalo, New York 14260

87 10 28 154

I. INTRODUCTION

Ever since the role of surface roughness was recognized as prominent in leading to such dramatic surface phenomena as surface-enhanced Raman scattering and other photochemical processes,¹ the problem of the decay rates for molecules in the vicinity of a spherical particle has been investigated intensively.²⁻⁵ While the classical electromagnetic approach has been followed to establish the results for the reduced (normalized) decay rates in both the electrostatic limit² and the more exact electrodynamical treatment,³⁻⁵ we feel that a complete analysis of such a problem has not yet been available in the literature. Given two possible orthogonal orientations of the molecule (radial/tangential), the two possible locations of the molecule (outside/inside the sphere) and the two different kinds of energy transfers during the decay process (radiative/nonradiative), there are altogether eight problems to be solved. In a paper following the analogous treatment of Chance, Prock and Silbey for a flat surface,⁶ Ruppin solved the complete problem for a molecule located outside the sphere.³ Very recently, Chew⁴ published results using the energy flux method^{3,6} for both the cases where the molecule is located outside and inside the sphere, and the equivalence with the results obtained from Green's dyadic method⁶ is proven in the limit where all the dielectric constants are real. Hence, all the nonradiative transfers are ignored in Chew's treatment.⁴ As a matter of fact, Eqs. (6) and (7) in Ref. 4 are identical to the results for radiative transfer for a molecule located outside the sphere as given in Eqs. (27) and (28) in Ruppin's work.³ Hence, combining the work of Ruppin³ and Chew,⁴ we conclude that six of the eight problems are solved, leaving the two problems of nonradiative rates for a molecule inside the sphere to be solved. Moreover, all these past treatments have been based on the Lorenz-Mie theory⁷ established by the expansion of the field quantities using vector spherical harmonics.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A185754

REPORT DOCUMENTATION PAGE

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/87/TR-55			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 NOS.		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT NO.		
11. TITLE Classical Decay Rates for Molecules in the Presence of a Spherical Surface: A Complete Treatment					
12. PERSONAL AUTHOR(S) Young Sik Kim, P. T. Leung and Thomas F. George					
13a. TYPE OF REPORT		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Yr., Mo., Day) October 1987	
				15. PAGE COUNT 25	
16. SUPPLEMENTARY NOTATION Prepared for publication in Surface Science					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	SPHERICAL SURFACE		
			NEARBY MOLECULE		
			CLASSICAL DECAY RATE		
			RADIATIVE AND NONRADIATIVE HERTZ VECTOR FORMALISM CAVITY AND AEROSOL		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A comprehensive treatment of the classical decay rates for a molecule in the vicinity of a spherical surface is presented through the application of the work of van del Pol and Bremmer and that of Fock. This theory takes full advantage of the Hertz vector formalism, which is mathematically simpler than the widely-adapted Lorenz-Mie approach which uses the complicated vector harmonic expansions. Results are obtained for both radiative and nonradiative transfer when the molecule is located outside or inside the surface. Numerical results are given for the cases of a surface, cavity and "aerosol", and comparisons with other works are made.					
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 NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0043

TECHNICAL REPORT No. 55

Classical Decay Rates for Molecules in the Presence of a Spherical
Surface: A Complete Treatment

by

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

Prepared for Publication

in

Surface Science

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

October 1987

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.



For	
DTIC	☒
ON&I	☐
DTIC TAB	☐
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or
	Special

In this present work, we present a complete solution of the eight problems via a different approach, namely, the Hertz vector formalism.^{5,6} This formalism has a mathematically simpler feature, since the expansions of the Hertz functions are more of a scalar type, and one can see easily from the Green's function property that there exists a simple transformation which relates the fields for the outside-molecule case to those where the molecule is located inside the sphere. Hence it is not necessary to solve again the boundary value problem for the inside-molecule case as is done in Chew's work.⁴ We elaborate the theory in Sec. II, where we shall see that for the case where the molecule is inside a sphere with a complex dielectric constant, a straightforward application of the methods of Ruppin³ and Chew⁴ is not appropriate, such that one must resort to more microscopic models for the treatment of the bulk decay rates (i.e., in the absence of the surface). Numerical examples are given in Sec. III, where we shall illustrate that the neglect of the nonradiative rates as in Chew's formalism can lead to serious errors in some cases. Discussion and conclusion of the present work are given in Sec. IV.

II. Theory

It is well known that the electromagnetic scattering problem in the presence of a dielectric sphere can in general be formulated in two different ways. While the scattering of a plane wave from a sphere has been well treated in both the Lorenz-Mie approach⁷ and the Hertz vector (Debye potential) approach,⁸ it seems that the problem of dipole-sphere interactions (hence the problem of molecular lifetimes) has always been treated by the former approach using the vector harmonics expansion.^{3,4} Here we want to solve the lifetime problem in the Hertz vector ($\vec{\Pi}$) formalism using expansions in ordinary spherical functions. For those mathematical results which have been obtained already by

the former approach, we shall only indicate briefly how the same results may be obtained in our present approach, with possible simplifications being emphasized.

For a dipole located outside the sphere, the problem has been solved for both the vertical (radial)⁹ and the horizontal (tangential)¹⁰ dipoles. Assuming nonmagnetic media and the region outside (inside) the sphere (of radius a) to be characterized by the local dielectric function ϵ_1 (ϵ_2), the Hertz vectors (along the radial direction) can then be expressed in the following series expansions in terms of the various "Mie coefficients":

For a vertical dipole located at $(d, 0, 0)$ with $y_1 = k_1 d$, $\rho_1 = k_1 a$ and $k_1 = \sqrt{\epsilon_1} \omega/c$,⁹

$$\Pi_1 = \begin{cases} ik_1 \sum_{n=0}^{\infty} (2n+1) h_n^{(1)}(y_1) [j_n(k_1 r) + B_n h_n^{(1)}(k_1 r)] P_n(\cos \theta) & , \quad a < r < d \\ ik_1 \sum_{n=0}^{\infty} (2n+1) [j_n(y_1) + B_n h_n^{(1)}(y_1)] h_n^{(1)}(k_1 r) P_n(\cos \theta) & , \quad d < r \end{cases} \quad (1)$$

$$\Pi_2 = \frac{ik_1^3}{k_2^2} \sum_{n=0}^{\infty} (2n+1) [j_n(\rho_1) + B_n h_n^{(1)}(\rho_1)] \frac{h_n^{(1)}(y_1)}{j_n(\rho_2)} j_n(k_2 r) P_n(\cos \theta) \quad , \quad r < a \quad (2)$$

where j_n and $h_n^{(1)}$ are the ordinary spherical Bessel and Hankel functions. The nonvanishing field components are then given by

$$E_r = \frac{1}{rd \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \Pi}{\partial \theta}) \quad , \quad (3a)$$

$$E_\theta = \frac{1}{rd} \frac{\partial^2}{\partial r \partial \theta} (r \Pi) \quad , \quad (3b)$$

$$H_{\phi} = -\frac{ic}{\omega} k^2 \frac{\partial \Pi}{\partial \theta} \quad (3c)$$

