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OFFICE OF NAVAL RESEARCH

Grant N00014-90-J-1193

TECHNICAL REPORT No. 23

Photodissociation Near a Rough Metal Surface: Effect of Reaction Fields

by

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Prepared for Publication

in

Journal of Chemical Physics

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

September 1990

Co

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

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/90/TR-23	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 Grant N00014-90-J-1193
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)*

Photodissociation Near a Rough Metal Surface: Effect of Reaction Fields

12. PERSONAL AUTHOR(S) Purna C. Das, Ashok Puri and Thomas F. George

13a. TYPE OF REPORT	13b. TIME COVERED FROM ______ TO ______	14. DATE OF REPORT *(Year, Month, Day)* September 1990	15. PAGE COUNT 31

16. SUPPLEMENTARY NOTATION

Prepared for publication in Journal of Chemical Physics

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

PHOTODISSOCATION, Chemical Reactions, SURFACE PLASMONS,
ROUGH METAL SURFACE, SILVER SUBSTRATE,
REACTION FIELDS, SURFACE BUMP, (JS)

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

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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

Journal of Chemical Physics, in press

Photodissociation Near a Rough Metal Surface: Effect of Reaction Fields

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Abstract

The modification of the photochemical dissociation rate of molecules in the presence of a rough metal surface is explored. Classical electromagnetic calculations are presented for the photodissociation rate of a point dipole near a rough surface modeled as a hemispheroidal bump on a semi-infinite flat plane. A correction is introduced by accounting for the reaction fields due to the dipole-substrate system radiating photons and coupling to delocalized surface plasmons. The effects of the shape and size of the bump and the separation of the molecule from the bump on the rate of photodissociation of the molecule are studied numerically.

1988 PACS Numbers: 82.65.Pa, 42.50.Kb, 68.35.Bs

I. Introduction

Ever since the discovery of surface-enhanced Raman scattering (SERS),[1] theoretical and experimental studies have been geared toward understanding the mechanism and possible applications of the interaction of laser radiation with atoms and molecules adsorbed on or near solid surfaces.[2] Gaining insight into the perturbations induced by the surface is the first step toward spectroscopic applications of a variety of surface optical phenomena which include vibrational spectroscopy of adsorbed molecules by SERS,[3] monitoring of surface processes by surface-enhanced nonlinear optics,[4-6] possible cooperative phenomena for an ensemble of admolecules,[7] surface-enhanced fluorescence for fabrication of sensor materials,[8-10] and possible enhanced photodissociation of adsorbates[11-18] with applications in chemical vapor deposition,[19] semiconductor fabrication,[20-25] and heterogeneous catalysis.[23,26]

Our interest in this paper lies in the possible enhanced photochemistry of adsorbates. Its potential technological applications to the fabrication and processing of materials depends not only on the cross section for a photodissociation process, but also on the subsequent photodynamics.[27] While the photochemistry of gas-phase molecules is relatively well understood, the role of the substrate and the degree of surface roughness in adsorbate photochemistry is a more recent topic of research. The presence of the surface allows energy and electron transfer mechanisms which may inhibit or enhance photofragmentation.[11-18] The type of substrate, whether metallic, insulator or semiconductor, also plays an important role in adsorbate photodissociation. Several groups have used insulator and semiconductor substrates, such as LiF(001),[14] Al_2O_3,[18] and Si(111) 7 × 7,[25] to study photochemistry. These substrates are good for detecting and measuring photodissociation and the associated dynamics of fragments, because the nonradiative relaxation rate of molecules on insulator and semiconductor surfaces is much less than that for metals, as predicted by the classical electromagnetic theory.[28,2,29] Rapid deexcitation of an adsorbate via nonradiative energy transfer to the metallic substrate has been attributed to the absence of photofragmentation of CH_2I_2 on Al or Ag, and phenyloctatrene on Ag.[18] More recently, for the adsorbate-metal systems CH_2CO/Pt(111) and CH_3Br/Pt(111),[15] and CH_3Br/Ni(111),[16] there is conclusive evidence that photofragmentation does take place without significant surface damping, but the photodynamics is perturbed due to charge transfer and collisional processes.[17,27] There is also evidence that much of UV surface photochemistry may be charge-transfer mediated at low coverages.[16,30]

The fragmentation yield is therefore determined by the relative rates of dissociation (direct as well as charge-transfer mediated) and nonradiative energy deposition into the substrate. Since nonradiative energy transfer to,[28,29] and photoemission from,[31] a rough surface are radically altered, one expects additional quenching of the photodissociation rate near a rough-surface. Furthermore, a model rough surface mav consist of a small particle above a flat surface. Therefore, one may expect rough surface effects to be a combination of the effects of a small particle and the flat plane.[32]

While model calculations of a dipole adsorbed on a silver sphere predicts some enhancement effects,[11] experimental results are mixed as far as enhancement of photodecomposition rate is concerned. For instance, photodegradation of rhodamine 6G shows no enhancement effects whatsoever.[12] On the other hand, enhanced photodissociation of surface-supported organic molecules has been reported.[13] The decomposition rate for about four monolayers of pyridine on a roughened silver surface has been found to have a peak for a spacer thickness of ~ 15 to 20 Å. It is believed that the discrepancies between the experiments are a result of the sensitive dependence of the effect on the nature of the surface and on the distance between the molecule and the surface. When chemical decomposition, which follows molecular excitation, is not fast relative to the surface-induced damping processes, which are dominant close to the surface, enhanced molecular absorption does not necessarily imply enhanced photochemical yield. The molecular energy transferred to the substrate, in turn causes excitation of electronic (surface plasmons) or ionic modes of the surface, or electron-hole pairs in the substrate.[27,33] If the surface modes are radiative,[34] part of the energy is recovered, while nonradiative surface modes act as a sink for the energy.

Typically, the electric field in the vicinity of a rough surface or a small particle, irradiated with an external source of light, is increased by two or three orders of magnitude over that in the absence of the surface. Therefore, under steady-state conditions, the power entering or leaving the molecule is increased by four to six orders of magnitude, although the power dissipated into any particular channel of decay is affected by the nature and characteristics of other channels of power flow. Representing the adsorbate-substrate system by a single "system dipole" above a flat surface and allowing this excited dipole to couple to surface plasmons of the underlying flat surface using the energy-transfer theory of Chance, Prock and Silbey,[28] and accounting for the loss of power to photon emission and resistive losses in the substrate medium electromagnetically, it has been shown[35] that the rates of decay of the dipole to both photons and surface plasmons are increased substantially, with increasing size of the bump, while the resistive loss rate remained unchanged. Under such enhanced power flow within the molecule-bump system, one is tempted to account for the electromagnetic reactions associated with the various modes of decay of the excited dipole. In fact, radiation damping alone has been shown,[36] in the context of SERS from a molecule near a spheroidal particle, to limit enhancement, particularly in the case of large-sized particles. Our goal in this paper, therefore, is to study the effect of correcting the local electromagnetic field, for reactive effects associated with photon radiation as well as coupling to a delocalized surface plasmon by the "system dipole". Within the domain of classical electromagnetism, the corrected local field is seen to better and more accurately predict the sensitive dependence of the photodissociation rate on molecule-surface separation.

