Giant Raman scattering of light by molecules adsorbed on the surface of a metal

V. I. Emel'yanov and N. I. Koroteev

M. V. Lomonosov Moscow State University
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A review is given of experimental and theoretical work on giant Raman scattering (GRS) by molecules adsorbed on the surface of submicroscopic particles of metals such as silver, gold, and copper. The GRS effect, i.e., the enormous (by a factor of 10^6) increase in the Raman cross section, is described together with experiments demonstrating the electromagnetic nature of the phenomenon. A model capable of quantitative explanation of the leading features of GRS is put forward.

CONTENTS

1. GENERAL DESCRIPTION OF THE EFFECT

The giant Raman scattering effect (GRS) consists of an enormous (by a factor of $10^5 - 10^6$) increase in the Raman scattering cross section of molecules adsorbed on the surface of precious metals such as silver, gold, and copper.[1-4] This phenomenon is attracting considerable attention among specialists in Raman spectroscopy and among chemists, and is being actively investigated. Suffice it to say that during the last (seventh) international conference on Raman spectroscopy (held in Ottawa in August 1980), a separate section was devoted to GRS and attracted twenty papers (seven of which were invited). Several reviews have now been published in this field.[5-7] This interest in the subject is due mainly to two factors.

An effect as strong as this was unexpected from the physical point of view, and its discovery has stimulated new investigations and the appearance of new concepts in the optics of surfaces. From the practical point of view, the GRS method promises to become a powerful spectroscopic technique for studying metal surfaces, the separation boundaries between solids, and the separation boundaries between electrodes and working mixtures used in electrochemical reactions. This will of course become possible once the effect itself is properly understood and can be controlled. The technique is capable of high spectral resolution and sensitivity to the details of the molecular environment of the surface. The giant amplification of the Raman signal at the surface of a metal can be used to detect small numbers of molecules and very weak lines.

The above effect attracted considerable attention after it was shown that a monomolecular layer of pyridine molecules, adsorbed on an electrochemically prepared rough surface of silver, produced a Raman signal that exceeded by several orders of magnitude the signal one would expect[1] from such a small amount of scattering molecules (surface density of the order of 10^4 cm^{-2}).

Much greater amplifications were reported in subsequent publications.[2-4,8] In the case of the monolayer of pyridine molecules on silver, excited with the 5145-Å line (50 mW), the observed GRS signal was of the order of 10^5 photomultiplier counts per second, which corresponded to an increase in the molecular Raman cross section by a factor of 10^6 as compared with Raman scattering within the body of the liquid.[2,3,9-11] The GRS effect has been recorded for a broad range of different molecules, including pyrazine[12] (in addition to allowed lines, a number of lines that were forbidden in the case of Raman scattering by free molecules was also observed), carbon monoxide,[13] methylpyridine,[14] CN$^-$ (additional low-frequency libration modes were observed),[15] ethylene and propylene,[16] CO$_3$, Cl$^-$, isonicotinic acid, and benzoic acid, adsorbed on silver, gold, and copper (apart from the dependence on the molecular species, silver gives rise to the strongest GRS effect).
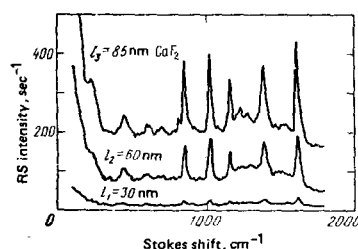

FIG. 1. GRS signal due to 4-pyridine-COH molecules on silver for three different values of the thickness l of the CaF$_2$ (l_1 = 30 nm $< l_2 < l_3$) corresponding to three different amplitudes h of surface roughness on silver ($h_1 < h_2 < h_3$).[22]

In addition to the electrochemical method of adsorbing molecules from solution,[1-4,8-10] molecules have also been adsorbed from vapor in air[1] and in vacuum chambers[13,18,19] (at vapor pressures 10^{-6}–10^{-7} Torr). The last method provides a particularly accurate control of the surface density of the molecules and can be used to investigate the dependence of the GRS effect on this density.[19] The GRS effect has also been observed for island films,[6] on colloidal metal particles,[20,21] and in diode structures.[22] A common feature of all these cases is the presence on the surface (or in the interior) of quasimicroscopic metal grains in the form of rods or spheroids (random dimensions of the order of 100–1000 Å), which are distributed randomly in space with separations of the same order as the linear dimensions of the grains. This picture emerges, for example, when surfaces are examined by electron microscopy.[5]

The GRS effect does not appear to have been observed on a sufficiently smooth metal surface. On the other hand, experiments[22] have shown that the GRS signal strength decreases monotonically as the degree of surface roughness is reduced (Fig. 1).

The GRS effect was observed in these experiments in tunnel diode structures prepared by successive deposition of layers of aluminum, monomolecular aluminum oxide, and CaF_2 on glass substrates. The surface profile was modulated by first depositing a CaF_2 layer on the glass substrate. The silver surface then had a random undulating form with undulation amplitude of 1–100 nm and transverse correlation length of 30–80 nm.

The amplitude of these undulations was found to increase with increasing thickness of the CaF_2, and there was a corresponding increase in the GRS signal which reached saturation when the amplitude was of the order of 10–100 nm. (These structures were simultaneously investigated by inelastic electron tunneling spectroscopy). An analogous behavior was also demonstrated in Ref. 19 where it was shown that the GRS signal was lost altogether in the accompanying noise when the surface roughness was of the order of 2–20 Å, whereas an amplification of 5×10^4 was recorded for surface irregularities of 500–2000 Å.