For a horizontal dipole located at $(d, 0, 0)$, we need two Hertz vectors with one along $\hat{r}$ and one along $\hat{\theta}$, given by $(i=1,2)^{10}$

$$\Pi_i^E = -\cos\phi \frac{\partial P_i}{\partial \theta} \quad (4)$$

$$\Pi_i^H = -\sin\phi \frac{\partial Q_i}{\partial \theta} \quad (5)$$

where P, Q are expressed in series form as (with $\psi_n(x) \equiv x j_n(x)$ and $\zeta_n(x) \equiv x h_n^{(1)}(x)$)

$$P_1 = \begin{cases} -\frac{1}{rd} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \zeta'_n(y_1) [\psi_n(k_1 r) + B_n \zeta_n(k_1 r)] P_n(\cos\theta) & , \quad a < r < d \\ -\frac{1}{rd} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [\psi'_n(y_1) + B_n \zeta'_n(y_1)] \zeta_n(k_1 r) P_n(\cos\theta) & , \quad d < r \end{cases} \quad (6)$$

$$P_2 = \frac{k_1^2}{ad} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} D_n^{-1} \zeta'_n(y_1) j_n(k_2 r) P_n(\cos\theta) \quad , \quad 0 < r < a \quad (7)$$

$$Q_1 = \begin{cases} k_1^2 \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} h_n^{(1)}(y_1) [j_n(k_1 r) + A_n h_n^{(1)}(k_1 r)] P_n(\cos\theta) & , \quad a < r < d \\ k_1^2 \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [j_n(y_1) + A_n h_n^{(1)}(y_1)] h_n^{(1)}(k_1 r) P_n(\cos\theta) & , \quad d < r \end{cases} \quad (8)$$

$$Q_2 = \frac{ik_1}{a} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} C_n^{-1} h_n^{(1)}(y_1) j_n(k_2 r) P_n(\cos\theta) , \quad 0 < r < a . \quad (9)$$

The nonvanishing field components are then given by

$$E_r = \frac{1}{r} L^2 \Pi^E \quad (10a)$$

$$E_\theta = -\frac{1}{r} \frac{\partial^2}{\partial r \partial \theta} (r \Pi^E) + \frac{i\omega}{c \sin\theta} \frac{\partial \Pi^M}{\partial \phi} , \quad (10b)$$

$$E_\phi = -\frac{1}{r \sin\theta} \frac{\partial^2 (r \Pi^E)}{\partial r \partial \phi} - \frac{i\omega}{c} \frac{\partial \Pi^M}{\partial \theta} , \quad (10c)$$

$$H_r = -\frac{1}{r} L^2 \Pi^M , \quad (10d)$$

$$H_\theta = \frac{ick^2}{\omega \sin\theta} \frac{\partial \Pi^E}{\partial \phi} + \frac{1}{r} \frac{\partial^2 (r \Pi^M)}{\partial r \partial \theta} , \quad (10e)$$

$$H_\phi = -i \frac{ck^2}{\omega} \frac{\partial \Pi^E}{\partial \theta} + \frac{1}{r \sin\theta} \frac{\partial^2 (r \Pi^M)}{\partial r \partial \phi} . \quad (10f)$$

with

$$L^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} .$$

The "Mie coefficients" in the above equations are defined as

$$A_n = \frac{j_n(\rho_1) \psi'_n(\rho_2) - j_n(\rho_2) \psi'_n(\rho_1)}{j_n(\rho_2) \zeta'_n(\rho_1) - h_n^{(1)}(\rho_1) \psi'_n(\rho_2)} ,$$

$$B_n = \frac{\epsilon_1 j_n(\rho_1) \psi'_n(\rho_2) - \epsilon_2 j_n(\rho_2) \psi'_n(\rho_1)}{\epsilon_2 j_n(\rho_2) \zeta'_n(\rho_1) - \epsilon_1 h_n^{(1)}(\rho_1) \psi'_n(\rho_2)} , \quad (11)$$

$$C_n = j_n(\rho_2) \zeta'_n(\rho_1) - h_n^{(1)}(\rho_1) \psi'_n(\rho_2) ,$$

$$D_n = \epsilon_2 j_n(\rho_2) \zeta'_n(\rho_1) - \epsilon_1 h_n^{(1)}(\rho_1) \psi'_n(\rho_2) .$$

From this formulation and by making use of the well-known properties of Green's functions, we can easily obtain via a simple transformation T the solution for the reflected and transmitted fields for the case where the dipole is located inside the sphere without having to solve again the boundary value problem.⁴ If we define T by

$$T \begin{pmatrix} j_n \\ h_n^{(1)} \\ k_1, \epsilon_1, \dots \\ k_2, \epsilon_2, \dots \end{pmatrix} = \begin{pmatrix} h_n^{(1)} \\ j_n \\ k_2, \epsilon_2, \dots \\ k_1, \epsilon_1, \dots \end{pmatrix} , \quad (12)$$

then it is not difficult to check that the "inside solutions" are easily obtained from the outside solutions through the operation with T .