The paper is organized in the following manner. In Sec. II, theoretical calculations of the cross section for photodissociation, the enhanced local field and the relative enhancement of molecular photochemistry near a surface are presented. In Sec. III, we present numerical results for the rate of photodissociation and its dependence on the shape and size of the bump, as well as on the separation between the molecule and the bump for a silver substrate, followed by a discussion.

II. Theory

Consider a molecule adsorbed on a rough surface and irradiated by an incident laser, whose electric field vector is denoted by $\vec{E}_0$. Let P be the total power transferred to the system while the molecule undergoes photochemical decomposition. The cross section σ for energy transfer to the molecule is defined as

$$\sigma = \left(\frac{8\pi}{c}\right) \Lambda \quad , \tag{1}$$

where $\Lambda \equiv P/|\vec{E}_0|^2$ and c is the speed of light in vacuum. If we denote the quantum efficiency of the molecule for photochemistry by η, then the cross section for photodissociation of the adsorbate is

$$\sigma_{pc} = \eta\sigma = \eta\left(\frac{8\pi}{c}\right) \Lambda \quad . \tag{2}$$

Defining $\sigma^0_{pc} \equiv \eta\left(\frac{8\pi}{c}\right) \Lambda^0$ as the surface-free cross section of an isolated molecule, we can obtain the surface enhancement ratio for photochemistry:

$$R_{pc} = \Lambda/\Lambda^0 \quad . \tag{3}$$

In the above formalism, we have assumed that the quantum efficiency η is unaffected by the presence of the surface.

A familiar model for a rough surface[37,35] is shown in Fig. 1. In terms of the spheroidal coordinates (ξ,η,ϕ), the hemispheroid surface is characterized by $\xi_0 = a/f$; the surface through the position of the molecule, considered as a polarizable point dipole, is given by $\xi_1 = (a + H)/f$, with the size parameter $f \equiv (a^2 - b^2)^{1/2}$; a and b are the semi-major and semi-minor axes of the hemispheroidal protrusion, respectively. The hemispheroid and the flat plane are considered as one piece with a complex dielectric constant $\epsilon(\omega)$. The incident laser field is taken to be propagating along the interface so that its electric field vector $\vec{E}_0$ is along the normal to the interface. The molecular dipole $\vec{\mu}$ is oriented along the z-direction. The local electric field at the location of the molecular dipole is obtained from the electric potential Φ_{II} in region II,[37]

$$\Phi_{II} = \sum_n B_n \, Q_n(\xi) \, P_n(\eta) - E_0 \, f \, \xi \, \eta$$

$$+ \frac{\mu}{f} \frac{\partial}{\partial \xi_1} \sum_n \frac{(2n + 1)}{f} \, P_n(\xi_<) \, Q_n(\xi_>) \, P_n(\eta) \quad . \qquad (4)$$

where P_n and Q_n are the Legendre polynomials of the first and second kind, respectively, and $\xi_< = \min(\xi, \xi_1)$ and $\xi_> = \max(\xi, \xi_1)$. Thus the local electric field at the location of the dipole is given by

$$E_{loc} = E_0 - \underline{B} \cdot \underline{q} \quad , \qquad (5)$$

where $q_n = Q_n'(\xi_1)/f$.

A formal solution for the coefficients B_n is obtained in the following form (quantities with single and double bars are vectors and matrices, respectively):[35,37]

$$\underline{B} = (\underline{\underline{T}}^{-1} \cdot \underline{\underline{S}} \cdot \underline{b}) \, \mu - (\underline{\underline{T}}^{-1} \cdot \underline{R}) \, E_0 \quad , \qquad (6)$$

where

$$T_{jn} = X_{jn} \, \{ [Q_n(\xi_0) \, P_j'(\xi_0) - \epsilon^{-1} \, Q_n'(\xi_0) \, P_j(\xi_0)]$$

$$+ (-1)^{j+n} \, \Delta_n \, [Q_n(\xi_0) \, P_j'(\xi_0) - Q_n'(\xi_0) \, P_j(\xi_0)] \} \quad , \qquad (7)$$

$$X_{jn} = \int_0^1 d\eta \, P_j(\eta) \, P_n(\eta) \quad , \qquad (8)$$

$$\Delta_n = \left[\frac{1+\epsilon^{-1}}{2} + (-1)^n \frac{1-\epsilon^{-1}}{2}\right] , \tag{9}$$

$$S_{jn} = X_{jn} \{Q'_n(\xi_1) \, [\epsilon^{-1} P_j(\xi_0) \, P'_n(\xi_0) - P'_j(\xi_0) P_n(\xi_0)]$$

$$+ (-1)^{j+n} \Delta_n P'_n(\xi_1) \, [P_j(\xi_0) \, Q'_n(\xi_0) - P'_j(\xi_0) \, Q_n(\xi_0)]\} , \tag{10}$$

$$R_j = f\xi_0 \left\{\frac{2}{3} \delta_{j1} \, \epsilon^{-1} - X_{j1} \, P'_j(\xi_0) \left[1 - \frac{(-1)^j}{\epsilon}\right]\right\} , \tag{11}$$

$$b_n = \frac{2n+1}{f^2} . \tag{12}$$

The system dipole moment is given[35,37] by $D = \left(\frac{B_1 f^2}{3}\right) + \mu$, and E_{loc} is the required field which polarizes the adsorbed molecule. Writing $B_n = W_n \mu - V_n E_0$, where $\underline{W} = \underline{\underline{T}}^{-1} \cdot (\underline{\underline{S}} \cdot \underline{b})$ and $\underline{V} = \underline{\underline{T}}^{-1} \cdot \underline{R}$, one gets

$$E_{loc} = E_0 - (\underline{W} \cdot \underline{q}) \, \mu + (\underline{V} \cdot \underline{q}) \, E_0 . \tag{13}$$

$(\underline{V} \cdot \underline{q}) \, E_0$ is the field produced by the polarization of the surface by the incident field E_0 in the absence of the molecule, and $-(\underline{W} \cdot \underline{q}) \, \mu$ is the electric field at the location of the molecule produced by the polarization of the surface by the near field of the molecular dipole. By substituting for B_1 we see that the system dipole consists of the molecular dipole μ, a dipole moment $- V_1 E_0 f^2/3$ induced in the bump by the incident field, and a moment $W_1 f^2 \mu/3$ induced in the bump by the molecule.