2. THEORETICAL MODELS FOR THE GIANT RAMAN SCATTERING EFFECT

It may now be regarded as firmly established that the presence on the surface (or in the interior) of geometrically bounded metal structures of submicroscopic size plays a decisive role in the appearance of the GRS effect (see Ref. 25 and the review of theoretical models of the GRS effect given in Ref. 7). This and many other facts (see below) enable us to choose from among the possible GRS mechanisms proposed so far.

GRS theories can be divided into the following groups, depending on the main physical process on which they are based.

(1) GRS explained as resonance Raman scattering due to the shift and broadening of the electronic molecular states on adsorption.[26-29] One of the processes that can give rise to the broadening and shift of these electronic states is the interaction with electromagnetic surface modes—the surface plasmons.[23,24,26,27] Level shifts can also be produced as a result of the appearance of molecule-metal complexes (chemical bonding).[38,29]

(2) Modulated surface reflection,[30] based on the assumption that variations in the charge associated with the chemical bond between the molecule and the metal produce a modulation of the reflectance of the metal surface because of the associated modulation of the susceptibility of the molecule-metal complex.

(3) Image dipole theory,[31-33] which relies on the idea of a singular increase in the polarizability of the molecules as they approach the metal surface, owing to the effect of the dipole image fields.

(4) Microscopic theories of the GRS effect, which rely on the excitation and relaxation of electronic and vibronic states in the metal and the molecule.[34-36]

(5) Electromagnetic theories of the GRS effect in which fields due to electronic oscillations in geometrically bounded submicroscopic structures (surface roughness or colloidal particles[37,25,30,38,46]) play the key role. These theories are essentially based on a resonance increase in the "local" light field acting on the adsorbed molecule. This field appears in the system of closely spaced submicroscopic particles of the precious metals (this phenomonon is also responsible for the specific optical properties of fine metal suspensions, for example, the finely dispersed gold in ruby glass and so on; see Ref. 39, Section 13.5). This theory gives the most complete description of existing experimental information on the GRS effect. For example, the processes upon which theories (1)–(4) are based are in no way connected with the surface roughness, so that they predict the GRS effect even for a perfectly smooth metal surface, which is in clear conflict with experiment.

On the other hand the effective-field theory introduces the geometrically bounded metal structures on the surface of the metal, or in the interior of films, as the key factor governing the GRS effect.

The physics of the GRS effect can be explained in this as follows (for a quantitative discussion, see Section 4).

A rough metal surface can be simplified to a set of submicroscopic metal particles, for example, ellipsoids (or spheroids) with random dimensions (smaller than the wavelength of the radiation), which are randomly distributed over the surface of the metal.

At the same time, the dimension of these particles must be large enough in comparison with the interatomic separation, so that they can contain the free-electron gas in the conduction band.

The localized oscillations in the electron density of such ellipsoids have associated oscillating dipole mo-

ments which interact with one another through the Coulomb field, forming collective modes. This ensures that the rough metal surface exhibits optical absorption maxima corresponding to the excitation of longitudinal and transverse (relative to the surface) plasmon oscillation modes. Such resonances are completely analogous to the optical absorption bands of thin (~100 Å) island films of silver, gold, and copper, which are shown by electron microscopy as consisting of submicroscopic "islands" whose transverse dimensions are much smaller than the wavelength of visible light.[40] These additional absorption bands are not observed for metals in bulk and lie in the yellow-red (or near infrared) parts of the spectrum. They have been actively investigated (see, for example, Ref. 41–43) and it has been found that they are due to the excitation of longitudinal (relative to the surface) collective electronic oscillations in the metal "islands" or localized surface plasmons by the incident light wave. The corresponding frequencies of "perpendicular" oscillations in the case of these metals lie in the ultraviolet and, because of strong interband absorption in this region, additional resonances are not observed.

Analogous additional absorption resonances in the visible range are also exhibited by other systems consisting of fine metal particles and suspensions.

Actually, the foundations of the theory of anomalous additional absorption by systems consisting of metal particles of size smaller than the wavelength of light were laid as far back as eighty years ago by Maxwell-Garnett[44] and by Mie[45] (see also Ref. 39, page 693).

It is important to emphasize that, in the frequency range containing these absorption bands, the ordinary ("bulk") permittivity of metals does not exhibit any resonances, and the appearance of the bands is wholly connected with the resonances between the local electric field of the light wave and the interior of the metal particles.

When molecules are adsorbed on the surface of such particles, they experience the resonance-enhanced local field E_{loc} (at the frequency of the incident light wave ω_i). The oscillations of the molecular dipoles excited by the field E_{loc} at the Stokes frequency $\omega_s = \omega_i - \Omega$ (where Ω is the frequency of intramolecular oscillations that are active in Raman scattering) in turn excite, through their Coulomb field, the collective modes of electron oscillations in the surface structures, which amplify the emission of the molecular dipoles by radiating at the frequency ω_s. The submicroscopic metal structures localized on the surface (or in the interior) are thus seen to act as accumulators of energy and effectively amplify both the incident and scattered radiation, which produces the effective increase in the Raman cross section.

