Enhanced electric fields near gratings: Comments on enhanced Raman scattering from surfaces

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We report calculations of enhanced electric fields near gratings which show that as the amplitude of the grating is increased, radiative damping of surface polaritons on the grating limits the maximum enhanced field to modest values. We then comment on the possible implications of this result on the origin of very large Raman signals found for adsorbed species on certain metal surfaces.

There has been considerable interest in the origin of very large Raman signals observed when molecules are adsorbed on the surface of simple metals.[1] We have been engaged in theoretical studies of the reflectivity of diffraction gratings and the evaluation of electric fields in their near vicinity, within a theoretical framework that does not treat the amplitude of the grating as a small perturbation, and which fully includes the effect of retardation on the field enhancements at the grating.[2] We believe our results, when set alongside recent experimental studies of Raman scattering from molecules on nominally smooth single-crystal surface,[3] and from molecules adsorbed on gratings[4] provide considerable insight into the origin of the enhancement and certain key factors which can influence its magnitude.

If σ_0 is the Raman cross section in the gas phase, we write the cross section $\tilde{\sigma}_s$ of the cross section on the surface in the form

$$\tilde{\sigma}_s = \sigma_0 \left(\frac{\sigma_s}{\sigma_0}\right)\left(\frac{E_I}{E_0}\right)^2\left(\frac{E_s}{E_0}\right)^2 , \tag{1}$$

where σ_s is the cross section of the adsorbed species on a perfectly smooth surface. The factor E_I/E_0 is the ratio of the intensity of the laser field at the adsorption site, normalized to its value far from the surface and, following Chen *et al.*[5] we recognize that a similar factor enters for the scattered photon. Large Raman signals may thus occur for adsorbed species either because the intrinsic cross section may be much larger than in the gas or liquid phase ($\sigma_s >> \sigma_0$), or because the incident and/or scattered photon have enhanced fields at the surface ($E_I/E_0 >> 1$ and/or $E_s/E_0 >> 1$). As numerous authors have proposed,[1] there may be substantial field enhancement from roughness present on the surface, or from protrusions produced in the process of preparing the sample.

Experiments which probe molecules adsorbed on diffraction gratings[4] allow the field enhancement effect to be studied directly, since one may sweep the incident laser through a reflectivity dip produced by grating induced coupling of the incident photon to surface polaritons which propagate along the structure. Our calculations explore this portion of the field enhancement. We note that Jha, Kirtley, and Tsang have calculated field enhancements near grating structures, under such conditions.[6] These authors treat the grating amplitude as small, and use a perturbation theoretic method to calculate the enhanced field. From the results reported here, the reader shall appreciate that such an approach is limited to gratings of rather small amplitude.

The calculations discussed here explore silver gratings of sawtooth profile, with the period a chosen equal to 8000 Å, the period of the gratings employed by the IBM group.[4] We have p polarized light incident at 45°, and the plane of incidence is oriented normal to the grooves of the grating. The wave-vector component of the incident photon parallel to the surface is thus $k_{\parallel}^{(0)} = (\omega/c)\sin\theta_I$, with $\theta_I = 45°$. Under these conditions, we find a reflectivity dip near 2.6 eV, as observed. This dip has its origin in the coupling of the incident photon to the surface polariton with wave vector $k_{\parallel}^{(0)} - 6\pi/a_0$.

We have calculated the electric field at the tip of the sawtooth structure, illustrated as point P in Fig. 1. If E_M is the maximum value found for the electric field as one scans through the reflectivity dip, the figure gives the ratio $|E_M/E_0|^2$ as a function of the half depth of the grating grooves. The principal feature in the calculation worth notice is that while $|E_M/E_0|^2$ increases with h initially, the maximum field *saturates* for modest values of the groove depth, then actually *decreases* as h increases further. The maximum field enhancement is modest, with $|E_M/E_0|^2 \sim 25$ at the maximum.[7]

The physical origin of the saturation effect is the following. As the amplitude of the grating increases, the surface polariton to which the incident photon is coupled suffers grating-induced radiative damping, in addition to damping provided by dissipation of energy in the substrate. As this wave becomes more heavily