We are interested in the sum of all the contributions to the local field including the reaction fields, associated with the coupling of the system dipole to photons and delocalized surface plasmon. Let us write E_R = RE_0 and $E_I = G\mu$, where $R(\omega) = \underline{V}\cdot\underline{q}$ and $G(\omega) = -\underline{W}\cdot\underline{q}$. To lowest order, the local field at any point above the surface consists of the incident field, the fields of photons radiated by both the molecular dipole and the dipole induced in the surface protrusion, and the field caused by the excitation of the surface plasmon by both the molecular dipole and the dipole induced in the bump. Therefore, we can imagine the system to consist of a single dipole of moment D, positioned very close to a flat surface.

If we denote the radiation reaction field by E_{rad} and the reaction field associated with the coupling to the surface plasmon by E_{sp}, then

$$E_{loc} = E_0' - \underline{B} \cdot \underline{q} \quad , \tag{14}$$

where $E_0' = E_0 + E_{rad} + E_{sp}$, and to maintain self consistency, we use $\underline{B} = \underline{B}(\mu, E_0')$ by replacing E_0 by E_0' in Eq. (6), and write the system dipole $D = D(\mu, E_0')$. The fields, E_{rad} and E_{sp}, are determined by using the results of Ref. 31 for the power radiated to photons,

$$P_{rad} = \frac{1}{3} |D|^2 \frac{\omega^4}{c^3} \left[1 + \frac{3}{2} \int_0^{\pi/2} d\theta \, \frac{\sin^3\theta \, \{(\epsilon^2 + 1) \cos^2\theta + (\epsilon - 1)\}}{(\epsilon - 1) \, \{(\epsilon + 1) \cos^2\theta - 1\}}\right] , \tag{15}$$

and the power lost to the excitation of surface plasmon,

$$P_{sp} = 4\pi\omega \, |D|^2 \, (\tfrac{\omega}{c})^3 \, \frac{(-\epsilon)^3}{(-\epsilon - 1)^{5/2} \, (1 - \epsilon)} \quad , \tag{16}$$

by the system dipole D, and demanding that the work done by the reaction force on the system dipole be equal to the negative of the corresponding energy lost during a given time. This calculation yields

$$E_{rad} = \frac{iD}{3}\left(\frac{\omega}{c}\right)^3 \left\{1 + \frac{3}{2}\int_0^{\pi/2} d\theta\, \frac{\sin^3\theta[(\epsilon^2 + 1)\cos^2\theta + (\epsilon - 1)]}{(\epsilon - 1)[(\epsilon + 1)\cos^2\theta - 1]}\right\} \tag{17}$$

and

$$E_{sp} = 4\pi iD\left(\frac{\omega}{c}\right)^3 \frac{(-\epsilon)^3}{(-\epsilon - 1)^{5/2}\,(1-\epsilon)} \quad . \tag{18}$$

Near the surface, the equation of motion of the molecular dipole, μ, may be taken to be of the Drude form,

$$\ddot{\mu} + \omega_0^2\mu + \gamma_0\dot{\mu} = \alpha_0\omega_0^2\, E_{loc}(t) \quad , \tag{19}$$

where ω_0 and γ_0 are the molecular frequency and decay rate in the bulk, respectively. Considering a steady state solution of Eq. (19) in the form $\mu(t) = \mu(\omega)e^{-i\omega t}$, the self-consistent dipole moment μ of the molecule and the power P absorbed by it in the presence of the corrected local field E_{loc}, are straightforwardly obtained:

$$\mu = \frac{\omega_0^2\alpha_0\, K_1 E_0}{(\tilde{\omega}_0^2 - \omega^2 - i\omega\tilde{\gamma})} \tag{20}$$

and

$$P = \frac{\omega^2\omega_0^2\alpha_0}{2} \frac{|K_1E_0|^2\tilde{\gamma}}{(\tilde{\omega}_0^2 - \omega^2)^2 + \omega^2\tilde{\gamma}^2} \quad , \tag{21}$$

where

$$K_1 = [1 + R(\omega)]/(1 + UV_1f^2/3) \quad , \tag{22}$$

$$\tilde{\gamma} = \gamma_0 + \frac{\omega_0^2\alpha_0}{\omega} \, \mathrm{Im}[G(\omega) + U(1 + \frac{W_1f^2}{3}) \, K_1] \quad , \tag{23a}$$

$$\tilde{\omega}_0^2 = \omega_0^2 - \omega_0^2\alpha_0 \, \mathrm{Re}[G(\omega) + U(1 + \frac{W_1f^2}{3}) \, K_1] \quad , \tag{23b}$$

and

$$U = U_{rad} + U_{sp} \tag{24}$$

is the factor resulting from the inclusion of reaction fields, $E_{rad} = U_{rad}D$ and $E_{sp} = U_{sp}D$, in the local electric field. V_n and W_n are the n-th elements of vectors $\underline{V}$ and $\underline{W}$, respectively.

Inspection of Eqs. (20) and (22) shows that when reaction fields are included, the effect of the driving field is cut down by a factor of $(1 + UV_1f^2/3)^{-1}$. Thus the absorbed power is reduced by the absolute square of the above factor from its value in the absence of reaction fields. Also, we find from Eq. (23) that surface-induced width and level shift have terms proportional to UK_1 and are thus dependent on $[1 + R(\omega)]$ when the reaction fields are accounted for. This is typical of situations where effects of the reaction fields are included.[36]

The ratio of P to P_0, the power absorbed by the molecule in the absence of any surface gives a measure of the photochemistry enhancement factor R_{pc}. This ratio can be expressed as

$$R_{pc} = \left(\frac{\tilde{\gamma}}{\gamma_0}\right) \left|\frac{E_{loc}}{E_0}\right|^2 , \tag{25}$$

or

$$R_{pc} = \left(\frac{\tilde{\gamma}}{\gamma_0}\right) \frac{|K_1|^2 ((\omega_0^2-\omega^2)^2 + \omega^2\gamma_0^2)}{((\tilde{\omega}_0^2-\omega^2)^2 + \omega^2\tilde{\gamma}^2)} . \tag{26}$$

If we neglect the small level shift (i.e., $\tilde{\omega}_0^2 \approx \omega_0^2$) and assume a near-resonance condition ($\omega \approx \omega_0$), then

$$R_{pc} \simeq \left(\frac{\gamma_0}{\tilde{\gamma}}\right) |K_1|^2 . \tag{27}$$

This is a familiar expression for R_{pc}, which contains two competing factors. The magnitude of R_{pc} is determined by the field enhancement factor $|K_1|^2$ and by the relative magnitudes of γ_0 and $\tilde{\gamma}$. $|K_1|^2$ contains the normal Raman enhancement factor $|1+R|^2$ and an add-on factor, $|1+UV_1f^2/3|^{-2}$, due to the inclusion of reactive effects.

