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Can photochemistry be enhanced on rough surfaces?

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Recent work[1] has shown that at least part of the surface enhanced Raman phenomenon[2] (SERS) is due to the intensified local electromagnetic field which occurs near a surface protrusion (10–10^3 Å scale) on a rough surface. Incident fields are locally enhanced near the protrusion by image, shape, and plasmon resonance effects. Consequently, all types of electromagnetic interactions should be affected. Indeed, enhanced absorption and subsequent luminescence have recently been reported.[3–5]

This communication addresses the question of whether photochemical processes may also be enhanced. Enhanced absorption does not necessarily imply enhanced photochemistry because of the existence on the surface of competing routes for molecular energy dissipation. These are (a) radiationless transfer of molecular energy to the surface and (b) thermal and photon induced desorption of adsorbed molecules. It is therefore necessary to study the time scale and the efficiency of the photochemical process relative to these competing channels. It is also necessary to find and model dielectric materials with resonances throughout the IR–UV photochemical range.

To investigate the feasibility of surface enhanced photochemistry we study a classical molecular dipole at a distance from the surface of a dielectric sphere of radius a and dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The molecule is modeled as a polarizable point dipole with characteristic frequency ω_0. Both a and d are much smaller then the field wavelength λ. The equations of motion for the molecule and the dipolar modes of the sphere are[7]

$$\ddot{R} + \omega_0^2 R + \Gamma \dot{R} = \frac{1}{m} \frac{\partial \mu}{\partial R} \cdot (\mathbf{E} + \bar{\mathsf{M}} \boldsymbol{\mu}_1) , \qquad (1a)$$

$$\ddot{\boldsymbol{\mu}}_1 + 2\gamma_1 \dot{\boldsymbol{\mu}}_1 + (\omega_1^2 + \gamma_1^2)\boldsymbol{\mu}_1 = \alpha_1(\omega_1^2 + \gamma_1^2)(\mathbf{E} + \bar{\mathsf{M}} \boldsymbol{\mu}) , \qquad (1b)$$

where R, $\mu(R)$, m, and ω_0 are the intramolecular coordinates, and the associated molecular dipole, mass, and transition frequency, respectively. For vibrational excitation $\omega_0^2 R$ may be replaced by $(1/m)\partial V(R)/\partial R$, where $V(R)$ is the intramolecular potential; for atomic transitions $|\mu(R)| = e|R|$, e and m being electronic charge and mass, respectively. $\boldsymbol{\mu}_1$ is the dipole induced on the sphere, ω_1 is the solution to $\epsilon_1(\omega_1) = -2$, $\gamma_1 = \epsilon_2(\omega_1)/\epsilon_1'(\omega_1)$, and $\alpha_1 = 6a^3\omega_1/[(\omega_1^2 + \gamma_1^2)\epsilon_1'(\omega_1)]$. $\mathbf{E} = \mathbf{E}_0 \cos\omega t$ is the

incident field, and $\bar{\mathsf{M}} = (3\hat{n}\hat{n} - \bar{\mathsf{I}})/(d+a)^3$, where $\hat{n}$ is a unit vector along the molecule–sphere center axis. Here $\epsilon_1' = \partial\epsilon_1/\partial\omega$. Finally, $\Gamma = \Gamma_0 + \Gamma_1$ is the molecular decay rate. Γ_0 is the free molecule term and Γ_1 (analogous to the surface induced decay term of molecule near a plane surface[6]) arises from the interaction of the molecule with all the nonradiative ($l > 1$) sphere modes.[7] These equations describe two coupled Drude dipoles in an external field. Equation (1b) is approximate and applies when ω_1 is not too different from ω. All the parameters in Eqs. (1) are estimated from available spectroscopic data.

We now consider two examples: I_2 photodissociation near 4500 Å is a one-photon process with a short ($\sim 10^{-14}$ sec) excited state lifetime. We simulate the continuous I_2 absorption by a broad Lorentzian resonance. Figure 1 shows the steady-state absorption line shape [e.g.,
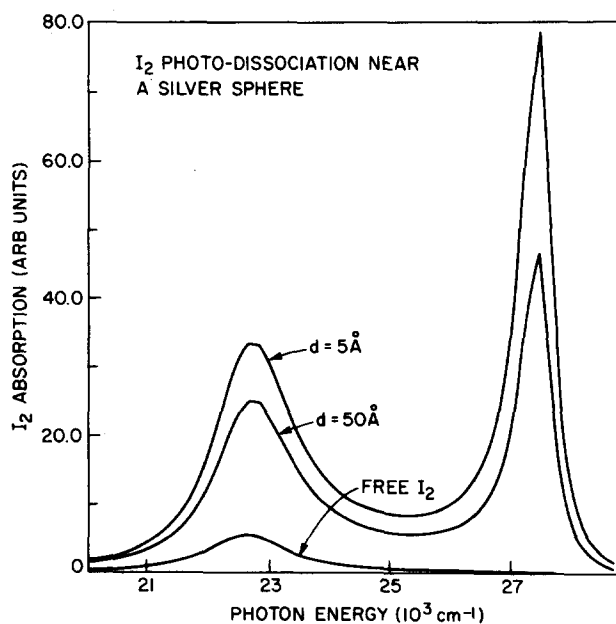