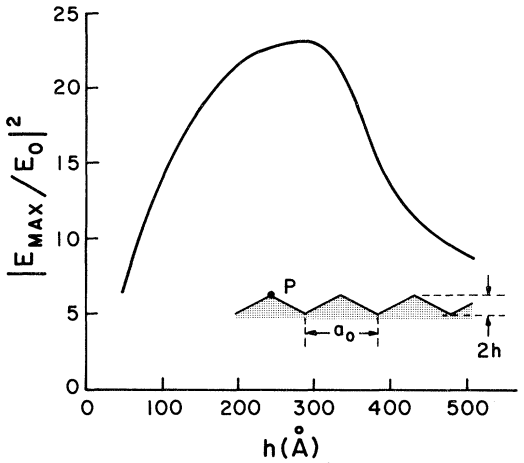

FIG. 1. The ratio $(E_M/E_0)^2$ in the reflectivity dip at 2.6 eV, for an Ag grating with period $a_0 = 8000$ Å. The angle of incidence is 45°.

damped, it is excited less efficiently by the incident photon. Since, in perturbation theory,[8] the radiative lifetime Γ_R scales as h^2 and the matrix element for coupling to the wave scales as h, we have $E_M/E_0 \sim h/[\omega-\omega_s-i(\Gamma_0+Ah^2)]$, with ω_s the surface polariton frequency, Γ_0 the width appropriate to the flat surface, and we write $\Gamma_R = Ah^2$. When $Ah^2 >> \Gamma_0$, then $|E_M/E_0| \sim h^{-2}$. In Fig. 2, we plot as a function of h the full width at half maximum of our calculated reflectivity dips, along with ΔR, its depth. One sees that ΔR initially increases with h, but saturates and begins to decrease, while the half width increases monotonically with h.

Our principal conclusion is then that the maximum fields which may be achieved near surfaces by coupling in through the surface polariton resonance are

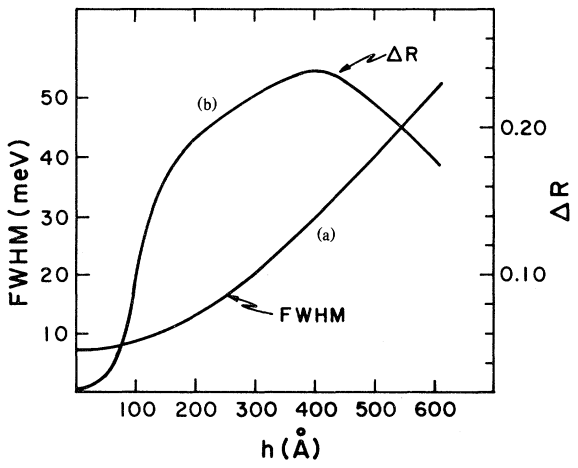

FIG. 2. We show values (a) of the full width at half maximum and (b) the change in reflectivity ΔR associated with the 2.6-eV dip, as a function of the grating height h.

rather modest (in the visible), because radiation damping sets in rapidly as the depth of the grating grooves increases. This limits the response of the grating structure, and leads to saturation and an eventual *decrease* in $|E_M/E_0|^2$ as h is increased. We note that Otto[9] has discussed coupling to surface polaritons in the attenuated total reflection (ATR) geometry, in language similar to that used here. As the spacing between the prism and substrate is decreased, coupling between the incident photon and surface polariton is increased, but at the same time the surface polariton becomes damped progressively more since it may radiate out through the prism. There is thus an optimum prism-to-substrate gap where the electric field near the substrate is a maximum.

A check on our grating results follows from the beautiful experiment reported in Ref. 4. These authors study Raman scattering from molecules adsorbed on gratings, under conditions (in one geometry) where the angle θ_s made by the scattered light with the normal to the film is fixed, and the angle θ_I is swept through the reflectivity dip in the visible. Such data provide a direct measure of the ratio $(E_I/E_0)^2$ in Eq. (1). For nitrobenzoic acid on Ag gratings, these authors quote a value of 25 for the maximum signal enhancement, remarkably close to our calculated maximum field enhancement displayed in Fig. 1.