The Raman cross section (power scattered per unit solid angle) of a free molecule is

$$\left(\frac{d\sigma}{d\sigma}\right)_{RS} = k_S^4 \,|\, d_S\,|^2, \tag{1}$$

where $k_s = \omega_s/c$, $\omega_s = \omega_i - \Omega$, $d_s = r E_i$ is the Stokes amplitude of the molecular dipole, r is the contraction of the Raman scattering tensor, and E_i, ω_i are the amplitude and frequency of the exciting light wave, respectively. In the case of Raman scattering by a molecule adsorbed on a rough surface of a metal, the Stokes amplitude of a dipole is $d_s = \tilde{r} E_{loc}$, where $\tilde{r}$ is the Raman scattering tensor of the adsorbed molecule (in which the possible shift of the molecular levels has been taken into account), and $E_{loc} = L(\omega_i) E_i$ is the local field. The effective dipole moment radiating at the frequency ω_s is

$$d_{eff}(\omega_s) = L(\omega_s)\, d_s = L(\omega_s)\, L(\omega_i)\tilde{r}\, E_i. \tag{2}$$

where $L(\omega_s)$ includes the contribution due to the dipole moments of the geometrically bounded metal structures.

Substituting (2) in (1), we obtain the Raman cross section of the molecule on the rough surface of the metal (or the surface of the colloidal particles):

$$\left(\frac{d\sigma}{d\sigma}\right)_{GRS} = \left(\frac{d\sigma}{d\sigma}\right)_{RS}\left|\frac{\tilde{r}}{r}\right|^2 \,|\, L(\omega_s)\,|^2\, |\, L(\omega_i)\,|^2. \tag{3}$$

If we neglect the change in the Raman scattering tensor on adsorption ($\tilde{r} = r$), we see from (3) that the gain is given by

$$\left(\frac{d\sigma}{d\sigma}\right)_{GRS} / \left(\frac{d\sigma}{d\sigma}\right)_{RS} \equiv G = |\, L(\omega_i)\,|^2\, |\, L(\omega_s)\,|^2. \tag{4}$$

It follows from Refs. 25 and 26 (see also Chapter 4) that the gain G may turn out to be of the order of 10^6–10^8 for particular metals under resonance conditions.

The other model of a rough metal surface, which leads to the appearance of additional optical resonances equivalent to those described above, involves the representation of the surface by a superposition of a large set of regular sinusoidal gratings with different amplitudes, different orientations of the "lines", and different separations between these "lines".[46, 22] The appearance of the additional absorption band in this system is connected with the excitation in one of the Fourier components (characterized by a reciprocal lattice vector q) of a coupled surface wave of collective electron-density excitations and electromagnetic oscillations (the so called surface plasmons[47]) when the system momentum is $k_t = K + q$ where k_t is the tangential component of the wave vector of the incident electromagnetic wave and K is the wave vector of the surface plasmon.

When the light is incident from vacuum on the metal surface, the dispersion relation for the surface plasmon is[47]

$$K^2 = \left(\frac{\omega}{c}\right)^2 \frac{\varepsilon}{\varepsilon - 1}, \tag{5}$$

where ω is the plasmon frequency, equal to the frequency ω_i of the incident light wave, and ε is the permittivity of the metal. In the region in which the surface plasmons exist we have $\mathrm{Re}\,\varepsilon \equiv \varepsilon' < 0$, so that
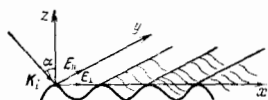
FIG. 2. Excitation of surface plasmons on a sinusoidally modulated silver surface by a light wave with the x-component of the electric field equal to $E_\perp$. The field $\mathbf{E}_\parallel$ does not excite surface plasmons. The GRS signal is observed only for the $\mathbf{E}_\perp$ configuration.[22]

$|\mathbf{K}| > |\mathbf{k}_t|$ for all angles of incidence, from which it follows that the surface plasmons cannot be excited by the light wave incident from vacuum on a level metal surface, since the system momentum cannot be conserved. However, when a regular-lattice perturbation with a definite vector $\mathbf{q}$, or a random roughness having a Fourier component with vector $\mathbf{q}$, is present on the surface, the system momentum is conserved, and the surface plasmon can be excited by the light wave, which is equivalent to an increase in the acting, i.e., local, field of the light wave. All effects governed by this local field also undergo this resonance increase, including Raman scattering by molecules adsorbed on the surface.

3. EXPERIMENTS CONFIRMING THE ELECTROMAGNETIC NATURE OF THE GRS EFFECT

Recent experiments provide strong evidence for the electromagnetic nature of the GRS effect and, at the same time, identify the role of the surface plasmons. Regularly modulated surfaces (holographic gratings with a period of 200–800 nm and amplitude up to 500 nm) were used in Ref. 22. A thin layer of silver was deposited on the surface of these gratings, repeating the modulation profile, and the molecules under investigation were deposited on this layer (Fig. 2). If the incident wave is polarized along the y axis ($\mathbf{E}_\parallel$), surface plasmons are not excited in the silver, and the Raman signal is not recorded. If the polarization vector of the wave has a component perpendicular to the "lines" ($\mathbf{E}_\perp$), the incident light excites the surface plasmons and a strong GRS signal is observed ("gain" $G \sim 10^5$), where the position of the angular maximum of the GRS intensity corresponds to the dispersion relation of the surface plasmon. Moreover, the angular maximum of the GRS effect coincides with the angular maximum in the absorption of light by the rough surface
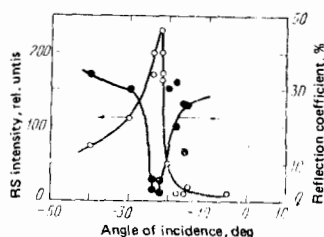
FIG. 3. GRS intensity and reflection coefficient as functions of the angle of incidence α of the laser beam on a sinusoidally modulated silver surface with absorbed molecules of 4-nitrobenzoic acid[22] (cf. Fig. 2).
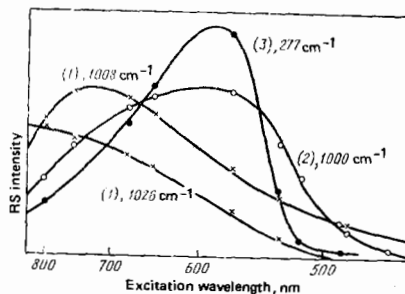
FIG. 4. GRS intensity on silver as function of the wavelength of exciting radiation for molecules with very different electronic structure[48]: 1—pyridene, 2—triphenylphosphene, 3—$[(NH_3)_5 RuOR_4(NH_3)_4OR_4(NH_3)_5]^{6+}$ molecule. The Raman line frequencies used are indicated.

