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RAMAN SCATTERING FROM A MOLECULE ADSORBED AT THE METAL SURFACE.
THE MOLECULAR CHARGE OSCILLATION MECHANISM

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Résumé - On présente un modèle de diffusion Raman exaltée de surface, dans lequel l'exaltation résulte de la modulation de la réflectivité par la charge moléculaire totale qui oscille avec la fréquence de vibration. Les oscillations de charge sont dues à la variation périodique de la position du niveau moléculaire.

Abstract - The model for Surface Enhanced Raman Scattering is presented in which the enhancement is a result of reflectivity modulation by the molecular total charge which oscillates with the vibrational frequency. The charge oscillations are caused by the periodical variation in the molecular level position.

I - INTRODUCTION

There are experimental reasons to believe now that a considerable part of the Raman Scattering (RS) enhancement is due to some short-distance mechanism closely related to nature and geometry of the molecular bonding to the metal substrate. Several experimental observations provide the evidence for such a mechanism: the first monolayer effect /1,2/; the effect of bonding geometry /3,4/; evidence for active sites at the metal surface /5-7/; influence of the tunneling barrier height between the molecule and the metal /8/; "activation" of the Pt surface by a monolayer of silver /9/. One can find a complete discussion of related works in /10/.

Another part of the RS enhancement displays a long-distance behaviour and depends on electromagnetic aspects of the molecule-metal interaction rather than chemical ones. The theory of electromagnetic enhancement which explains the effect of Surface Enhanced Raman Scattering (SERS) in terms of the classical local-field enhancement induced by plasma resonances at the rough or specially shaped surfaces can provide successful interpretation of data in many cases, especially in metal colloids /11/ and silver structures produced by microlithography /12/. Thus there is unambiguous evidence for the electromagnetic mechanism to be responsible for at least a part of the enhancement.

However there is no suitable theory for the "chemical" enhancement. The system consisting of an adsorbed molecule and a metal is too complicated for any microscopic calculation. Therefore most of the theories are based on purely speculative arguments, or employ a highly approximate description of the molecule-metal interaction. Hence there are no reliable predictions which could allow one to find out the nature of the "chemical" enhancement.

Here a simple model for the "chemical" enhancement is presented which gives clear predictions avoiding at the same time complicated microscopic calculations. Some results of this theory were published earlier /13/. We shall discuss here mainly qualitative aspects of the theory and related experimental results.

II - THEORY

A general property of the adsorbate system is that conduction electrons of the metal can be involved in the RS process. They take part in collective plasma resonances at the rough surface microstructures /14/. They can also be involved in the charge transfer process providing the resonance RS in visible /15,16/. But apart from these effects conduction electrons could serve as scatterers of light. The scheme of this scattering is the following: the incident laser light (frequency ω_i) induces current (or polarization) in the metal; molecular vibrations modulate this current at the vibrational frequency ω_v and the light emission at the frequencies $\omega_i \pm \omega_v$ appears as a result. This mechanism can be very effective for the RS enhancement due to large polarizability of conduction electrons in visible.

The idea about the possible role of conduction electrons as scatterers was proposed by OTTO /17/ who considered RS in terms of the metal reflectivity modulation by the molecular vibrating dipole. However, the dipole cannot produce effective modulation of the electronic current at the flat surface; only at the rough surface the breaking of the momentum conservation law causes the growth of the dipole contribution to RS /13/. Another modulating mechanism involves oscillations of the total molecular charge driven by vibrations in the molecule. This mechanism was considered by McCALL and PLATZMAN /18/ in their model of a vibrating ion periodically dipping into electron gas, by AUSSENEGG and LIPPITSCH /19/ by analogy with charge transfer in ionic compounds and by the author /13/ in terms of oscillation in occupancy of molecular orbitals in chemisorbed molecule.

A basic assumption of the latter model is the existence of the molecular electronic level near the Fermi energy E_F . In an isolated molecule this level is discrete and may be occupied by one or two electrons or be empty. Thus, the molecular orbital includes an integer quantity of electrons. However, for the chemisorbed molecule this is not the case; due to mixing of this molecular orbital with the continuum of electronic states in the metal the level will acquire the width Γ and its occupancy could be varied continuously depending on Γ and the level position relative to E_F . It should be mentioned that this position does not coincide with that for an isolated molecule; it can be shifted significantly as a result of interaction with the metal. Thus, in a chemisorbed molecule we have the continuum spectrum of electronic states with the density centered about the shifted energy E_a . The Anderson-Newns model predicts for this density of states the Lorentzian form. Therefore, the occupancy n is given by

$$n = \int_{E_F - B}^{E_F} D(E) dE \quad (1)$$

where $D(E) = \frac{2}{\pi} [(E - E_a)^2 + \Gamma^2]^{-1}$ and B is the conduction zone bandwidth. In the eq.(1) B can be safely taken as ∞ if $\Gamma \ll B$.

The connection between the occupancy of the level and molecular vibrations is now directly seen from the eq.(1). The molecular vibrations adiabatically drive the level position and hence the occupancy and the total molecular charge. For example, energies of π and π^* orbitals in hydrocarbons are sensitive to the C-C stretch mode. For occupancy variation Δn we get from(1):

$$\Delta n = D(E_F) \Delta E_a, \quad (2)$$

where ΔE_a is the variation of E_a during one normal mode oscillation Δq , $\Delta E_a = (dE_a/dq) \Delta q$. It should be mentioned that all this adiabatic picture of charge periodically flowing into and from the molecule is correct only if the adiabatic condition $\Gamma \gg \omega_v$ is fulfilled.