III. Results and Discussion

Here, we consider the photodissociation rate of a molecule held at a distance H from a silver surface. The molecule is characterized by the parameters ω_0 , γ_0 and α_0. The rough surface consisting of the semi-infinite flat plane and the hemispheroidal protrusion is made up of silver, whose complex dielectric function $\epsilon(\omega)$ is taken from Ref. 38. To obtain finer adjustments in the neighborhood of resonance frequencies (for both molecular and plasmon resonances), we have numerically fitted the data to obtain the following empirical relation for $\epsilon(\omega)$ in the Drude form,

$$\epsilon(\omega) = \left[4.74 + \frac{0.12}{\omega^2}\right] + 0.24i \quad , \tag{28}$$

where ω is the frequency of the incident light. In what follows, all quantities are expressed in atomic units (a.u.).

Numerical calculations are done for the molecule resonating with both the incident laser frequency ω as well as with the ground-state resonance frequency of the bump-plane system, whose surface geometry gives rise to electromagnetic resonances called "shape resonances"[35]. One way of characterizing the shape resonance is through the value of the real part of the dielectric constant at the resonance frequency. For $a/b = 2$, 3 and 4, the ground states correspond to $\mathrm{Re}\,\epsilon(\omega) = -7.34$, -11.3 and -15.9, respectively. These data, along with Eq. (28), give the ground-state resonance frequency of the bump, which is 0.1, 0.086 and 0.076 a.u., for aspect ratios of 2, 3 and 4, respectively. A ten-dimensional $\underline{B}$-vector was chosen for numerical computation. For fixed a/b, a and H, reasonable convergence in R_{pc} was obtained using this $\underline{B}$ vector, with $a \leq 1000$ a.u. and $H \leq 140$ a.u.

Figure 2 shows $|K_1|^2$ (----) and $|1 + R(\omega)|^2$ (——) as a function of the distance H for various aspect ratios of the bump. $|1 + R(\omega)|^2$ is regarded as the field enhancement factor when $U = 0$ and $|K_1|^2$ is the corresponding factor when $U \neq 0$. For a given H, there is a significant reduction in the magnitude of the field enhancement factor when reaction field contributions are included. For example, for $a/b = 2$, there is at least two orders of magnitude reduction. As the bump becomes more needle-shaped, the value of $|K_1|^2/|1 + R(\omega)|^2$ becomes larger, because of the lightening-rod effect. The relative magnitude of $|K_1|^2$ with respect to the normal Raman enhancement factor $|1 + R(\omega)|^2$ for various aspect ratios and semi-major axes of the bump are given in Table 1.

The enhancement factor for photochemistry, R_{pc}, depends on $|K_1|^2$ and $\tilde{\gamma}$, besides other molecular parameters. Since K_1 is the surface-modified field-enhancement factor (when $U \neq 0$) and since it also occurs in $\tilde{\gamma}$, it is easy to see how the molecular width γ changes as a function of H when reaction fields are included. It turns out that the numerical value of $\mathrm{Im}[U(1 + W_1 f^2/3)K_1]$ is small compared to Im(G), and consequently $\tilde{\gamma}$ changes slightly with respect to γ unless we consider extremely large-sized ($a >$ 1000 Å) bumps. $|K_1|^2$ in the numerator of Eq. (26) is thus the dominant factor in deciding the effects of including reaction fields on photochemistry. On the same ground, since the polarizabilty α_0 enters the expression for R_{pc} through $\tilde{\gamma}$, the effect on R_{pc} of going from weak ($\alpha_0 = 0.1$) to strong ($\alpha_0 = 10.0$) polarizabilities is expected to be minimal.

Figure 3 shows R_{pc} as a function of H for three different aspect ratios for a fixed size of the bump (fixed a). The solid curves are obtained when $U = 0$, and the dashed curves are for $U \neq 0$. The molecular frequency ω_0 is chosen to coincide with the ground state of the bump for each value of a/b. Since R_{pc} is directly proportional to $|K_1|^2$, these curves mimic those of Fig. 2. The reactive effects are evidenced by the decrease in R_{pc} by several orders of magnitude when $U \neq 0$ from that when $U = 0$. As one goes away from the surface, the enhancement factor declines for a given eccentricity of the hemispheroid, and appreciable enhancement persists out to large distances.

Figure 4 gives the enhancement ratio R_{pc} for a molecule located at 40 a.u. from the surface as a function of the semi-major axis a of the hemispheroid for various aspect ratios. A complete resonance condition ($\omega_0 \approx \omega \approx \omega_s$, where ω_s is the ground-state resonance frequency of the bump-plane system) is assumed. Other molecular parameters used are $\gamma_0 = 10^{-3}$ a.u. and $\alpha_0 = 10$ a.u. These graphs show the effects of both including (----; $U \neq 0$) and excluding (——; $U = 0$) the reaction fields in the calculation. For extremely small values of a (< 200 a.u.), the effect of including the reaction fields is negligible. On the other hand, for a given shape of the bump (a/b fixed), the enhancement with $U \neq 0$ decreases to signficantly lower values than those for $U = 0$ with increasing a. This is understandable since the effects of including the reaction fields are expected to be substantial for large-sized roughness features.[36] For a = 300 Å, it is seen that the reduction in enhancement can be nearly two orders of magnitude when $U \neq 0$ for a hemispheroid with a/b = 2. The magnitude of the attenuation in enhancement decreases with increasing eccentricity of the bump, because one would expect the strongest intrinsic electric fields near the sharpest protrusions. The value of a where R_{pc} peaks may be taken as the size of the bump at which reaction field contributions start to bear significant effect. For an eccentricity of 3, for example, the semi-major axis of the bump has to be roughly ~ 300 a.u. before reactive effects are significantly noticeable.