at which the light energy is transformed into the energy of the surface plasmons (Fig. 3).

In the experiment reported in Ref. 48, the GRS process was investigated by recording the frequency dependence of the GRS signal strength for different molecules adsorbed on the silver surface. Despite the considerable difference between the electronic structures of the molecules, the GRS maxima are only slightly shifted relative to one another and lie in the region of the surface plasmon resonance (Fig. 4). A similar situation is observed in the case of gold and copper, but the GRS maxima are then shifted toward longer wavelengths and so are the maxima of surface plasmon absorption.

It has been shown[37] that metals exhibiting the collective electron resonance in the visible region include silver, gold and copper, for which the GRS effect has also been observed. The possibility of observing the GRS effect in transition metals (V, Cr, Ti, Mn, Ni, Co, Fe, and Pd) has also been investigated.[49] Data obtained show that the surface plasmon resonances in these metals lie in the ultraviolet ($\hbar\omega_1 \sim 3$–4 eV), and the best candidate is Pd (the absorption and Raman amplification peak lies at 3.3 eV, i.e., at $\lambda_1 = 375$ nm).

We note, however, that the position of the resonance should depend on the geometry and the statistics of surface inhomogeneities [see Chapter 4, equation (14)]. It follows that the resonance can, in principle, shift toward longer wavelengths. For example, Knasser[50] has reported the first observation of GRS (in CO, C_2H_4, and other molecules) on the surface of small (of the
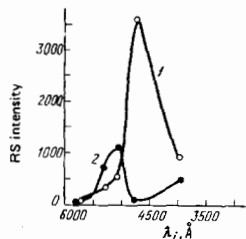
FIG. 5. GRS intensity due to the molecular complexes $CO:H_2$ on the surface of colloidal particles of nickel as a function of the wavelength of exciting radiation.[50] The Raman line is $\nu = 2912$ cm^{-1}. The two curves correspond to different CO to H_2 ratios: 1—$CO:H_2 = 1:1$, 2—$CO:H_2 = 1:4$.

order of 100 Å diameter) colloidal nickel particles excited by visible radiation (Fig. 5). An important condition for the observation of the GRS effect is that the resonance frequency should lie below the threshold for absorption due to interband transitions (short-wave limit of the GRS effect). When this condition is not satisfied, surface plasmons are not efficiently excited by the incident light wave.

If the local plasmon field is responsible for the GRS effect, a small displacement of the molecule from the surface of the metal should not have a critical effect on GRS (in contrast to the case of chemical bonding between the molecule and the metal). When the molecule is displaced from the surface through a small enough distance R, the gain G should decrease in accordance with the expression $G \sim (r_0/R)^{12}$, where r_0 is the characteristic size of the inhomogeneity. For example, for a polarized sphere of radius r_0, the Coulomb field is $E \sim r_0^3/R^3$, so that $d_s \sim (r_0/R)^3$, $d_{eff}(\omega_s) \sim (r_0/R)^6$ and $G \sim (r_0/R)^{12}$ (see, for example, Ref. 51). This means that the GRS effect may appear immediately after the deposition of a few molecular monolayers on the metal surface.

Multilayer structures were used in Ref. 52 to investigate the dependence of GRS on the distance of the molecules from the surface. It was shown that the departure of the molecules from the surface even by 50 to 100 Å had no important effect on the GRS signal strength. This shows that a sufficient condition for GRS to show itself is that the molecules should simply be *near* the rough surface (physical adsorption).

Recently, a group at the Bell Laboratories in the USA performed a series of experiments[40] that have resulted in strong evidence in favor of the electromagnetic nature of GRS. A controlled variation of the surface density of an island silver film deposited on a dielectric substrate (this simulated the regular variation in the roughness of a solid metal surface) was used to perform parallel measurements of the Raman intensity scattered by molecules adsorbed on the surface of the metal islands (the radicals CN⁻), elastic Rayleigh scattering, and optical absorption in the film. Figure 6 shows the results obtained in this comparative experiment. The figure plots the scat-
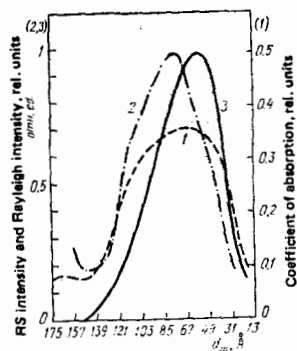

FIG. 7. Theoretical imaginary part of effective permittivity ε'' and local field factor $|L|^4$ compared with the measured Raman intensity as a function of the grain size d_m in the film: 1—$\tilde{\varepsilon}''(\omega t)$, 2—Raman intensity, (3) local field factor.

tered intensity as a function of the quantity $d_m = m/\rho$ where m is the mass of the metal deposited on a unit area of the substrate and ρ is the bulk density. The ratio d_m is a measure of the average size of the silver islands. It is clear that all the optical characteristics depend nonmonotonically on d_m. Electron microscopy has shown that, when $d_m < 60$ Å, the film consisted of individual semiellipsoidal islands whose average dimensions were of the order of the separation between the islands. The islands were found to coalesce for $d_m > 60$ Å, and formed a continuous and relatively level metal layer for $d_m > 150$ Å.

