

Theory of Enhanced Light Scattering from Molecules Adsorbed at the Metal-Solution Interface

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We present a theory to explain the anomalous enhancement of light scattering from molecules adsorbed at a metal-solution interface. It is found that tunneling of electrons between a surface molecule and the metal induces a resonance at a point in the vicinity of the Fermi surface. A dynamical equilibrium due to photoionization and recombination stabilizes the system near resonance.

Observations of grossly enhanced Raman scattering from molecules in the vicinity of the liquid-solid metal interface have recently been reported.¹⁻⁵ It is the purpose of this Letter to offer an explanation for the origin of this enhancement. It is the purpose of this Letter to offer an explanation for the origin of this enhancement.

We adopt the philosophy that Raman scattering may be regarded as the sidebands of Rayleigh scattering which are generated by molecular vibrational motions. Our attention will therefore focus on Rayleigh scattering and at a later stage

our conclusions may be extended to the Raman scattering case. In our proposed model the coupling to the solid is obviously crucial. The electron absorbs a photon, is promoted to an excited state of the coupled molecule-solid system, and finally reradiates the photon. We shall first consider the case where a positive ion exists in the intermediate state. The molecule-solid coupling leads to a larger effective polarizability, which is the physical origin of the enhancement.

Our model is described by the Hamiltonian (in units where $\hbar = 1$)

$$H = \sum_{\sigma} [\epsilon_a a_{\sigma}^{\dagger} a_{\sigma} + (\epsilon_b - i\frac{1}{2}\gamma) b_{\sigma}^{\dagger} b_{\sigma} + \sum_{\vec{k}} \epsilon_{\vec{k}} C_{\vec{k}\sigma}^{\dagger} C_{\vec{k}\sigma}] + \sum_{\vec{q}\lambda} [d_{\vec{q}\lambda}^{\dagger} d_{\vec{q}\lambda} + \frac{1}{2}] \omega_{\vec{q}\lambda} - \sum_{\vec{k}\sigma} [V_{\vec{k}} C_{\vec{k}\sigma}^{\dagger} b_{\sigma} + V_{\vec{k}}^* b_{\sigma}^{\dagger} C_{\vec{k}\sigma}] - i \sum_{\vec{q}\lambda\sigma} (2\pi\omega_{\vec{q}\lambda})^{1/2} [\langle a | \vec{\mu} \cdot \hat{\epsilon}_{\vec{q}\lambda} | b \rangle a_{\sigma}^{\dagger} b_{\sigma} + \langle b | \vec{\mu} \cdot \hat{\epsilon}_{\vec{q}\lambda} | a \rangle b_{\sigma}^{\dagger} a_{\sigma}] [d_{\vec{q}\lambda} - d_{\vec{q}\lambda}^{\dagger}]. \quad (1)$$

The molecule has been idealized as a two-level system with a ground state $|a\rangle$ and an electronically excited state $|b\rangle$. A state of an electron in the solid is symbolized by $|\vec{k}\rangle$. The corresponding electronic energies⁶ are denoted by ϵ_a , ϵ_b , and $\epsilon_{\vec{k}}$, while the associated annihilation operators are a_{σ} , b_{σ} , and $C_{\vec{k}\sigma}$. The spin index is denoted by σ . The photon energy is $\omega_{\vec{q}\lambda}$ and its annihilation operator is $d_{\vec{q}\lambda}$. The tunneling integral, $V_{\vec{k}}$, permits an electron to shuttle between the molecule and the solid.⁷ The final term in H represents the dipole approximation to the molecule-radiation interaction, $\vec{\mu}$ being the electric dipole operator. A decay rate γ has been included to account for radiative and nonradiative decays of the excited molecule in solution.

Rather than introduce a set of Coulomb repulsion integrals, as would be appropriate to the Hubbard model, we shall simply exclude negative molecule-ion states. The consequence of this exclusion is equivalent to solving the Anderson model in the limit where the Coulomb repulsion integrals are all very strong. For this situation, their contributions to the energy denominator of the light-scattering matrix element from an electron configuration where states a and b are simultaneously occupied are suppressed with respect to the contributions from configurations where electrons are either in level a or b . The result is the appearance of the Fermi factor, which otherwise would cancel out, in the energy denominator of the matrix element.