One may inquire if this behavior is special to grating structures, or whether radiation damping will also limit the maximum fields near bumps and protrusions on surface. We believe the following argument, admittedly qualitative at this point, suggests the answer is in the affirmative, at least for features with linear dimensions greater than 200 Å. Consider a sphere of radius R in free space, filled with electrons of plasma frequency ω_p, so the dielectric constant is $\epsilon(\omega) = \epsilon_\infty - \omega_p^2/\omega(\omega = i/\tau)$, where we assume $\omega_p\tau >> 1$. Such a sphere has a dipole resonance strongly coupled to light, with frequency $\omega_0 = \omega_p/\sqrt{2+\epsilon_\infty}$. We find this resonance has halfwidth $\Gamma_0 = 1/\tau$ in the absence of radiative damping, and we calculate the radiative damping rate Γ_R to be given by $\Gamma_R = [2\omega_0/(\epsilon_\infty+2)]\,(\omega_0 R/c)^3$, when $\omega_0 R/c << 1$. If for Ag we take $\omega_0 = 3$ eV and $\tau = 10^{14}$ sec, then we find $\Gamma_0 = \Gamma_R$ when $R = 125$ Å. The rapid increase of Γ_R with R ensures that radiative damping will limit the amplitude of the dipole resonance of the sphere, for values of R larger than those for which $\Gamma_0 = \Gamma_R$. We note that in a recent study which fully includes retardation effects and consequently radiation damping, Kerker[10] and his colleagues have explored the role of field enhancement in the Raman cross section, for a molecule placed near an Ag sphere. They find "giant enhancements" [factors of 10^6 for the combination $|E_I/E_0|^2|E_s/E_0|^2$ in our Eq. (11)] only for particles with the rather small radius of 50 Å, and

the enhancement factor decreases by two or three orders of magnitude as one moves to larger spheres, a result consistent with the crude estimate above. (See Fig. 2 of Ref. 9.) It appears as if the possible role of radiative damping has not been considered in a number of theoretical estimates[11,12] of enhanced fields near features on the surface; our experience with the grating calculation and also the work of Kerker *et al.* suggests this may lead one to overestimate $|E_M/E_0|$ by a very substantial amount, for particles with linear dimensions greater than those where $\Gamma_R = \Gamma_0$.

We now turn to the question of whether one may account for the large Raman signals from adsorbed species, if radiation damping strongly limits the maximum field one may realize near gratings, rough surfaces, and near well-defined surface features. Ushioda and collaborators[3] have studied Raman scattering from pyridine on nominally smooth single-crystal Ag surfaces, prepared in ultrahigh vacuum. They have measured the ratio of the Raman cross section of the adsorbed species, to that in the liquid. For present purposes, we assume their data provide values for the cross section of the molecule on a perfectly smooth surface. They then find $\sigma_s/\sigma_0 \sim 600$, in the notation of Eq. (1).[13] We suppose such an enhancement of the cross section may have its origin in the excited state of the adsorbed species near 1.5 eV, absent in the liquid phase, which have been studied by optical spectroscopy[14] and electron energy-loss spectroscopy.[15] Now if on a roughened surface, such as that found on an evaporated film, we assume that the ratios $(E_I/E_0)^2$ and $(E_s/E_0)^2$ are limited by radiation damping to the modest values we find from our grating calculations, then with $\sigma_s \cong 600\sigma_0$, $(E_I/E_0)^2 = (E_s/E_0)^2 \cong 25$, the cross section for the adsorbed species can be larger than σ_0 by the factor 3.6×10^5, which is in the range often quoted in the literature. If the surface contains sharp protrusions, then field enhancements substantially larger than estimated above may result. Within the framework of a calculation which ignores radiation damping, Wang and Kerker[16] have found field enhancements considerably larger than appropriate to a sphere, particularly near a spheriod of prolate form. In our view, it is unlikely that sharp protrusions will be present on the evaporated films used in many experimental studies, however.

The discussion in the previous paragraph is speculative since we have little direct knowledge of field enhancements near real rough surfaces, but it is internally consistent. That is, if the maximum field enhancement near rough surfaces is modest because of the strong role played by radiation damping, then it is clear that the data of Ref. 3 truly measure the cross section of species adsorbed on flat portions of the surface, simply because the field enhancement will be too small to boost scattering from that very small fraction of the adsorbed molecules located near steps or defects to the point where it dominates the signal. If one assumes then, that Ref. 3 provides us with σ_s/σ_0 in Eq. (1), one is forced to conclude that $(E_I/E_0)^2$ and $(E_s/E_0)^2$ assume modest values rather not far from those provided by our grating calculation.