Transmission and reflection data for the film can be used to calculate (from the Fresnel formulas) the effective complex permittivity of the film $\tilde{\varepsilon} = \tilde{\varepsilon}' + i\tilde{\varepsilon}''$, and hence the local field factor $|L(\omega)|^4$. Figure 7 shows the corresponding dependence of $\tilde{\varepsilon}''$ and $|L|^4$ on d_m. It is clear that the local field and the Raman intensity have practically the same dependence on d_m for $d_m \leqslant 60$ Å. For larger values of d_m the two functions depart from one another to some extent, but remain qualitatively similar. The authors of Ref. 40 were therefore fully justified in concluding that their data could be regarded as strong evidence in favor of the GRS model based on the resonance increase in the local field near rough metal surfaces.

FIG. 6. Optical absorption coefficient (1), Rayleigh intensity (2), and the intensity of the Raman line (2144 cm⁻¹, CN⁻) (3) as functions of the grainsize d_m in the silver film.
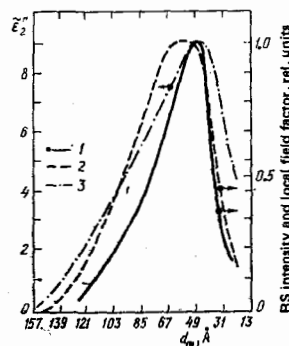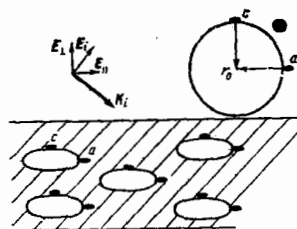

FIG. 8. Model of dielectric film containing metal colloidal particles in the field E_i of the light wave. The metal ellipsoids of revolution are represented by the oval figures and the dielectric by the shaded area. Top right—spherical colloidal particle with absorbed molecules. The molecules under consideration lie at points a and c.

It is, however, important to note that, in many cases, the nature of the bonding between the adsorbed molecule and the surface is important for the GRS effect. For example, it has been shown[5,9] that the molecules of benzoic acid exhibit the GRS effect on silver when the chemical bond with the surface involves the COOH group (chemical adsorption), but the effect does not occur when the benzene ring is simply near the surface (physical adsorption). These results suggest that the electromagnetic mechanism is not the only one in certain cases. For example, modulation of surface reflection[30] provides both qualitative and quantitative explanation of the results of the experiment[53] in which the radical CN^- was chemically strongly bonded to the silver surface (through the carbon atom) and the two modes ω_+ and ω_- were observed (ω_+ and ω_- are, respectively, the relative oscillations of the atoms and the oscillations of the molecule as a whole relative to the metal). The measured intensity ratio of the GRS lines was found to be $I_+/I_- \approx 0.1$, which is in good agreement with the theoretical value[30] of about 0.15.

Other possible situations are those in which the electromagnetic mechanisms combines with other GRS amplifying mechanisms. Thus, the gain observed in the case of GRS in diode structures[22] is $G \sim 10^5$ whereas the estimated pure electromagnetic gain should be about 10^3. The additional amplification may be due to the dipole images.[31-33] Moreover, a new GRS mechanism ($G \sim 10^4 - 10^8$) has also been examined[22] for molecules in the region of the potential barrier of the diode, in which this barrier is modulated by molecular vibrations.[46]

4. GRS EFFECT AND LOCAL FIELDS DUE TO COLLECTIVE ELECTRON OSCILLATIONS (THEORETICAL ANALYSIS)

The above review of experimental data shows that the main mechanism responsible for the GRS effect is the resonance increase in the local field of the light wave near rough metal surfaces and in colloidal films.

We shall now use a simple model to calculate the main parameters of this mechanism.

The medium in which the GRS effect takes place will be taken in the form of a thin dielectric film containing randomly distributed colloidal particles whose dimensions are smaller than the wavelength of light and the thickness of the film. For the sake of simplicity, we shall suppose that these particles are identically oriented ellipsoids of revolution (with semiaxes r_a and r_c and volume v_e; Fig. 8). We shall assume that the molecules studied with the aid of the Raman effect are adsorbed on the surface of these particles. We note, by the way, that similar models have been used [37,25] to calculate resonance optical absorption by thin colloidal films, and to consider GRS on the surface of a metal.

Suppose that a light wave with electric field $\mathbf{E}_i = \mathbf{E}_\parallel$ parallel to the film surface is incident on the system

(the case where the field is perpendicular to the surface can be considered in a similar way; Fig. 8). The field inside the ellipsoid (the local field $\mathbf{E}_{loc}$) consists of the field due to the incident wave, the depolarization field of the ellipsoid, and the "Lorentz field" due to the contribution of the dipole moments of the surrounding ellipsoids (collective effect)

$$\mathbf{E}_{loc}(\omega_1) = \mathbf{E}_1 - \mathcal{L} 4\pi \mathbf{P}_e + \beta 4\pi \mathbf{P}, \qquad (6)$$

where $\mathcal{L} = \mathcal{L}_\parallel$ is the depolarization factor determined by the geometry of the particle (1/3 for a sphere and much less than unity for an elongated ellipsoid), $\mathbf{P}_e$ is the dipole moment per unit volume of the ellipsoid, i.e., its polarization, β is the Lorentz field constant, $\mathbf{P} = n_e \mathbf{d}_e$, n_e is the number of ellipsoids per unit volume, and $\mathbf{d}_e = \mathbf{P}_e v_e$ is the dipole moment of the ellipsoid.