The light-scattering matrix element may be written in a form valid to all orders in perturbation the-

ory:

$$M=A \left\{ \left[\epsilon_a + \omega - \epsilon_b + i \frac{\gamma}{2} + \sum_{\vec{k}\sigma} |V_{\vec{k}}|^2 f_{\vec{k}}^{(+)} \frac{1}{\epsilon_{\vec{k}} - \epsilon_a - \omega - i0^+} \right]^{-1} + \left[\epsilon_a + \omega' - \epsilon_b + i \frac{\gamma}{2} + \sum_{\vec{k}\sigma} |V_{\vec{k}}|^2 f_{\vec{k}}^{(+)} \frac{1}{\epsilon_{\vec{k}} - \epsilon_a + \omega' - i0^+} \right]^{-1} \right\}. \quad (2)$$

The perturbation series leading to this result is depicted in Fig. 1. We have let

$$A = 2\pi(\omega\omega')^{1/2} \langle b | \vec{\mu} \cdot \hat{\mathcal{G}} | a \rangle \langle a | \vec{\mu} \cdot \hat{\mathcal{G}}' | b \rangle. \quad (3)$$

The factor $f_{\vec{k}}^{(+)}$ is a Fermi factor guaranteeing that the electron, when making its excursion through the solid, lies above the Fermi sea. In the zero-temperature limit it is simply a step function at the Fermi energy ϵ_F . In Eq. (2) the incident and outgoing frequencies are denoted by ω and ω' and the corresponding polarization vectors by $\hat{\mathcal{G}}$ and $\hat{\mathcal{G}}'$. The first term in Eq. (2) is the "resonant" term and the second is the "antiresonant" term. Our attention will be directed towards the former.

For simplicity's sake assume $V_{\vec{k}}$ to depend only on energy and introduce a density-of-states function $D(\epsilon)$ for the solid. The resonant denominator may then be written as

$$Q(\omega) = \epsilon_a + \omega - \epsilon_b + i \frac{\gamma}{2} + \int_{\epsilon_F}^{\infty} d\epsilon \frac{D(\epsilon) |V(\epsilon)|^2}{\epsilon - \epsilon_a - \omega - i0^+}. \quad (4)$$

As we shall soon see, it is the range where $\epsilon_a + \omega - \epsilon_F$ is small that is of primary interest.

In addition to describing light scattering, the Hamiltonian of Eq. (1) describes photoionization of an electron from the molecule to a state in the conduction band of the solid. The photoionization cross section is

$$\sigma_I = \frac{4\pi^2\omega}{c} \frac{|V(\epsilon)|^2 D(\epsilon)}{|Q|^2} |\langle b | \vec{\mu} \cdot \hat{\mathcal{G}} | a \rangle|^2 \Theta(\epsilon_a + \omega - \epsilon_F), \quad (5)$$

where $\epsilon = \epsilon_a + \omega$ and Θ is a unit step function. We start with the ground-state neutral molecule, Fig. 2(a). If $\epsilon_a + \omega > \epsilon_F$ the effect of the photoionization process will be the transfer electrons from some molecules on the illuminated surface to the solid [Fig. 2(b)]. This will cause a rise in the Fermi level of the solid relative to the ground (and excited) states of the molecule, the rise being due to an electrostatic potential difference. This rise will continue until $\epsilon_a + \omega = \epsilon_F$, at which point the one-photon photoionization process will terminate. Thus, even if we start with a situation where $\epsilon_a + \omega > \epsilon_F$, the system will develop a potential step between the metal and the inner Helmholtz plane and adjust itself to the condition $\epsilon_a + \omega = \epsilon_F$ as illustrated in Fig. 2(c).

If the Fermi level were to be elevated beyond the above point, e.g., by varying the electrode potential, some electrons would return from the metal to the adlayer to restore the condition $\epsilon_a + \omega = \epsilon_F$. The recombination process, although small, may not be neglected because the photoionization process is cut off. Direct tunneling, radiative recombination, and electronic currents in the cell may contribute to the recombination. Thus a dynamic equilibrium between the adlayer and the metal will be established.

In order to be able to take into account time-varying electrode potentials or to be able to analyze situations in which inhomogeneous surface potentials are present, we must consider the neighborhood of the point $\epsilon_a + \omega = \epsilon_F$. This will also be important in discussing the Raman effect. Returning to Eq. (4) let $x = \epsilon_F - \epsilon_a - \omega$ and $y = \epsilon - \epsilon_F$.