Now let us apply the above results for our decay rate problem. According to the classical approach, there are two different methods for calculating the decay rate of the molecule as induced by the presence of the surface. In the Green's dyadic approach, the dipole is modeled as a damped harmonic oscillator being driven by the surface field. The induced decay rate is then given by⁶

$$\gamma = \gamma_0 + \frac{a}{\omega} \text{Im } G , \quad (13)$$

where γ_0 is the decay rate in the absence of the boundary surface (i.e., with the whole space filled with the dielectric medium in which the dipole is located), $\alpha = e^2/m$, ω being the emission frequency (which is assumed to change negligibly), and $\text{Im } G$ is the imaginary part of the dyadic function defined as the surface field (E_R) reflected at the dipole site per unit dipole moment ($\vec{\mu}$). The other approach would be to calculate the rate of the energy carried away from the molecule, which can further be divided into that radiated to infinity [radiative (R) transfer] and that lost in the form of Joule heat into any dissipative medium present [nonradiative (NR) transfer]. Hence, combining these two approaches, the total rate given by Eq. (13) can be written as

$$\gamma = \gamma^R + \gamma^{NR} \quad (14)$$

with³

$$\gamma^R = \frac{1}{W} \int_{(r \rightarrow \infty)} d\Omega \, r^2 \, \vec{S} \cdot \hat{n} \quad , \quad (15)$$

and

$$\gamma^{NR} = \frac{1}{2W} \int_V d\tau \, \sigma \, |\vec{E}|^2 \quad . \quad (16)$$

Here $\vec{S} = \frac{c}{8\pi} \text{Re}(\vec{E} \times \vec{H}^*)$ is the Poynting vector, $\sigma = \frac{\omega}{4\pi} \text{Im } \epsilon$ is the conductivity of the dissipative medium, and $W = \omega^2 \mu^2 / 2\alpha$ is the average energy of the dipole. The integral in Eq. (15) is over a surface at infinity, and that in Eq. (16) is over the volume of the dissipative medium. Very often, the Joule heat integral is quite complicated,³ and one can obtain it indirectly through Eqs. (13)-(15). We

shall apply the fields obtained from Eqs. (1)-(10) to calculate the γ 's given in Eqs. (13)-(15) for the following three cases:

Case (1): The surface problem

Here $\vec{\mu}$ is located in vacuum ($\epsilon_1 = 1$) outside a sphere of dielectric constant $\epsilon_2 = \epsilon' + i\epsilon''$, and γ_0 is then given by $\frac{1}{3}ck_1^4\mu^2/W = 2ak_1^3/3\omega$. Using Eqs. (1), (3a) and (13), we obtain for a vertical dipole⁴

$$\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} (2n+1)n(n+1)B_n \left[\frac{h_n^{(1)}(y_1)}{y_1} \right]^2. \quad (17)$$

Furthermore, using Eqs. (1)-(3), the Poynting vector can readily be calculated, and from Eq. (15) we obtain^{3,4}

$$\frac{\gamma_1^R}{\gamma_0} = \frac{3}{2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \left| \frac{j_n(y_1) + B_n h_n^{(1)}(y_1)}{y_1} \right|^2. \quad (18)$$

Similarly, using Eqs. (4)-(10), (13) and (15), we obtain the corresponding results for a horizontal dipole

$$\frac{\gamma_1}{\gamma_0} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} (n+\frac{1}{2}) \{ B_n \left[\frac{\zeta_n'(y_1)}{y_1} \right]^2 + A_n [h_n^{(1)}(y_1)]^2 \}, \quad (19)$$

$$\frac{\gamma_1^R}{\gamma_0} = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \{ |j_n(y_1) + A_n h_n^{(1)}(y_1)|^2 + \left| \frac{\psi_n'(y_1) + B_n \zeta_n'(y_1)}{y_1} \right|^2 \}. \quad (20)$$

The nonradiative rates can then be obtained from the difference between the total and radiative rates.

Case (ii): The cavity problem

Here $\vec{\mu}$ is located inside a spherical vacuum ($\epsilon_2 = 1$) with a dielectric ($\epsilon_1 = \epsilon' + i\epsilon''$) occupying the whole space outside the vacuum. The total decay rates can readily be obtained from the outside solutions (Eqs. (17) and (19)) through the transformation T (Eq. (12)) as discussed above, whereby we obtain¹¹

$$\frac{\gamma_{\perp}}{\gamma_0} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} (2n+1)n(n+1) E_n \left[\frac{j_n(y_2)}{y_2} \right]^2, \quad (21)$$

$$\frac{\gamma_{\parallel}}{\gamma_0} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} \left(n + \frac{1}{2} \right) \left\{ E_n \left[\frac{\psi'_n(y_2)}{y_2} \right]^2 + F_n j_n^2(y_2) \right\}, \quad (22)$$

with E_n and F_n given by

$$E_n = T\{B_n\}, \quad (23)$$

$$F_n = T\{A_n\}. \quad (24)$$

We want to remark that in this configuration the decay rates can only be purely radiative or purely nonradiative, depending on whether the outside medium is transparent ($\epsilon'' = 0$) or dissipative ($\epsilon'' \neq 0$) with respect to the molecular emission frequency. Furthermore, it is interesting to note that in the perfectly-conducting limit ($|\epsilon_2| \gg |\epsilon_1|$) where we have⁴

$$A_n \approx -j_n(\rho_1)/h_n^{(1)}(\rho_1) ,$$

$$B_n \approx -\psi_n'(\rho_1)/\zeta_n'(\rho_1) , \quad (25)$$

both Eqs. (21) and (22) vanish. Thus, in the present classical treatment, the molecular lifetime becomes infinite in a perfectly-conducting cavity. This is understandable since in this approach only two mechanisms can "cause" the molecule to decay, i.e., either for energy being brought to infinity (radiative transfer) or dissipated into a host medium (nonradiative transfer). Since no field can penetrate into the perfect conducting environment and hence both these transfers cannot occur, it is not surprising to see that both decay rates vanish in Eqs. (21) and (22). In the more exact quantum treatment, however, the vanishing of the decay rates in a perfectly-conducting cavity can only restrictively occur.¹²

Case (iii): The "aerosol" problem¹³

Here $\vec{\mu}$ is located inside a dielectric sphere ($\epsilon_2 = \epsilon' + i\epsilon''$) with the outside being vacuum ($\epsilon_1 = 1$). We shall further divide this into the following two cases for discussion:

(a) Transparent dielectric

This case has already been treated by Chew.⁴ In the present approach, the total decay rate can again be obtained directly from Eqs. (17) and (19) through T . With γ_0 being given by $\frac{1}{3}ck_2^4\epsilon_2^{-3/2}\mu^2/W = 2\alpha k_2^3/3\omega\epsilon_2$,⁴ we obtain the same expressions as given in Eqs. (21)-(24). The radiative transfers in this case can similarly be obtained as in Eqs. (18) and (20) via the transformation $\vec{E}_{in} = T\{\vec{E}_{out}\}$ to give⁴

$$\frac{\gamma_{\perp}^R}{\gamma_0} = \frac{3}{2} \epsilon_2^{3/2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \left| \frac{j_n(y_2)}{\rho_2 y_2 D_n} \right|^2, \quad (26)$$

$$\frac{\gamma_{\parallel}^R}{\gamma_0} = \frac{3}{4} \epsilon_2^{3/2} \sum_{n=1}^{\infty} (2n+1) \left\{ \left| \frac{\psi'_n(y_2)}{\rho_2 y_2 D_n} \right|^2 + \left| \frac{j_n(y_2)}{\rho_2 \sqrt{\epsilon_2} C_n} \right|^2 \right\}. \quad (27)$$

In this case, since ϵ_2 is real (transparent, $\epsilon'' = 0$), there is no dissipative (nonradiative) effects, and it has been shown explicitly by Chew that the radiative rates in Eqs. (26) and (27) are identical to the total rates as given in Eqs. (21) and (22).