The polarization of the ellipsoid is related to the local field by the formula

$$\mathbf{P}_e = \frac{\varepsilon(\omega_1) - 1}{4\pi} \mathbf{E}_{loc}, \qquad (7)$$

where $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ is the permittivity of the metal. Accordingly

$$\mathbf{P} = \frac{\varepsilon - 1}{4\pi} q \mathbf{E}_{loc}, \qquad (8)$$

where $q = v_e n_e$ is the volume occupied by the metal in a unit volume of the film. For the sake of simplicity, we shall suppose that the permittivity of the dielectric filling the space between the ellipsoids is equal to unity.

From (6)–(8) we obtain the following formula for the local field:

$$\mathbf{E}_{loc}(\omega_1) = \frac{\mathbf{E}_1}{1 + (\varepsilon(\omega_1) - 1)(\mathcal{L} - \beta q)} \equiv L(\omega_1) \mathbf{E}_1. \qquad (9)$$

The values of the effective local fields acting on the molecules at points a and c on the surface of the ellipsoid (see Fig. 8) will be different from one another. At point c, the continuity of the tangential component ensures that the acting field is given by

$$\mathbf{F}_c = \mathbf{E}_{loc} = L(\omega_1) \mathbf{E}_1 \equiv L_c \mathbf{E}_1, \qquad (10)$$

whereas the discontinuity in the normal component at a gives

$$\mathbf{E}_a = \mathbf{E}_{loc} + 4\pi\sigma n = \mathbf{E}_{loc} + 4\pi \operatorname{Re} \mathbf{P}_e. \qquad (11)$$

From (7) and (11) we find that the acting field is

$$\mathbf{F}_a = \varepsilon'(\omega_1) \mathbf{E}_{loc} = \varepsilon'(\omega_1) L(\omega_1) \mathbf{E}_1 \equiv L_a \mathbf{E}_1. \qquad (12)$$

Equation (9) then shows that the local field factor $|L(\omega_1)|$ reaches its maximum at the resonance value $\omega_1 = \omega_r$ which is obtained by demanding that the real part of the denominator should vanish:

$$1 + [\varepsilon'(\omega_r) - 1](\mathcal{L} - \beta q) = 0. \qquad (13)$$

The "additional" (unrelated to the Im ε resonance) light absorption maximum of the field should be observed at the same frequency. In fact the absorption coefficient is equal to the ratio of power dissipated per unit volume to power transmitted per unit area of the surface:

$$\alpha_{abs}(\omega) = \frac{\varepsilon'' q\omega \,|\, E_{loc}\,|^2}{4\pi}\left(\frac{c\,|\,E_1\,|^2}{4\pi}\right)^{-1} = q\varepsilon''(\omega)\frac{\omega}{c}\,|\,L(\omega)\,|^2.$$

Since $\varepsilon''(\omega)$ is a monotonic function of ω in the region of the resonance variation of $|L(\omega)|^2$, the optical absorption resonance is in fact given by (13).

To calculate ω_r we can use in (9) the explicit expression for $\varepsilon'(\omega)$ from the theory of collisionless plasma of conduction electrons: $\varepsilon' = \varepsilon_0 - \omega_p^2/\omega^2$ where ε_0 is the contribution due to interband transitions (it is constant in the region of the resonance), and $\omega_p^2 = 4\pi n_e e^2/m_e$ is the square of the plasma frequency of the electron gas. From (9) and (13) we then find that, near the resonance,

$$|\,L(\omega)\,|^2 = \frac{(\varepsilon'(\omega_r)-1)^2\,\omega^4\omega_r^4/\omega_p^4}{(\omega^2-\omega_r^2)^2+(\omega^4\omega_r^4/\omega_p^4)[\varepsilon''(\omega)]^2}, \tag{14}$$

where

$$\omega_r = \omega_p\left(\varepsilon_0 + \frac{\beta q - \mathscr{L} + 1}{\mathscr{L} - \beta q}\right)^{-1/2}. \tag{14'}$$

In the special case where $\mathscr{L} = 1/3$ (sphere) and $\beta = 1/3$ (Lorentz field), the formula given by (14') becomes identical with the formula for the resonance optical absorption wavelength of the colloidal film reported in Ref. 37.

It is clear from (14') that the resonance occurs only when the medium contains metal particles of finite dimensions, which are characterized by the depolarization factor $\mathscr{L}$ and the mutual influence factor β (if we turn off the interaction between the particles, $\beta = 0$, and (14) gives the absorption resonance of one such particle). The resonance vanishes as we pass to the limit of a continuous medium ($\mathscr{L} \to 0$, $\beta \to 0$, $q \to 1$).

We note that (14') predicts a long-wave shift of ω_r between silver and gold and copper (since $\text{Ag}\,\varepsilon_0 = 4$ and $\text{Au}\,\varepsilon_0 = 8$, whereas $\text{Cu}\,\varepsilon_0 = 10.9$), and this is confirmed by experiment.