For small x we have

$$Q \cong \epsilon_a + \omega - \epsilon_b + i \frac{\gamma}{2} + \int_0^{\Delta} dy \frac{D(\epsilon_F) |V(\epsilon_F)|^2}{V+x-i0^+} \cong \epsilon_F - \epsilon_b + i \frac{\gamma}{2} + \rho \left[\ln \left| \frac{\Delta}{x} \right| + i\pi\Theta(-x) \right], \quad (6)$$

where $\rho = D(\epsilon_F) |V(\epsilon_F)|^2$, and Δ is a typical energy scale over which the quantity $D(\epsilon) |V(\epsilon)|^2$ varies. Typically it will be on the order of a characteristic bandwidth of the solid. This point has been supported by elementary model calculations. Aside from the presence of the damping term γ , Q will have a zero

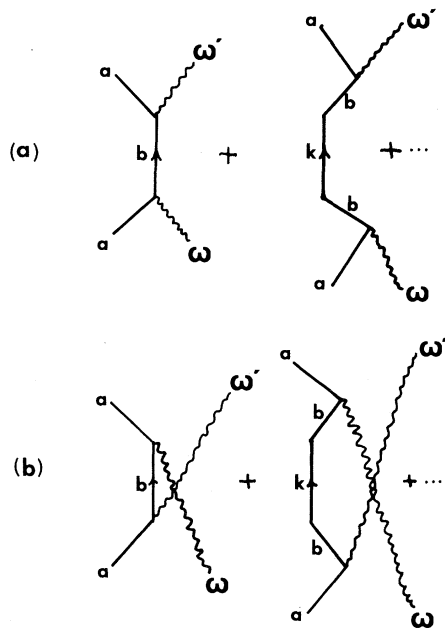


FIG. 1. The perturbation series corresponding to the scattering matrix element of Eq. (2). In (a) are the resonant terms and in (b) are the antiresonant terms.

at approximately

$$x_0 = \Delta \exp[-(\epsilon_b - \epsilon_F)/\rho]. \quad (7)$$

Thus we would expect an anomalously large light-scattering matrix element at a point where the photon excites the electron to an energy slightly below the Fermi surface, i.e.,

$$\epsilon_a + \omega = \epsilon_F - \Delta \exp[-(\epsilon_b - \epsilon_F)/\rho]. \quad (8)$$

The light-scattering intensity is proportional to $|M|^2$. From Eqs. (2) and (6) we see that the peak value of this function is

$$|M|_{\max}^2 = 4A^2/\gamma^2. \quad (9)$$

$$\frac{d\sigma}{d\Omega'} \cong \left(\frac{\omega}{c}\right)^4 \frac{|\langle b | \vec{\mu} \cdot \hat{\mathcal{G}} | a \rangle \langle a | \vec{\mu} \cdot \hat{\mathcal{G}}' | b \rangle|^2}{[\epsilon_a + \omega - \epsilon_b + \rho \ln |\Delta / (\epsilon_F - \sigma_a - \omega)|]^2 + [\frac{1}{2}\gamma + \pi\rho\Theta(\epsilon_a + \omega - \epsilon_F)]^2}. \quad (13)$$

This is a highly skewed function of energy. At the point where $\epsilon_a + \omega = \epsilon_F$ the logarithmic divergence in the denominator should force the scattering to fall to zero. At a point slightly below this [given by Eq. (8)] the light-scattering intensity peaks. For still lower values it gradually decreases because of the logarithmic denominator in Eq. (13). The effect of an inhomogeneous distribution of micropotentials at the surface (due to thermal fluctuations) would be to average

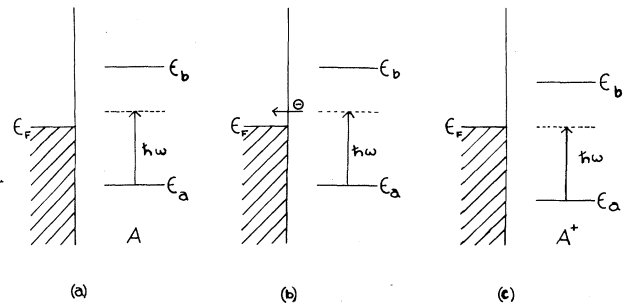


FIG. 2. Energy level diagram of the metal-molecule system. (a) Metal-neutral molecule A on illumination immediately before tunneling. (b) Tunneling to the metal. (c) Adjustment of energy levels on formation of A^+ .