(b) Dissipative dielectric

This is the case which has not been discussed before in the context of "surface problems". Nevertheless, the same problem for a molecule in the bulk of an adsorptive medium has received considerable attention in the literature.¹⁴ The difficulty lies in the evaluation of γ_0 in Eq. (13). Obviously, the decay in a dissipative medium of infinite extent can only be nonradiative. However, if one applies Eq. (16) directly to calculate γ_0 in this case, one will get divergences in the integral due to the predominance of the near field in this case, unless one adopts a cutoff volume (forbidden volume¹⁴) in the lower bound of the integral.¹⁵ Moreover, this approach has been criticized by Agranovich and Dubovskii (AD),¹⁶ who proposed a more exact microscopic treatment which shows that the result from such macroscopic theory¹⁵ can be correct only under certain restrictive conditions. In the following, we shall make use of the results of AD to investigate the surface effects in Eq. (13).

According to AD, under the condition that the "Mössbauer-type" effect (in the optical region)¹⁷ can be neglected, γ_0 can be expressed in a form which is very similar to that obtained from Feinberg's theory,¹⁵

$$\frac{\gamma_0}{\gamma_{sp}} = \frac{32}{64\pi^4} \epsilon'' N_0 \lambda^3, \quad (28)$$

where γ_{sp} is the spontaneous decay of the free molecule, N_0 is the molecular number density of the dielectric medium, λ is the emission wavelength, and Z is a numerical factor depending on the lattice structure of the medium. A rough estimate gives $Z \sim 10$.¹⁶ Eq. (28) holds as long as λ is much greater than the lattice constant of the medium and the spatial dispersion of the dielectric constant ϵ'' can be neglected.¹⁶ Using Eqs. (13), (21), (22) and (28), we finally obtain the total decay rates for $\vec{\mu}$ in a dissipative dielectric sphere as

$$\frac{\gamma_{\perp}}{\gamma_0} = 1 + \frac{3}{2} f(\omega) \operatorname{Re}\{\sqrt{\epsilon_2} \sum_{n=1}^{\infty} (2n+1)n(n+1) E_n \left[\frac{j_n(y_2)}{y_2} \right]^2\}, \quad (29)$$

$$\frac{\gamma_{\parallel}}{\gamma_0} = 1 + \frac{3}{2} f(\omega) \operatorname{Re}\{\sqrt{\epsilon_2} \sum_{n=1}^{\infty} (n+\frac{1}{2}) [E_n \left(\frac{\psi'_n(y_2)}{y_2} \right)^2 + F_n j_n^2(y_2)]\}, \quad (30)$$

where $f(\omega) \equiv \gamma_{sp}/\gamma_0$ is the reciprocal ratio as given in Eq. (28). The radiative rates can analogously be obtained from Eqs. (26) and (27) by multiplying each of them by $f(\omega)$. The nonradiative rates can then be obtained again from the difference between the total and the radiative rates. Furthermore, for $\vec{\mu}$ located at the center of the sphere, we have results analogous to those for the case of a transparent sphere obtained by Chew⁴ where for a dissipative sphere are given by

$$\frac{\gamma_{\perp}}{\gamma_0} = \frac{\gamma_{\parallel}}{\gamma_0} = 1 + f(\omega) \operatorname{Re}(\sqrt{\epsilon_2} E_1) \quad , \quad (31)$$

$$\frac{\gamma_{\perp}^R}{\gamma_0} = \frac{\gamma_{\parallel}^R}{\gamma_0} = f(\omega) \left| \frac{\epsilon_2}{\rho_2 D_1} \right|^2 \quad . \quad (32)$$

III. Numerical Results

We have performed numerical studies for each of the above three classes of problems. For simplicity, we treat one of the two media as a vacuum ($\epsilon = 1$). The other medium, if it is transparent to the molecular emission, is taken to be glycerol with $\epsilon = 2.16$,^{4,13} and if it is dissipative, it is taken to be silver at $\lambda = 413$ nm with $\epsilon = -4.42 + 0.73 i$.¹⁸ Figure 1 shows the results for a dipole above a Ag spherical surface of radius $a = 100$ Å. We see that while the neglect of the nonradiative transfer (as in Chew's formulation) leads to somewhat lower values for γ for the radial dipole case, it leads to tremendous differences for the tangential dipole case as $r \rightarrow a$. This phenomenon also occurs in the flat-surface case, with its origin due to the parallel (antiparallel) orientation of the "image dipole" with respect to the normal (tangential) orientation of the source dipole.⁶ Of course, the extremely large values of the rates at $r = a$ are not physical either, and it is known that more reasonable values for γ at $r = a$ can be obtained by considering the spatial dispersion of the dielectric function of the substrate at close distances.¹⁹ Nevertheless, we should add that in all the numerical calculations of Ref. 4, the substrate sphere is taken either as transparent ($\epsilon'' = 0$) or as perfectly conducting (hence no penetration of fields and $\gamma^{NR} = 0$), so that the neglect of the nonradiative rates does not lead to any error in these cases.⁴

Figure 2 shows the results for a dipole in a cavity of radius $a = 4000 \text{ \AA}$. The outside medium is taken to have a real $\epsilon_1 = 2.16$. We observe that both radial and tangential dipoles decay at the same rate $(= 1 + \text{Re}E_1 \text{ (see Eq. (23))})^4$ at the center, with the tangential dipole showing appreciable oscillating behavior as the dipole is moving towards the cavity wall. We also note that both enhanced and diminished values (with respect to the free molecule case) for γ can occur in this case. Figure 3 shows the results for the same cavity problem with the outside medium being absorptive (Ag at $\lambda = 413 \text{ nm}$). We notice that there is no oscillating behavior, and the decay for this case is very small (unless the dipole is far away from the center) and purely dissipative in nature (we recall that in the extreme limit where the outside medium becomes perfectly conducting, the decay is zero as discussed in Sec. II).