When $\omega_i = \omega_r$, equations (9), (12) and (13) show that the Raman gain at a is a maximum and is given by

$$|\,L_a\,|^2 = \frac{\varepsilon'^2(\omega_r)\,(\varepsilon'(\omega_r)-1)^2}{\varepsilon''^2(\omega_r)}, \tag{15}$$

whereas the maximum Raman gain at c is

$$|\,L_c\,|^2 = \frac{(\varepsilon'(\omega_r)-1)^2}{\varepsilon''(\omega_r)^2}. \tag{16}$$

The additional Raman gain occurs because the molecular Stokes dipoles [excited by the local fields (10) and (12)] in turn induce dipole moments in the ellipsoids which oscillate and radiate at the frequency ω_8. To estimate this effect, let us consider the simple case of a sphere of radius r_0 and then proceed to the case of the ellipsoid by analogy. A molecular dipole d_S placed at the origin produces the following field at the

point $\mathbf{R}$:

$$\mathbf{E}_S(\mathbf{R}) = \frac{-d_S + 3\,(d_S\hat{\mathbf{R}})\,\hat{\mathbf{R}}}{R^3}, \qquad \hat{\mathbf{R}} = \frac{\mathbf{R}}{|\mathbf{R}|}.$$

If the molecule is in configuration c on the surface of the sphere (see Fig. 8), the field at the center of the sphere is

$$|\,\mathbf{E}_S(r_0)\,| = -\frac{d_S}{r_0^3}. \tag{17}$$

The local field inside the sphere is given by a formula analogous to (6) and (9)

$$\mathbf{E}_{loc}(\omega_S) = \mathbf{E}_S(r_0) - \mathscr{L}_s 4\pi\mathbf{P}_s(\omega_S) + \beta 4\pi\mathbf{P}(\omega_S).$$

The dipole moment of the sphere can be obtained from (17) with $\mathscr{L}_s = 1/3$:

$$d_s(\omega_8) = \frac{4}{3}\pi r_0^3\,\frac{\varepsilon(\omega_S)-1}{4\pi}\,|\,\mathbf{E}_{loc}(\omega_8)\,| = \mathscr{L}_s\,(\varepsilon(\omega_S)-1)\,L(\omega_S)\,d_S.$$

In the case of an ellipsoid, we substitute $\mathscr{L}_s \to \mathscr{L}_e$. The effective dipole moment of the molecule in position c, which radiates at frequency ω_8, is

$$d_c(\omega_S) = d_S + d_e = \{1 - \mathscr{L}\,[\varepsilon(\omega_S)-1]\,L(\omega_S)\}d_S. \tag{18}$$

Similarly, for a molecule at point a

$$d_a(\omega_S) = \{1 + (1-\mathscr{L})\,[\varepsilon(\omega_S)-1]\,L(\omega_S)\}\,d_S. \tag{19}$$

Using (2) with (19) or (18), we obtain the second factor in the Raman gain in (15), which depends on the position of the molecule on the surface of the colloidal particle as follows:

at the point a (see Fig. 8)

$$|\,L_a(\omega_S)\,|^2 = |\,1 + (1-\mathscr{L})\,(\varepsilon(\omega_S)-1)\,L(\omega_S)\,|^2$$
$$\approx (1-\mathscr{L})^2\,|\,\varepsilon(\omega_S)-1\,|^2\,|\,L(\omega_S)\,|^2, \tag{20}$$

at the point c

$$|\,L_c(\omega_S)\,|^2 = |\,1 - \mathscr{L}\,(\varepsilon(\omega_S)-1)\,L(\omega_S)\,|^2 \approx \mathscr{L}^2\,|\,\varepsilon(\omega_S)-1\,|^2\,|\,L(\omega_S)\,|^2. \tag{21}$$

From (5) and (15) and (20) or (16) and (21), we obtain the expression for the maximum Raman gain ($\omega_8 \approx \omega_i = \omega_r$) at a:

$$G_a = (1-\mathscr{L})^2\left[\frac{\varepsilon'(\omega_r)}{\varepsilon''(\omega_r)}\right]^4[\varepsilon'(\omega_r)-1]^2\,|\,\varepsilon(\omega_r)-1\,|^2, \tag{22}$$

whereas at c:

$$G_c = \mathscr{L}^2\left[\frac{\varepsilon'(\omega_r)}{\varepsilon''(\omega_r)}\right]^4\,|\,\varepsilon(\omega_r)-1\,|^2. \tag{23}$$

It is clear from the last two expressions that molecules adsorbed at a have a much greater Raman gain:

$$\frac{G_a}{G_c} = \frac{(1-\mathscr{L})^2}{\mathscr{L}^2}\,|\,\varepsilon(\omega_r)-1\,|^2 \sim \frac{\varepsilon'^2(\omega_r)}{\mathscr{L}^2} \gg 1,$$

since $|\varepsilon'(\omega_r)| \gg 1$, and $\mathscr{L} \ll 1$ (for example, $\mathscr{L} = 0.2$ when the ratio of semiaxes of the ellipses is $r_a/r_c \sim 2.5$). Similar results can be obtained for a rough metal surface.[25]

Let us now estimate the numerical values of the GRS

gain and the resonance wavelength $\lambda_r = 2\pi c/\omega_r$ in the case of silver. For this special case $\beta = \mathscr{L} = 1/3$ (acting Lorentz field in the case of metal spheres), equation (14) yields

$$\lambda_r = \lambda_p \sqrt{\varepsilon_0 - \frac{q-2}{1-q}},$$

where $\lambda_p = 2\pi c/\omega_p$. The characteristic values of λ_r for silver lie in the range 600–700 nm (see Fig. 4) and $\lambda_p = 136$ nm (i.e. $\lambda_r/\lambda_p \approx 5$), $\varepsilon_0 = 4$ (see Ref. 37). We then have $q \approx 0.86$ and $\varepsilon'(\omega_r)$. The values of ε'' for thin films are much greater than for the material in bulk because of the surface scattering of plasmons and the increase in the number of lattice defects.[54-56] If we take $\varepsilon'' = 5$ (which exceeds the bulk value by an order of magnitude), we find from (22) and (23) that $G_c \sim 500$ and $G_a \sim 10^6$. The effective gain is obtained by averaging over all the positions of the molecule on the surface.