FIG. 1. Effective absorption cross section vs incident frequency for a model of I_2 photodissociation. d is the distance from the surface of a silver sphere of radius $a = 500$ Å. The molecular dipole lies along sphere radius.
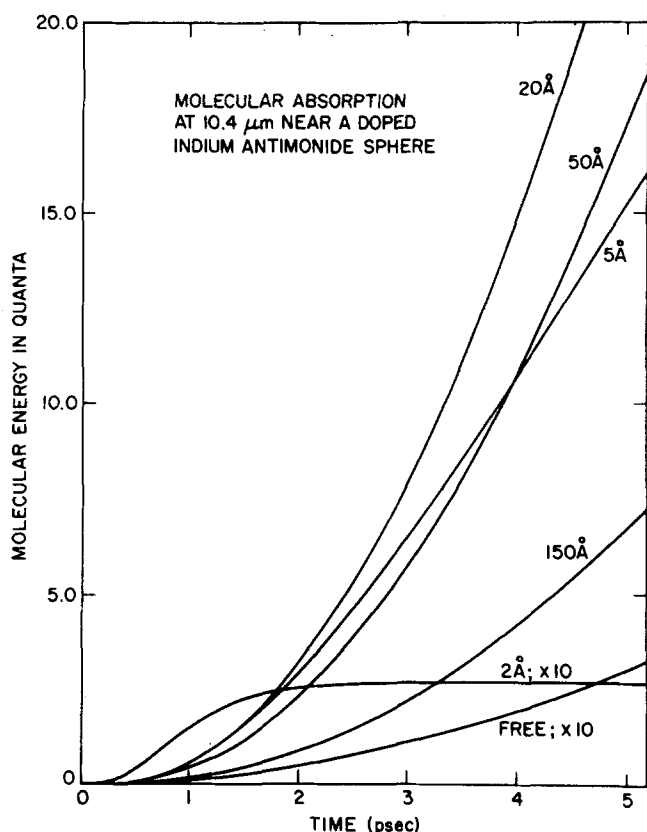
FIG. 2. Energy accumulation in an anharmonic molecule (ω = 965 cm^{-1}, radiative lifetime corresponding to the 0–1 ν_3 transition in SF$_6$ and nonradiative lifetime corresponding to 10^{-6} cm^{-1}) as a function of time for different distances from a n-type InSb sphere with dipole resonance at 967 cm^{-1}. $a = 500$ Å.

rate of energy pumping into the I$_2$ calculated from Eq. (1)] for several values of distance d near an Ag sphere ($\omega_1 = 28\,230$ cm^{-1}, $\Gamma_1 = 382$ cm^{-1}). The line shape in Fig. 1 directly gives the excitation spectrum for I atom production in view of the short I$_2^*$ lifetime. There are two effects leading to enhanced photochemistry: (a) The 4500 Å I$_2$ absorption increases as d decreases due to the enhanced local field at this wavelength; (b) there is a new photodissociation maximum at the sphere wavelength of 3540 Å, resulting from sphere absorption followed by energy transfer to I$_2$.

As a second example we consider the IR multiphoton excitation of a molecule (modeled as a damped harmonic oscillator with parameters corresponding to the 0 → 1 ν_3 transition of SF$_6$, $\omega_0 = 965$ cm^{-1}) near an n-type InSb sphere doped to give a free carrier plasmon resonance nearly coinciding with a CO$_2$ laser line.[8] The resonance corresponds to $\omega_1 = 967$ cm^{-1} and $\Gamma_1 = 16.2$ cm^{-1}. Figure 2 shows the time evolution of molecular energy accumulation for an incident field intensity 2 $\times 10^8$ W/cm^2 as a function of d. Enhancement ratios of 10^2–10^3 relative to the free molecule are observed.

These results show that photochemistry may be enhanced on rough surfaces. Figure 1 demonstrates that (in contrast to plane surfaces) small particles or surface protrusions may absorb light and transfer energy to nearby molecules (leading to the ~28 000 cm^{-1} peak in

Fig. 1). Figure 2 demonstrates that enhanced IR pumping may compete successfully with damping into nonradiative surface modes provided that d is not too small.[9] The requirement that d be not too small is qualitatively different than in SERS, where Raman scattering is maximum on the surface. The short psec time scale of the pumping rate and the long range of the effect (appreciable even at $d/a \sim 0.25$) imply that pumping may also compete successfully with thermal desorption processes. This example also demonstrates the use of doped semiconductors to enhance IR radiation fields. We could alternatively employ an ionic crystal such as SiC whose dielectric response[10] leads to a optical phonon sphere resonance near $\omega_1 \sim 930$ cm^{-1}. We conclude that efficient photochemical catalysis may occur on appropriately rough surfaces. Processes involving coherent multiphoton absorption steps (which will be highly enhanced due to the nonlinear dependence on the local field intensity) suggest themselves as candidates in attempts to verify this prediction.

Finally, note that we demonstrate an effect which in practice will have more complex resonance conditions due to the various shapes and interaction among the dielectric particles.

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