As mentioned earlier, U consists of two parts: $U = U_{rad} + U_{sp}$. U_{rad} corresponds to the inclusion of photon radiation damping, and a nonzero U_{sp} represents the inclusion of reaction in the decay of the system dipole to delocalized surface plasmons, which is the primary relaxation mechanism very close to the surface.[2,28,29] The effect of only $U_{rad} \neq 0$ was disucssed in Ref. 36 in the context of SERS. To see how a nonzero U_{sp} additionally modifies the enhancement of photochemistry near a rough surface, we show R_{pc} as a function of the semi-major axis a in Fig. 5 for three different situations: $U \neq 0$ (curve a), $U = 0$ (curve b) and $U_{rad} \neq 0$ but $U_{sp} = 0$ (curve c). Curve c is in qualitative agreement with previous results[36] as evidenced by the attenuation of enhancement for larger-sized bumps. Comparative inspection of the curves in Fig. 5 shows that for photodissociation of a molecule near a rough silver surface, the effect of including the surface plasmon reaction field in the calculation is substantial for both intermediate and larger-sized bumps. It clearly illustrates the importance of taking into account the reaction field corresponding to the excitation of surface plasmons by the system dipole. The peak positions of curves a and c set a lower bound for values of the semi-major axis a at which radiation and surface plasmon dampings, respectively, become important.

The above results lead us to a simple conclusion that enhancement in photochemistry near a rough surface is not only dependent, very sensitively, on the shape and size of the roughness feature, but also the theory should take the radiation as well as the surface plasmon damping into consideration, particularly for large-sized features, for a correct prediction of experimental results. If one wants to produce a predetermined enhancement in photochemistry for a molecule held at a fixed distance from the surface, the surface morphology has to be designed accordingly. On the other hand, if the surface roughness is specified, one needs to put the molecule at a certain, predetermined, distance away from the surface to get maxmimum enhancement.

The "system dipole" referred to in this article has a moment which is the sum of the molecular dipole moment and the dipole moment associated with the "single" roughness feature. For the near-resonance condition, where the laser frequency coincides with a resonance of the molecule and the bump, each dipole may have its moment increased by a factor of ~50 to 100. Thus the system dipole in this model calculation is much stronger than gas-phase molecular dipole. Consequently, the coupling of an adsorbed molecule to the delocalized surface electronic excitation of the flat substrate in the case of flat-surface adsorbate photochemistry is much weaker than that in the case of a rough surface. One may therefore neglect the reactive effects associated with radiation and surface plasmon dampings in flat surface photochemistry.

Like the energy-transfer mechanism, charge-transfer processes, to[39] and from[17,30] the surface, are short-range quenching mechanisms. The photochemical process involves excitation of the molecule to a repulsive state and subsequent fragmentation. The repulsive state is attained either by electronic excitation or by dissociative electron attachment,[17,30] where the surface looses an electron to the adsorbate. In either case, quenching of photochemistry occurs very close to the surface (i.e., at very low coverages and/or when the inert spacer layer between the molecule and surface is absent), since the molecule may return to a nonrepulsive state before fragmentation occurs. This is possible because of the strong overlap between the molecule and the surface at short range, so that the attached electron as well as the excited electron can tunnel through to the surface. On the other hand, very far from the surface, the excited molecule has sufficient time to undergo fragmentation without appreciable quenching by charge transfer. Because of the very weak molecule-surface overlap and the potential barrier that the surface electron has to overcome (to get through the first few layers of molecules or the spacer layer), electron-transfer-mediated photochemistry is practically absent at large distances. There is hence an optimum distance from the surface,[17] where the cross section for photodissociation is expected to peak.

Although from the above discussion, the characteristics of both energy-transfer and charge-transfer quenching mechanisms are similar, we have made no attempt to include the latter effect here. While the energy dissipation to a rough surface can be easily accounted for by the classical electromagnetic theory,[37] detiled quantum theoretical insight into the charge-exchange processes in the presence of a "rough" surface is needed.

In summary, we have considered a correction to the electromagnetic theory of surface-enhanced photochemistry by taking into account the radiation and the surface plasmon reaction fields. We chose a model where decay to delocalized plasmons, besides photon emission, by the system is possible. It is found that while surface plasmon damping can be important for both small as well as large-sized roughness features, the radiation damping has an effect only for very large-sized roughness features. It should be pointed out that the rough surface chosen is only a model surface. Realistic rough surfaces are quite different and difficult to model. Nonetheless, the qualitative conclusions drawn from these results should help guide experimentalists in choosing correct parameters to maximize enhancement. Given the surface preparation techniques known to date, it is perhaps possible to check the predictions of this calculation experimentally on microlithographically-prepared surfaces.[40]

Acknowledgments

This research was supported in part by the National Science Foundation under Grant CHE-8922288 and the Office of Naval Research. PCD wishes to acknowledge the computational assistance of Mr. Donald Wheaton. We also acknowledge valuable discussions with Prof. J. P. Cowin.

	$\lvert K_1 \rvert^2 / \lvert 1 + R(\omega) \rvert^2$		
a (a.u.)	a/b = 2	a/b = 3	a/b = 4
400	0.08	0.2	0.3
600	0.01	0.03	0.07
800	0 .002	0.008	0.02

Table 1. The ratio of the field-enhancement factor $|K_1|^2$ (when $U \neq 0$) to $|1 + R(\omega)|^2$ (when $U = 0$) as a function of the semi-major axis a of the hemispheroid for different a/b values.

Figure Captions

1. Geometry of the surface protrusion. The semi-major axis is a, and the semi-minor axis is b. The spheroid surface is $\xi = \xi_0$, and the surface passing through the molecule is $\xi = \xi_1$.

2. $|1 + R(\omega)|^2$ (——) and $|K_1|^2$ (----) as a function of the molecule-surface distance H for three different a/b values: (a) a/b = 2; (b) a/b = 3; (c) a/b = 4. For each case, a = 800 a.u., α_0 = 10 a.u., and ω_0 is equal to the ground-state resonance frequency of the bump-plane system.

3. Enhancement factor R_{pc} as a function of H for three a/b values: (a) a/b = 2, ω_0 = 0.1 a.u.; (b) a/b = 3, ω_0 = 0.086 a.u.; (c) a/b = 4, ω_0 = 0.076 a.u. The solid curves are for U = 0, and the dashed curves are for U ≠ 0. Here, a = 800 a.u., α_0 = 10 a.u. and $\gamma_0 = 10^{-3}$ a.u.

4. Enhancement factor R_{pc} as a function of the semi-major axis a of the bump for three different aspect ratios: (a) a/b = 2, ω_0 = 0.1 a.u.; (b) a/b = 3, ω_0 = 0.086 a.u.; (c) a/b = 4, ω_0 = 0.076 a.u. The solid cuves are for U = 0, and the dashed curves are for U ≠ 0. Here, H = 40 a.u., α_0 = 10 a.u. and $\gamma_0 = 10^{-3}$ a.u.