5. CONCLUSIONS

The GRS effect that we have reviewed in this paper is a clear example of the substantial change in the optical parameters of molecules as they approach the surface of submicroscopic metal structures which act as accumulators and amplifiers of the incident and scattered radiation.

Other linear and nonlinear optical effects should be amplified under similar conditions. For example, it is known[57,58] that the intensity of luminescence emitted by a monolayer of dye molecules increases by an order of magnitude when it is deposited on a rough silver surface. Similar amplification effects occur when light (or luminescence) are scattered inelastically by electron-hole excitations on the surface of a metal.[4,8]

Chen et al.[59] have observed a sharp increase in the second harmonic generation on a rough silver surface as compared with a polished surface. The size of this effect ($G \sim 10^4$) was found to be in close agreement with estimates based on the local-field model. This group has also subsequently reported[60] a further increase in the above efficiency when a monolayer of noncentrally symmetric molecules was first placed on the rough silver surface.

We may thus conclude that the main reason for the appearance of the giant resonances in Raman scattering by molecules adsorbed on rough metal surfaces and island and colloidal films is now understood. It is the sharp increase in the local field of the light

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[1] It is clear that local fields can undergo a resonance increase not only as a result of the excitation of surface plasmons on the rough metal surface, as in the above case, but also for a number of other reasons that produce an increase in the local field factor $L(\omega)$. In particular, the increase in the imaginary part of the usual "bulk" permittivity of a continuous medium (for example, colored liquid or crystal containing defects) in the region of absorption bands should also lead to an increase in the local field of the light wave incident on the molecules of the nonabsorbing component of the solution or crystal, since $L(\omega) = (\varepsilon(\omega) + 2)/3$ in the Lorentz model.

wave near the surface structures discussed above, which is due to a resonance with the localized collective oscillations of conduction electrons, i.e., with localized surface plasmons. The frequencies of these resonances in the case of yellow precious metals (copper and gold) and silver lie in the visible range; in the case of other metals, they are probably located at shorter wavelengths.[1]

However, there are many features of the GRS effect and some accompanying phenomena that still await an adequate description. This refers above all to the nature of the noncoherent broad-band emission accompanying GRS and having a dependence on roughness and exciting wavelength similar to that of GRS. Although there is considerable evidence that this emission is generated by surface luminescence,[61] there are some facts that contradict this. The role of chemisorption and, in general, the nature and strength of the chemical bonding of the molecule to the metal in the GRS effect are still not entirely clear. Existing theories of the local field are too approximate and do not take into account some of the finer details of the properties of the surfaces, adsorbed molecules, and so on.

These shortcomings of the "classical" theory of the local field indicate that this theory may not be as universal and comprehensive as it might appear at first sight. There is some experimental evidence that surface roughness of metal substrates with linear dimensions of 100 Å or less, and in particular surface defects such as adatoms, may play an important role in GRS (see the review given in Ref. 67 and the papers in Refs. 68–74). It must, however, be admitted that these experiments were carried out with electrolytically prepared surfaces and not films deposited in a vacuum. Moreover, the authors of these papers also emphasize the importance of chemisorption which also frequently gives rise to the GRS phenomenon.

Nevertheless, the recent attainment of a clear understanding of the important role played by local field resonances near separation boundaries has led to a new concept in surface optics and has revealed new possibilities in the study of surface molecular states by optical spectroscopy.

Although the electron spectroscopy of surfaces and adsorbed molecules is now traditional, well developed, and sensitive enough to detect small fractions of molecular monolayers (see, for example, Refs. 62 and 63), the introduction of optical methods into this field is exceedingly desirable, since this should yield new data complementing electron-spectroscopic data. It should also increase the spectral resolution (a resolution of 1 cm^{-1} is quite realistic in Raman spectroscopy and compares favorably with a resolution of about 50 cm^{-1} in inelastic electron scattering spectroscopy), provide a way of investigating separation boundaries in the interior of sandwich structures, and so on.

Nonlinear optical methods are particularly promising in this respect. The extension of active coherent Raman spectroscopy (ACRS)[64] to the study of monolayers of adsorbed molecules should ensure that many projects

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that until quite recently appeared impossible will become realistic.[65] One of the most interesting directions in this field is the application of nonstationary ACRS with mode-locked laser pumping as a way of direct determination of the picosecond relaxation times of the oscillatory modes of adsorbed molecules. Some results on these times have already been reported[61] for molecules under GRS conditions. Successful experiments have also been carried out on the application of nonlinear modulation Raman spectroscopy of molecular monolayers that do not exhibit the GRS effect.[66] Finally, we have already mentioned the interesting attempts to develop a sensitive method for the detection of small amounts of adsorbed monolayers by second harmonic generation.[60]

There is thus every reason to anticipate rapid progress in the development of optical methods for the investigation of surface phenomena, and it would appear that nonlinear optics will play a leading role in this process.

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