The total electric charge on the molecule which oscillates with the frequency ω_v induces the electric field $E(\omega_v)$ inside the metal which, in its turn, modulates the linear response to the applied field $E(\omega_i)$ of laser light. This creates the emission of light at frequencies $\omega_i \pm \omega_v$. The modulated metal response can be calculated by analogy with the RUDNICK and STERN /20/ theory of the second-harmonic generation. However, now we have two interacting fields $E(\omega_i)$ and $E(\omega_v)$ to yield $E(\omega_i \pm \omega_v)$ instead of second-harmonic generation where $E(\omega_i)$ "interacts" with itself to give $E(2\omega_i)$. These calculations /13/ give the RS enhancement about 10^2 for unsaturated hydrocarbons (the UPS data /21/ were used) and about 10^3 for CO on Cu(100) using data on the vibrational lifetime for CO on Cu(100) /22/ (see below). But it is more interesting to discuss qualitative result which follows directly from this model and do not depend on details of calculations.

III - DISCUSSION

The cross section for RS is equal to

$$\sigma = f(\omega_i, \omega_v) (\Delta n)^2, \quad (3)$$

where Δn is given by the eq.(2) and the factor $f(\omega_i, \omega_v)$ is determined by the nonlinear metal response and may include also the local field enhancement factors.

The amplitude of the occupancy oscillation Δn includes all information on the adsorbate system. But the calculation of Δn in a real adsorbate system is rather difficult, especially if the molecule forms a complex with an adatom or other defect sites at the surface. It is possible to estimate Δn only in simple cases when the molecule adsorbs at single crystal surfaces and the bonding geometry is known. Such estimation had been made for hydrocarbons with the use of UPS data to calculate $D(E)$. However, single crystal surfaces are not SERS active. The real SERS active sites at the rough surface and bonding geometry are not known. In spite of this some conclusions can be made.

a) As it has been shown /23/, occupancy oscillations cause changes in vibrational spectra. These are the shift in the vibrational frequency and the decrease of the vibrational lifetime. The same approach was used to explain an observable (by EELS) decrease of the lifetime of the stretch mode CO and N_2 on single crystal surfaces of some metals /22/. An important fact is that this lifetime is proportional to $(\Delta n)^{-2}$. Therefore a conclusion follows: the width (and shift) of any line in the SERS spectrum increases with its intensity. It should be noted that this width appears due to excitation of electrons in the substrate. Hence, it does not depend on temperature and looks as an inhomogeneous broadening. MOSKOVITS et al /24/ observed the corre-

lation between the broadening and SERS intensity in spectra of CO and N_2 adsorbed at Ag and Li surfaces. The authors noted that this correlation is a general property of SERS spectra. Independent measurements of FWHM of vibrational spectra by EELS in SERS "active" systems would allow to get a simple estimation for Δn and σ .

b) The cross section σ from (3) has its maximum when $E_a = E_F$. In this case the level at the Fermi surface provides a resonance channel for electronic tunneling between the metal and the molecule. The correlation between the effective barrier height and the SERS effect was observed in tunnel junctions / 8/. Intense signals were correlated with lower effective barriers.

c) Any factor which changes Γ or the position of E_a could influence the SERS intensity. One could shift the level E_a by coadsorption of ionic species (such as chloride ions) or by the applied potential in an electrochemical cell. Potential dependence of SERS was observed in /25/. However, the potential behaviour of SERS was different for different incident light frequencies. This behaviour does not follow from (3) and seems to support strongly the model of the resonance RS in adsorbate complexes /15,16/. However, the model of oscillating charge could also explain this effect. The factor $f(\omega_i, \omega_v)$ is also dependent on the potential. There are two contributions to the nonlinear response of the metal. One of these is long-range modulation of the metal polarization (skin-depth) and the other is the surface contribution /20/. The former does not depend on the potential. However, the latter varies with applied voltage. Both of them display different frequency dependence. Therefore some frequency dependent shift of σ vs potential curve should take place. The calculation of this effect is now in progress.

d) A general property of any mechanism which involves modulation of reflectivity is the sharp angular dependence of σ . This dependence has nothing in common with the angular resonances observed on gratings and could be observed even at flat substrates. Resonance occurs when components of wavevectors k_i and k_s parallel to the surface satisfy the equation $\Omega_{sp}(k_s - k_i) = \omega_v$, where $\Omega_{sp}(k)$ is the surface plasmon-polariton dispersion curve. This condition is that of the "resonance" modulation of reflectivity. The surface (random) roughening should lead to broadening of the resonance while the grating periodicity will result in appearance of satellites.

e) The concept of "adatoms" or "active sites" can be easily included in the model proposed here. One may argue that the "active site" is the site where the electronic level is close to the Fermi energy. For example, chloride ions change the local work function of the metal and, consequently, shift the π -level of pyridine up to the Fermi level. One should mention that the level E_a in $D(E)$ is not necessary a molecular one. It should belong to any surface state, possibly to the state located at the adatom. In the surface complex molecular vibrations can "drive" this level as the molecular one.

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