5. Enhancement factor R_{pc} as a function of the semi-major axis a for a fixed a/b = 3. Curves (a) and (b) correspond to U ≠ 0 and U = 0, respectively. Curve (c) is obtained when only the photon radiation damping is taken into account ($U_{rad} \neq 0$, $U_{sp} = 0$). Here, H = 40 a.u., ω_0 = 0.086 a.u., α_0 = 10 a.u. and $\gamma_0 = 10^{-3}$ a.u.

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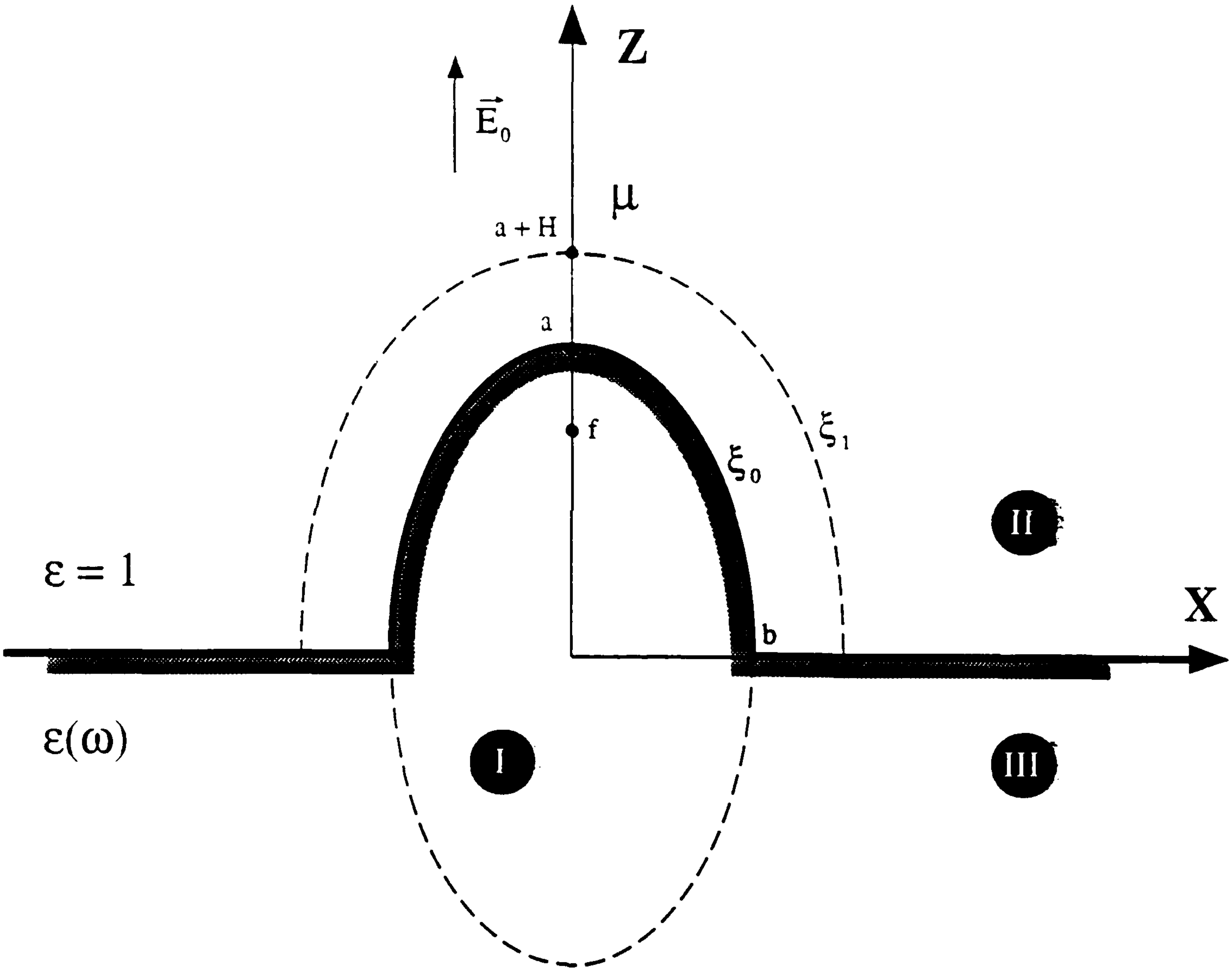
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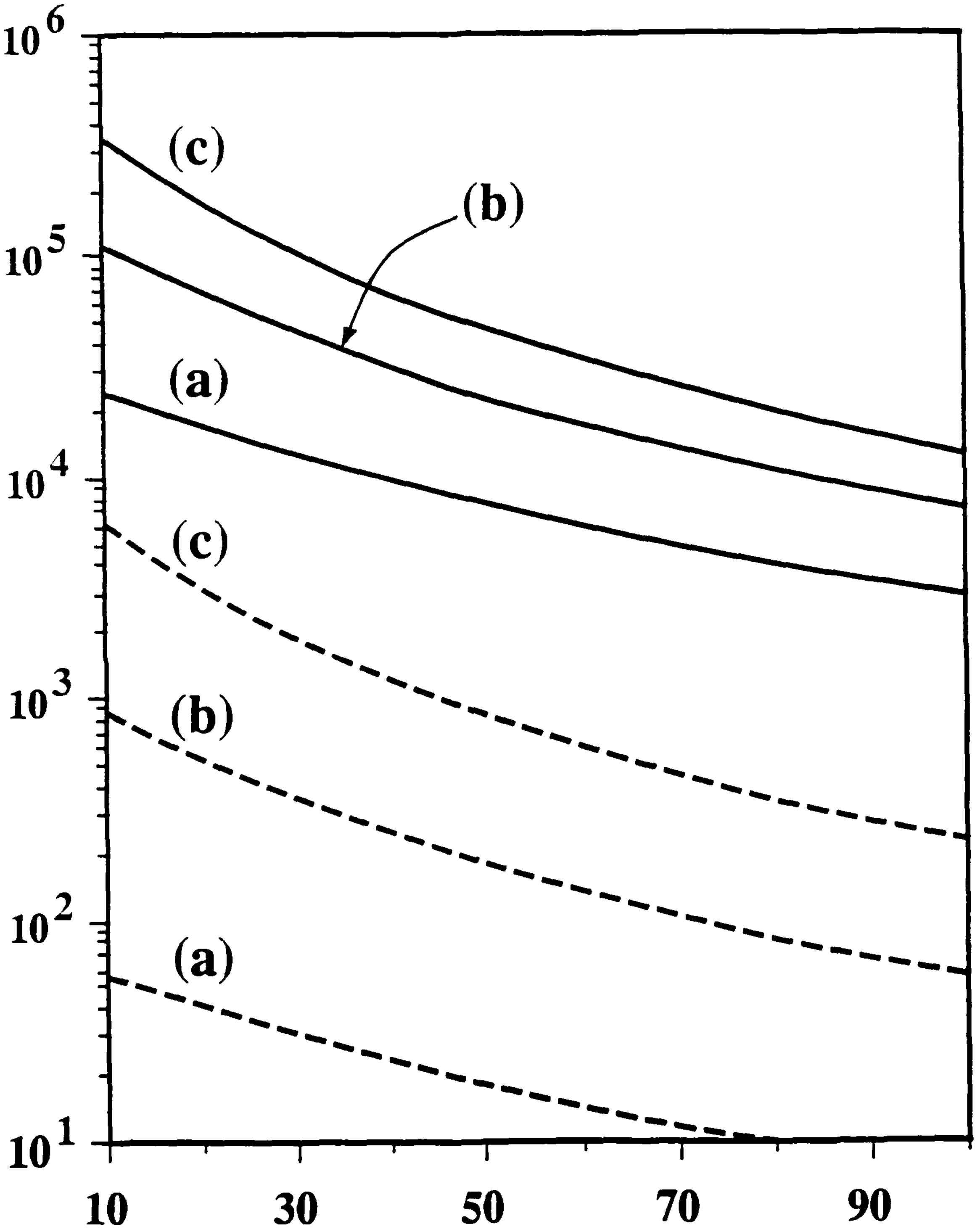