Figures 4 and 5 show results for a dipole inside an "aerosol" of transparent and dissipative media, respectively. For the transparent case (radius $a = 4000 \text{ \AA}$), we again observe similar oscillatory behavior as for the flat-surface case and a possible "diminution effect" for the decay rate. For the dissipative case (radius $a = 1000 \text{ \AA}$), it is interesting to note that (for both orientations) most of the decays are nonradiative in nature, and the surface effect is hardly noticeable except when the molecule is very close to the surface. This means that most of the molecular deexcitation energy is dissipated within a very small region of the medium around the molecule, which can be understood from Eq. (28) showing that γ_0 is very large for molecular emission wavelengths. To have appreciable surface effects, one must look for much higher emission frequencies, which can occur, for example, in nuclear spectroscopy in the γ -ray range. Thus for our interest here which focuses on molecular lifetimes, the surface effect is hardly manifested.

IV. Conclusion

We have in this paper presented a complete treatment of the classical decay rates of a molecule in the vicinity of a spherical surface. We have adopted a different formulation of the dipole-sphere interaction problem via the Hertz vector formalism, which is distinct from the more common approach via the Lorenz-Mie expansions of the field quantities in terms of complicated vector spherical harmonics. We have explored all the eight problems as stated in the Introduction within this classical approach. Since this approach is limited to only two kinds of mechanisms (radiative and dissipative transfers) through which the molecular decay rates can be examined, some interesting features (e.g., possible enhanced decays for a perfectly-conducting cavity)¹² cannot be obtained in the present formalism. Recently, a quantum electrodynamical formalism (QED) of the spherical cavity problem was published,²⁰ although the electrostatic image concept was adopted and hence the dynamical nature of the dipole field was omitted. It would therefore be interesting to incorporate the dynamical dipole fields, as treated in our present paper, into the QED formalism to see if it would give rise to new interesting phenomena for the decay rate.

Acknowledgments

This research was supported by the Office of Naval Research, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, and the National Science Foundation under Grant CHE-8620274. The United States Government is authorized to reproduce and distribute reprints notwithstanding any copyright notation hereon.

References

1. See, e.g., H. Metiu, Prog. Surf. Sci. 17, 153 (1984); M. Moskovits, Rev. Mod. Phys. 57, 783 (1985).
2. J. I. Gersten and A. Nitzan, Surf. Sci. 158, 165 (1985) and references therein.
3. R. Ruppin, J. Chem. Phys. 76, 1681 (1982).
4. H. Chew, J. Chem. Phys. 87, 1355 (1987).
5. P. T. Leung and T. F. George, J. Chem. Phys. (in press). This article compares the static and the dynamic theories and gives an assessment of the accuracy of the former theory.
6. R. R. Chance, A. Prock and R. Silbey, Adv. Chem. Phys. 37, 1 (1978).
7. See, e.g., M. Kerker, The Scattering of Light and Other Electromagnetic Radiation (Academic, New York 1969).
8. See, e.g., A. B. Pluchino, Applied Optics 20, 2986 (1981).
9. B. van del Pol and H. Bremmer, Phil. Mag. XXIV, 141 (1937).
10. V. A. Fock, Sov. Phys. JETP 19, 916 (1949) (in Russian); see also V. A. Fock, Electromagnetic Diffraction and Propagation Problems (Pergamon, New York, 1965).
11. The solutions obtained here are essentially the dynamical version for the reaction fields in the Onsager model (cf. L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936)).
12. See e.g., M. Levenstein, T. W. Mossberg and R. J. Glauber, Phys. Rev. Lett. 59, 775 (1987), and references therein.
13. See, e.g., L. M. Polan, S. Arnold and S. D. Druger, Chem. Phys. Lett. 118, 322 (1985); J. Chem. Phys. (in press).
14. See the classic monograph by V. M. Agranovich and M. D. Galanin, Electronic Excitation Energy Transfer in Condensed Matter (North Holland, Amsterdam, 1982), and references therein.
15. E. L. Feinberg, JETP Lett. 7, 20 (1968).
16. V. M. Agranovich and O. A. Dubovskii, Sov. Phys.-Solid State 12, 1631 (1971).
17. A. Maradudin, Solid State Physics 18, 274 (1966).
18. See, e.g., E. D. Palik, Handbook of Optical Constants of Solids (Academic, New York, 1985).
19. G. W. Ford and W. H. Weber, Surf. Sci. 109, 451 (1981).

20. A. O. Barut and J. P. Dowling, Phys. Rev. A 36, 649 (1987).

Figure Captions

1. Transition rates for the two polarizations of an oscillator molecule outside a dielectric sphere of radius $a = 100 \text{ \AA}$ for $\lambda = 4133 \text{ \AA}$ and $\epsilon_2 = -4.42 + 0.73i$. The molecule is located at a distance d from the center, and T and R stand for the total and radiative transition rates, respectively. The solid curve is for the radial dipole, while the dashed curve is for the tangential dipole.
2. Transition rates for the two polarizations for an oscillator molecule in a vacuum cavity ($\epsilon_2 = 1$) of radius $a = 4000 \text{ \AA}$ for $\lambda = 4133 \text{ \AA}$ and $\epsilon_1 = 2.16$. The molecule is located at d from the center. The solid curve is for the radial dipole while the dashed curve is for the tangential dipole.
3. Same as Fig. 2, except that $\epsilon_1 = -4.42 + 0.73i$.
4. Transition rates for the two polarizations for an oscillator molecule inside a dielectric sphere of radius $a = 4000 \text{ \AA}$ for $\lambda = 4133 \text{ \AA}$ and $\epsilon_2 = 2.16$. The molecule is located at d from center. The solid curve is for the radial dipole while the dashed curve is for the tangential dipole.
5. Same as Fig. 4 except that $\epsilon_2 = -4.42 + 0.73i$ and $a = 1000 \text{ \AA}$.