This number should be compared with the corresponding light-scattering intensity of an isolated molecule, which is given by

$$|M|_{\text{mol}}^2 = A^2 / [(\epsilon_a + \omega - \epsilon_b)^2 + \frac{1}{4}\gamma^2]. \quad (10)$$

The peak enhancement ratio, R , is the quotient of these two numbers, i.e.,

$$R = [(\epsilon_a + \omega - \epsilon_a + \omega - \epsilon_b)^2 + \frac{1}{4}\gamma^2] / \frac{1}{4}\gamma^2. \quad (11)$$

One notes that the peak intensity given by Eq. (9) is precisely the same as the intensity given by Eq. (10) for exact molecular resonance conditions. The molecule-solid coupling has, in essence, moved the resonance point to the vicinity of the Fermi surface! The integrated intensity of this line, however, is less than that of the isolated molecule. For molecules in solution γ may typically be two to three orders of magnitude less than $\epsilon_b - \epsilon_a$, and so peak enhancement ratios in the range 10^4 to 10^8 can be expected.

The Rayleigh scattering cross section is

$$\sigma = (2\pi/c) \int |M|^2 \delta(\omega' - \omega) d\Omega' / (2\pi)^3, \quad (12)$$

and so the differential scattering cross section is

Eq. (13) over some small energy range. If we assume the width of the distribution to be comparable to x_0 [see Eq. (7)] the net scattering would be given approximately by

$$\left\langle \frac{d\sigma}{d\Omega'} \right\rangle = \frac{1}{N} \left(\frac{\omega}{c}\right)^4 \frac{|\langle b | \vec{\mu} \cdot \hat{\mathcal{G}} | a \rangle \langle a | \vec{\mu} \cdot \hat{\mathcal{G}}' | b \rangle|^2}{(\gamma/2)^2}, \quad (14)$$

where N is approximately 2. This is because ϵ_a

$+\omega$ is about equally likely to be above as below ϵ_F . The frequency dependence of this result is reminiscent of nonresonant Raman scattering although its origin is seen to be due to a resonance effect.

Let us now generalize our considerations to the case of Raman scattering. We make the adiabatic approximation and regard M as depending on the set of normal coordinates Q_i of the molecule. Upon expanding M in a power series in Q_i , retaining the linear terms, and forming matrix elements between different vibrational states, one obtains the Raman scattering amplitudes. Thus if M undergoes enhancement, so must $\partial M/\partial Q_i$, so that the Raman scattering is also enhanced. In computing the actual Raman scattering cross section we must also modify the energy-conservation δ function of Eq. (12) to include the Stokes or anti-Stokes shift.

While we have originally formulated the theory in terms of an adsorbed layer which is composed partially of positive molecule ions and partially of neutral molecules, we could equally well have formulated it in terms of an admixture of negative ions and neutral molecules. The process is now viewed as a photon promoting an electron from the Fermi surface to the excited state of the molecule and involving the tunneling of a hole to the metal could also be formulated. The dynamic equilibrium that stabilizes the process now involves photoionization from the metal onto the molecule forming a negative ion. Recombination processes neutralize these ions.

The idealized model presented allows the following experimentally verifiable predictions. Any molecule which adsorbs on the metallic surface, has a stable cation radical at the interface, and can be promoted to a virtual state near the Fermi level should exhibit an enhanced Raman spectrum. Likewise, any adsorbed molecule which has a stable anion radical at the interface should exhibit the effect if the laser excitation can promote the electrons in the metal to the lowest unoccupied orbital of the molecule. The model further predicts that for a process involving

cation radicals the entire effect will cut off if the electrode potential is made sufficiently negative, and for a process involving anion radicals the entire effect will cut off if the electrode is made sufficiently positive. In addition, on the basis of our model it should be possible to observe a feeble photocurrent due to the photoionization process. The direction of this photocurrent would allow one to determine whether an anion or cation is involved and from its magnitude one should be able to measure the photoionization cross section. Finally, recombination processes will occur which should give rise to a continuum radiation on which the Raman spectrum of the adsorbed molecule is superimposed.

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