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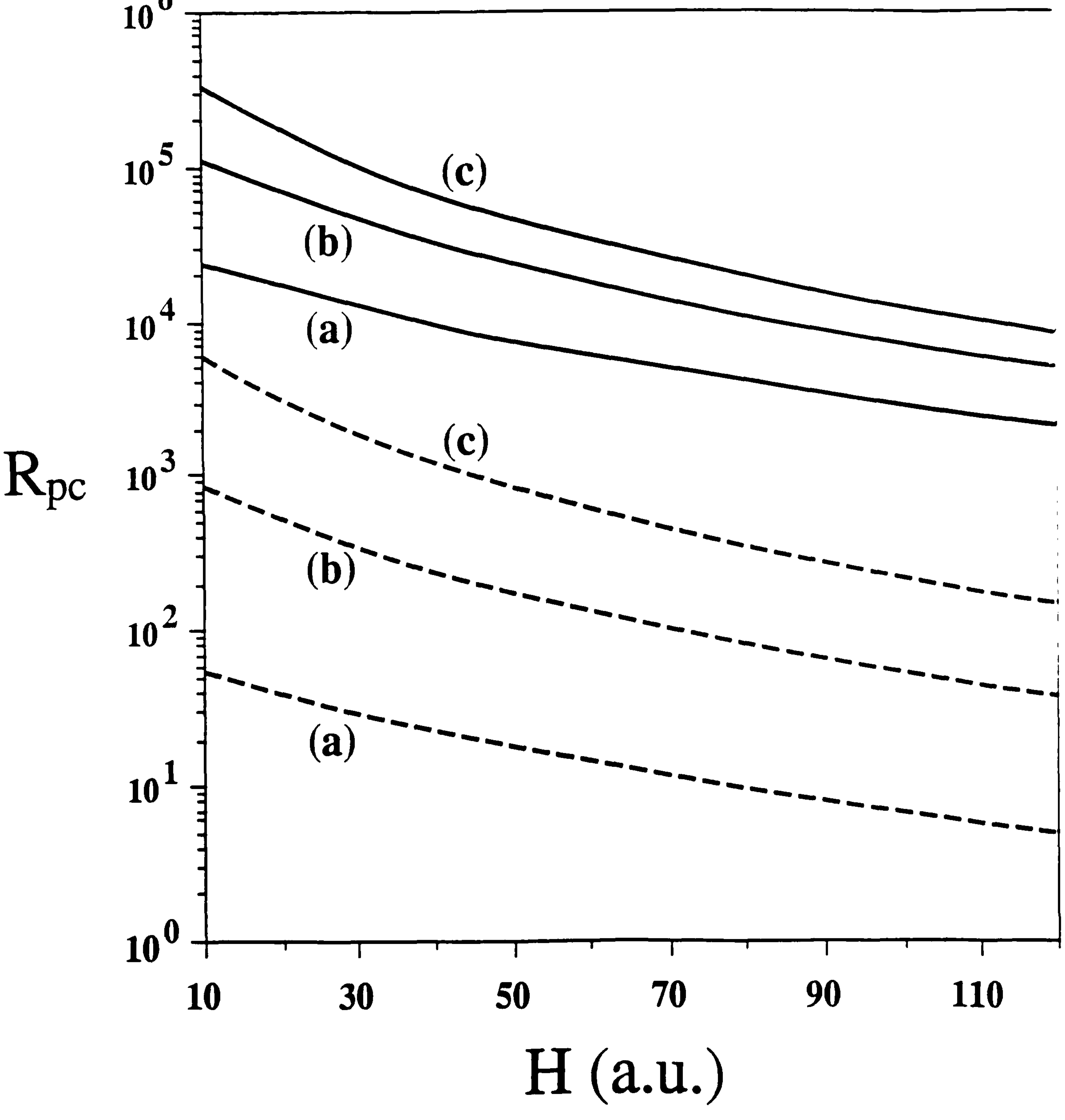
Fig. 3