Fig. 1

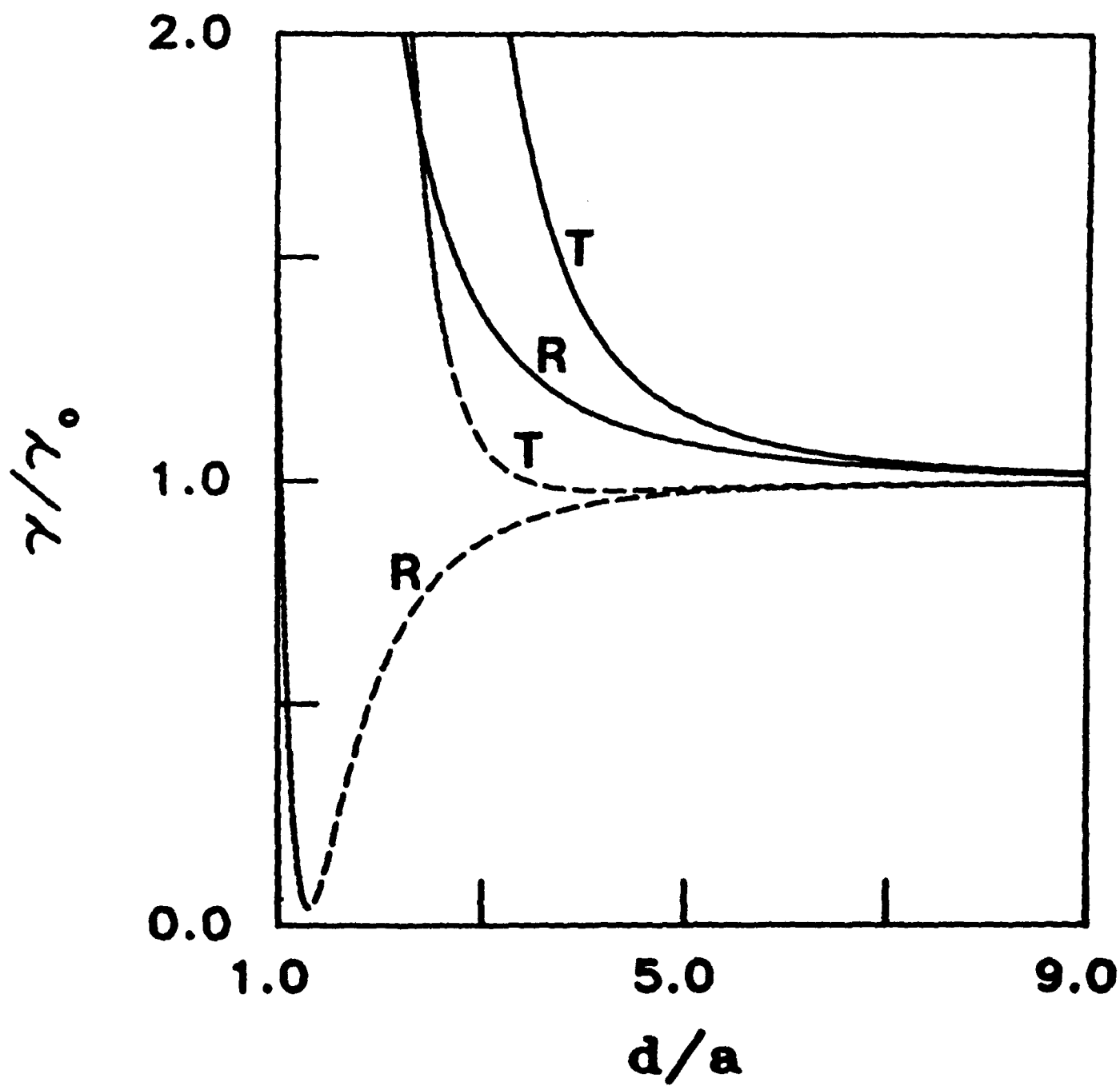


Fig. 2

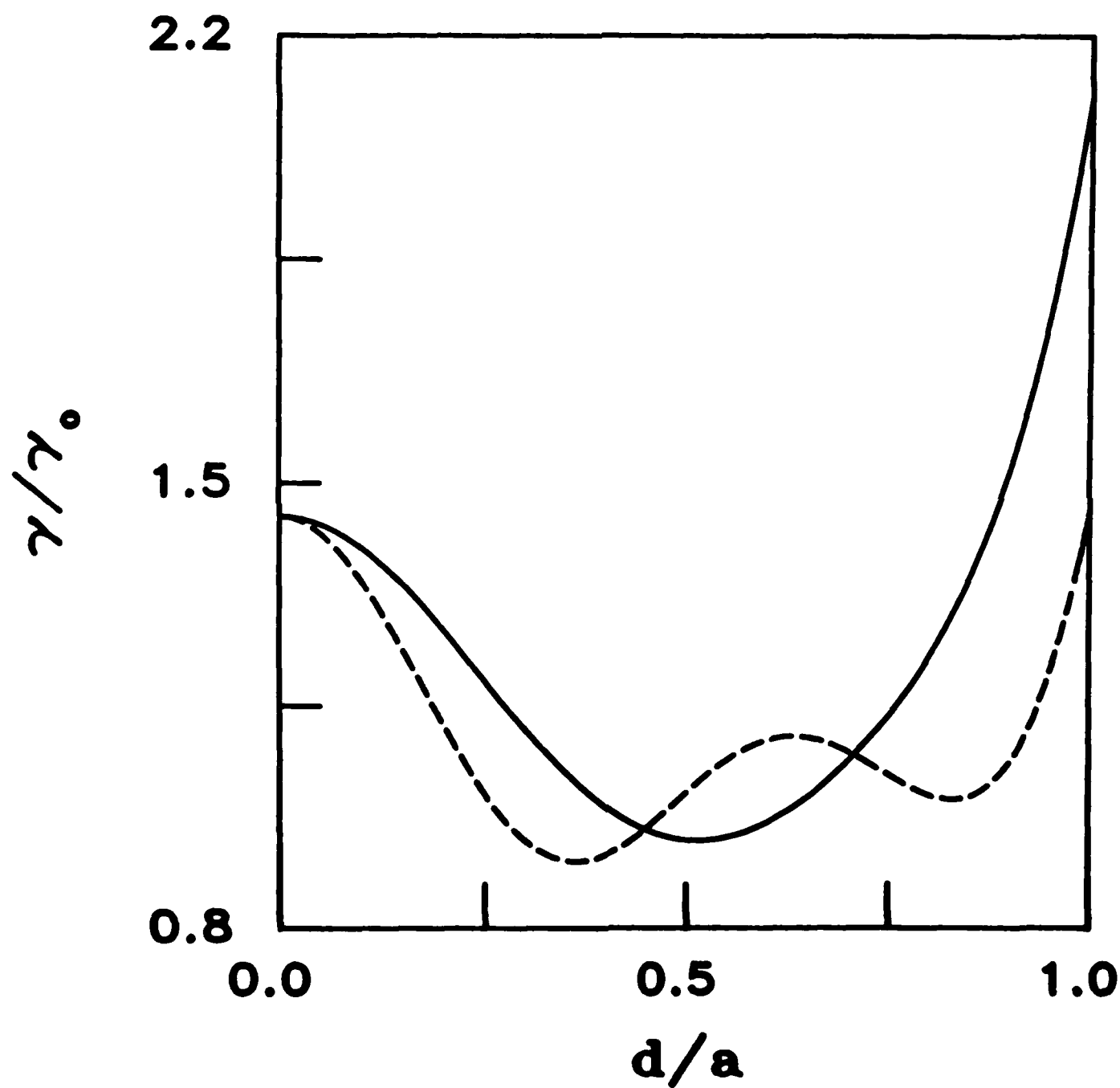


Fig. 3

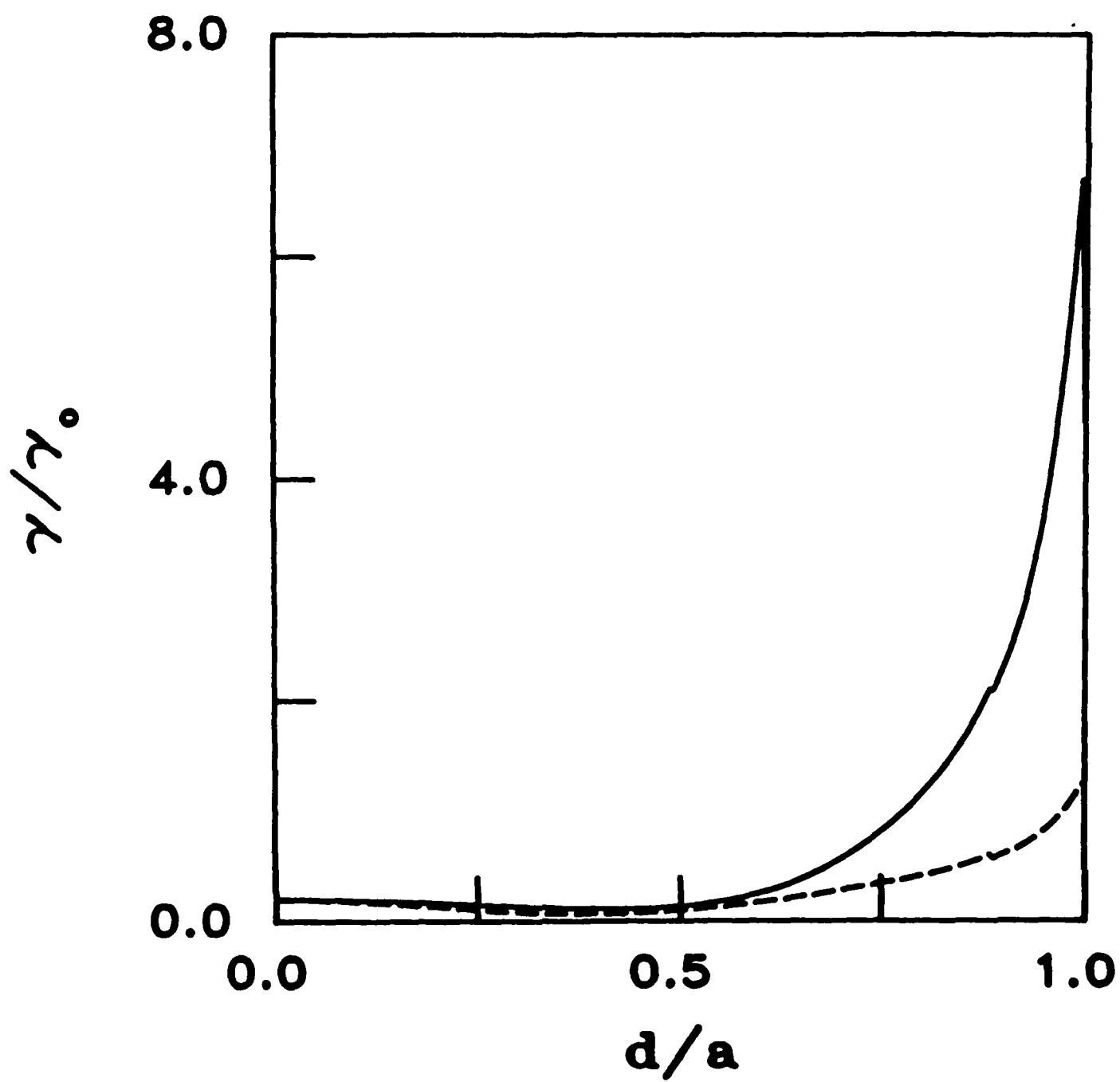


Fig. 4

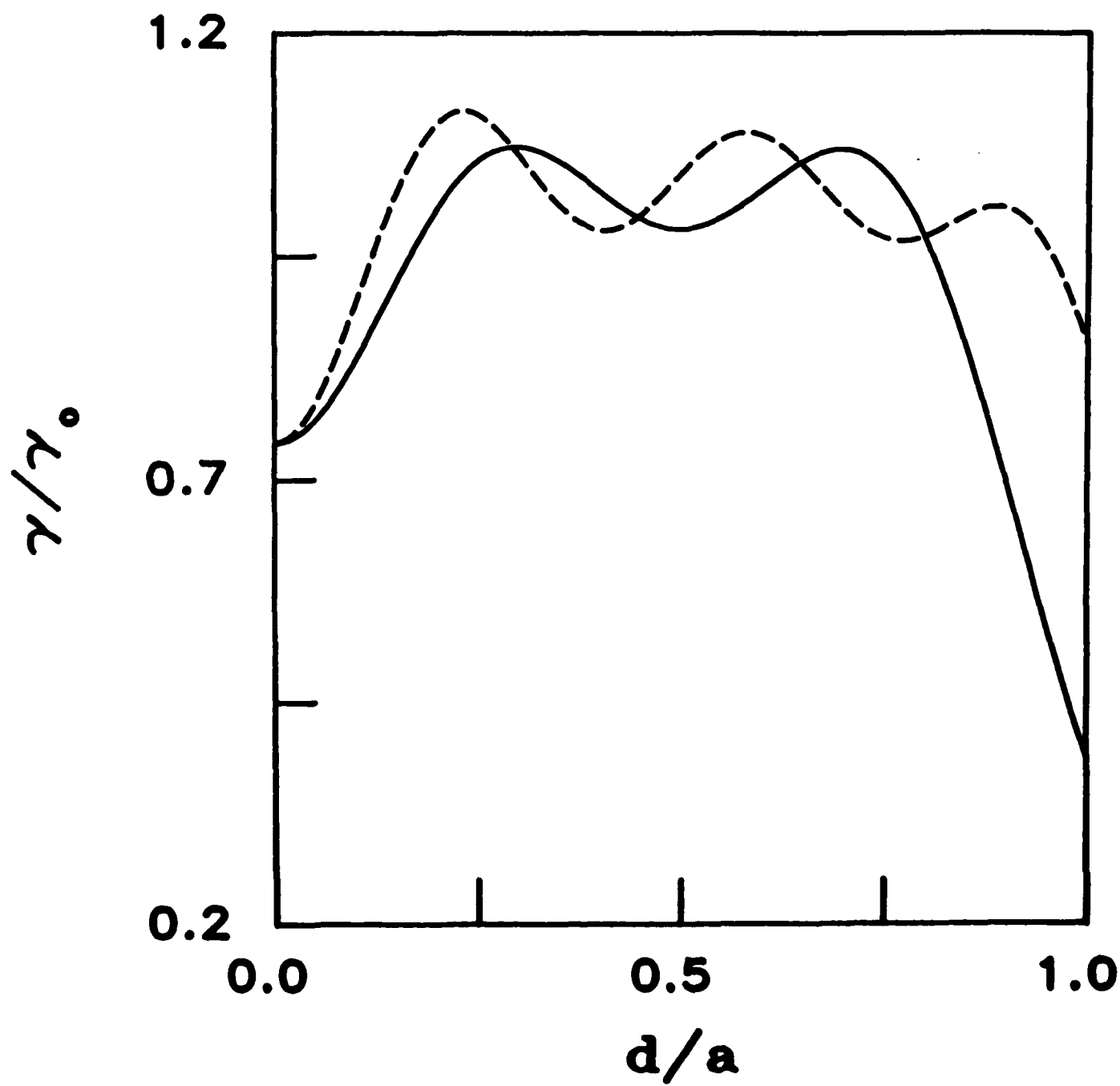
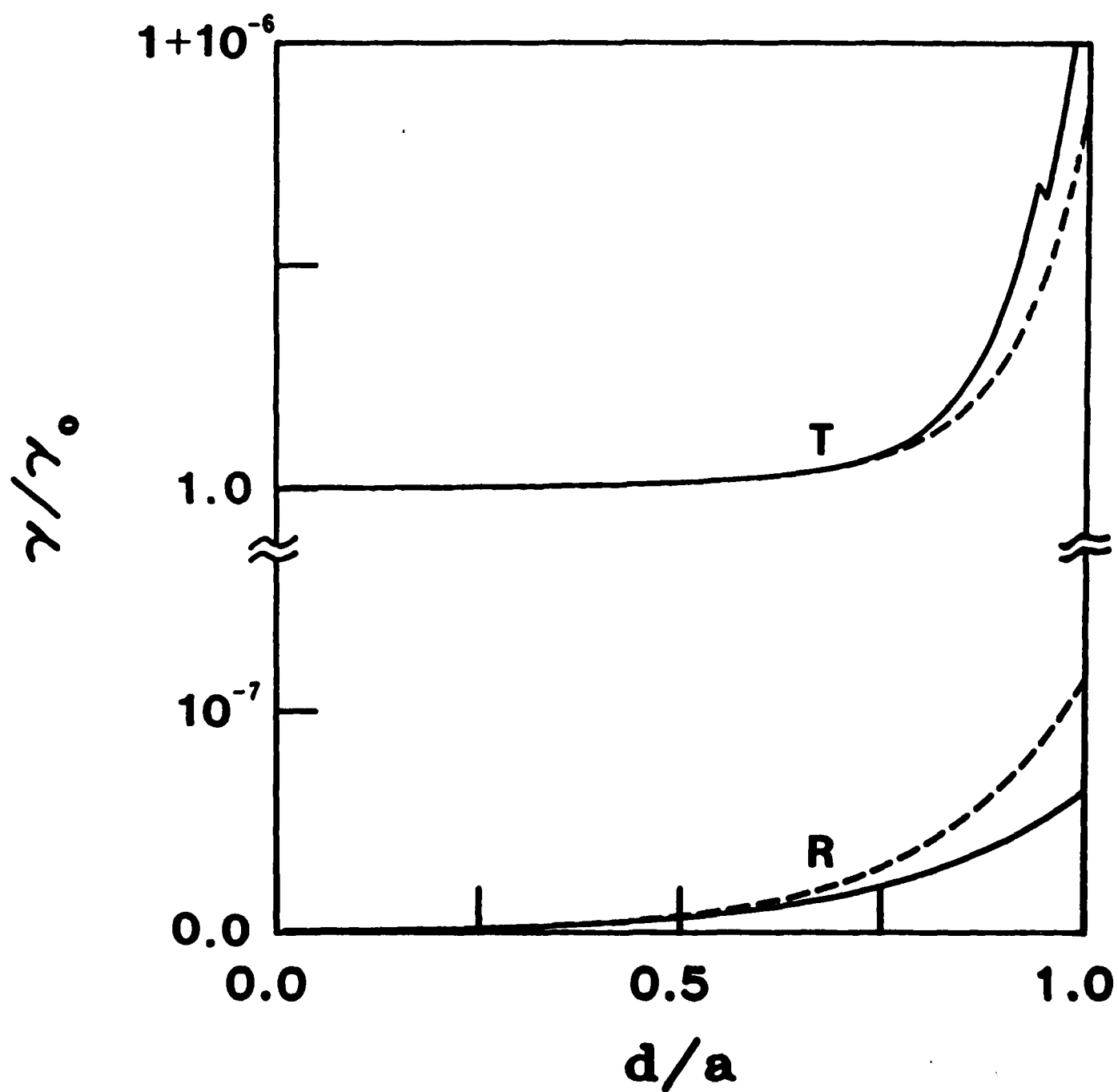


Fig. 5



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

Dr. A. Reisman
Microelectronics 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. 20375-5000

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

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

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

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

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

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

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

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

END

12-87

DTIC