The suggestion that a substantial fraction of the total enhancement comes from the factor σ_s/σ_0 implies that this portion of the enhancement should be short ranged, and thus influenced by microscopic aspects of the surface composition. Recent data reported by Kester are consistent with this notion.[17] Kester coats a Ag surface with submonolayer coverages of Tl,[7] to find the enhanced signal disappears. Auger spectroscopy shows the adsorbed molecules are moved away from the surface as the Tl is adsorbed, and Kester concludes direct contact between the Ag surface and the adsorbed molecule must be established for "giant Raman signals" to be observed, i.e., a substantial portion of the enhanced cross section has its origin in effects of very short range.

Since this paper was submitted for publication, we have learned that Numata[18] has calculated enhanced fields near gratings of sinusoidal profile, to obtain results in remarkable quanitative agreement with those reported here. This suggests that under the conditions explored in this paper, the value of the enhanced fields near gratings may not be very sensitive to the details of the profile, for grating amplitudes near those where maximum field enhancement occurs.

ACKNOWLEDGMENTS

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[1]See the volume *Surfact Enhanced Raman Scattering,* edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1981).

[2]We have applied an elegant method proposed by F. Toigo, A. Marvin, V. Celli, and N. R. Hill, Phys. Rev. B 15, 5618 (1975). We find the method converges nicely for grooves with depths up to 1000 Å ($h = 500$ Å in the present notation), for gratings with 8000-Å periods. Extensive studies

of large amplitude diffraction gratings have been carried out by a rather different method by Petit and his colleagues. See the volume *Electromagnetic Theory of Gratings,* edited by R. Petit (Springer-Verlag, Berlin, 1980).

[3]M. Udagawa, Chih-Cong Chow, J. C. Hemminger, and S. Ushioda, Phys. Rev. B 33, 6843 (1981).

[4]J. C. Tsang, J. R. Kirtley, and T. N. Theis, Solid State Commun. 35, 667 (1980).

[5]Y. J. Chen, W. P. Chen, and E. Burstein, Phys. Rev. Lett. 36, 1207 (1976).

[6]S. S. Jha, J. R. Kirtley, and J. C. Tsang, Phys. Rev. B 22, 3972 (1980).

[7]We understand that R. Reinisch and M. Neviere have also found this behavior, in an analysis of fields near gratings, in studies carried out in the 1-μm spectral region. Their maximum fields are somewhat larger than ours (factor of 3 in E_M/E_0). [R. Reinisch and M. Neviere (unpublished).] We believe this is because near 1 μm, the surface polaritons on Ag are much less tightly bound to the surface than they are in the visible. As a consequence, they radiate less efficiently, and the influence of radiation damping is less severe than it is at visible frequencies.

[8]For small amplitude gratings, the radiation rate may be calculated by suitable adaptation of results given by D. L. Mills, Phys. Rev. B 12, 4036 (1973).

[9]A. Otto, in *Polaritons* (Proceedings of the First Taormina Research Conference on the Structure of Matter, Taormina, Italy), edited by Elias Burstein and Francesco de Martini (Pergammon, New York, 1974), p. 117.

[10]Milton Kerker, Dau-Sing Wang, and H. Chew, Appl. Opt. 19, 4159 (1980).

[11]Enhanced fields near a sphere, with radiation damping neglected, are discussed by S. L. McCall, P. M. Platzman, and P. A. Wolff, Phys. Lett. 77A, 381 (1980). Within a similar framework, Ruppin has discussed enhanced fields near a hemispherical bump on an otherwise flat surface. R. Ruppin, Solid State Commun. 39, 903 (1981).

[12]P. K. Aravind, R. W. Rendell, and H. Metiu, Chem. Phys. Lett. 85, 396 (1982). These authors consider field enhancements near a small sphere placed in the vicinity of a flat surface, and when the enhancement in both the incoming and scattered channels is included, they predict cross-section enhancement factors as large as 10^{10} or 10^{12}, which are astonishingly large.

[13]While the value published for this ratio is 440, we understand that an improved calculation of the coverage measurement has raised the value to 600 [S. Ushioda (private communication)].

[14]A. Tadjeddine and D. M. Kolb, J. Electroanal. Chem. 111, 119 (1980).

[15]P. N. Sanda and J. E. Demuth, Phys. Rev. Lett. 47, 57 (1981); J. E. Demuth and Ph. Avouris, *ibid.* 47, 61 (1981).

[16]D. S. Wang and M. Kerker, Phys. Rev. B 24, 1777 (1981).

[17]J. J. Kester, Bull. Am. Phys. Coc. 27, 244 (1982).

[18]H. Numata (unpublished). We are grateful to Professor S. Ushioda for informing us of this work.