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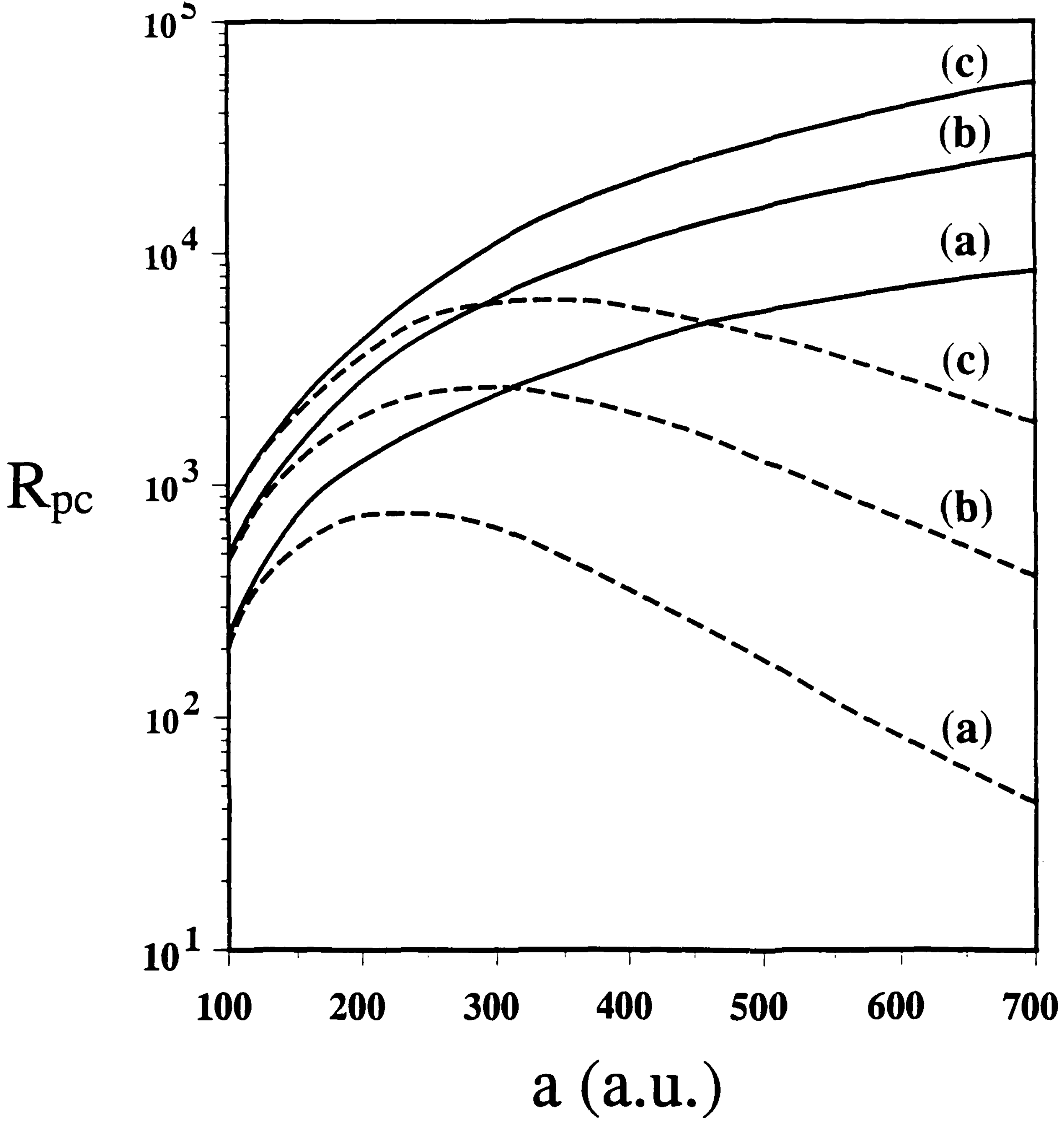
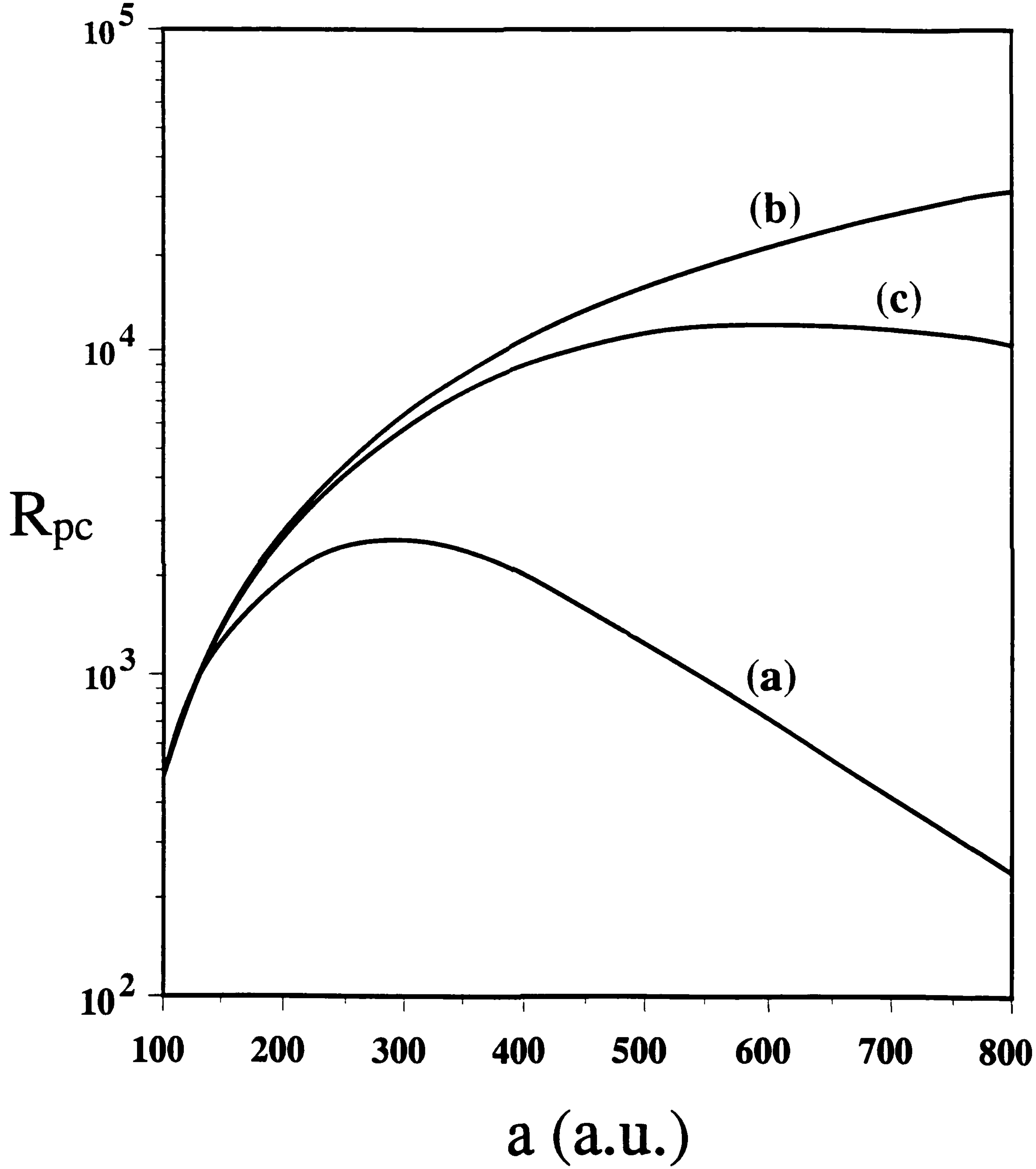


Fig. 5



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