SURFACE RAMAN SPECTROSCOPY: A NEW ANALYTICAL TECHNIQUE IN SURFACE SCIENCE

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ABSTRACT

Recent applications of the resonance Raman process and the discovery of surface-enhanced Raman scattering have led to the promising technique of surface Raman spectroscopy. With the development of highly sensitive optical multi-channel analysers, it is argued that this new technique will become a powerful method to study adsorption of molecules on a solid surface and general surface reactions in natural conditions. Along with a brief review of other techniques presently available for surface studies, an overview of the surface Raman spectroscopy is presented.

INTRODUCTION

FOR the last fifty years, Raman spectroscopy[1,2] involving inelastic scattering of light due to vibrational excitations of molecules in a gas or liquid and excitations of phonons in solids has been one of the well known analytical techniques for physical and chemical analysis of materials. Together with the methods of x-ray diffraction, optical absorption and fluorescence spectroscopies, it has played a crucial role in the development of modern chemistry, biology and physics. With the advent of highly tunable and intense lasers, there has indeed been a renaissance in this field, both in terms of its extension to other types of elementary excitations and higher order nonlinear processes and in terms of its applications to more diverse analytical problems. A high resolution Raman spectrum can easily lead to the basic information on the identities as well as detailed arrangements of atoms and molecules in the system. However, Raman scattering due to vibrational excitations in a typical molecule is a very weak optical process arising from the modulation of the electronic polarization induced by the incident light by the ionic motion in the molecule. The Raman cross section for such excitations being only about 10^{-30} - 10^{-31} cm^2 per molecule, Raman spectroscopy could not be used till very recently for studying adsorbed molecular monolayers on a solid surface, with only about 10^{12} - 10^{13} molecules in the interaction region.

In the study of atomic and molecular processes at a solid surface, the weak Raman signal cannot be increased by simply increasing the incident laser intensity, because due to local heating that alters the physical system itself. Thus, until a few years ago Raman spectroscopy did not have any major role in the development of as important an area as surface science. With the use of resonance Raman scattering and the discovery[3,4] of surface-enhanced Raman scattering (SERS), together with the development of highly sensitive optical multi-channel analysers (OMCA), this situation is changing fast. In fact, surface Raman spectroscopy may soon develop into one of the most important techniques in the study of surface science, because unlike the case of other present day sensitive methods a sample can be studied in its natural state here without any high vacuum requirements.

Before discussing the recent developments of SERS and OMCA which have given great impetus to the new technique of surface Raman spectroscopy, first a brief review of the types of problems which are studied in surface science and the usual techniques available in the field will be presented. We will then discuss the new developments which have led to the surface Raman spectroscopy and speculate on the future for this technique.

SURFACE SCIENCE

Matter is normally found in a solid, liquid, gaseous or plasma state. The boundary between any of these two phases is the so-called surface region, the structure and properties of which are studied in surface science. Many physical properties and phenomena, *e.g.*, electron emission, adsorption of molecules and oxidation, friction, adhesion, nucleation and epitaxial crystal growth, electrical conduction and surface superconductivity, surface reactions and catalysis, etc., depend critically on surface conditions, which by their very nature are highly sensitive to contaminations by unwanted foreign atoms and defects. However, with the rapid progress in semiconductor and ultra-high vacuum technologies in recent years, one is now in a position to obtain various types of atomically clean and controlled solid surfaces which may be used in a proper scientific study of their physical properties. In other words, it is only now that we are in a position to study meaningfully microscopic physical processes taking place at any solid surface with a given environment. Of course, surface science ranges over many disciplines, including the important areas of biology, metallurgy, industrial chemistry and solid state physics.

While dealing with solid surfaces, with which we will be concerned here in this article, one usually studies:

(1) Structure and physical properties of pure intrinsic surfaces, without any contaminations.

(2) Surface atomic diffusion.

(3) Adsorption of atoms and molecules and surface reactions.

(4) Crystal growth, etc.

In the important fields of surface atomic diffusion and surface reaction science, the basic problems involve (a) physical mechanisms for heterogeneous catalysis, etc., (b) electrode reactions, corrosion, etc., (c) surface oxidation processes, (d) mass transport or shape changing processes, such as sintering, etc., (e) transport across biological membranes, etc., each of which is of obvious technical and fundamental importance. For example, if one can develop an efficient catalytic agent, whether metallic or otherwise, which can greatly increase the rate of photochemical reaction for converting water into hydrogen, one would have solved the basic "energy" problem for ever! It should be added here immediately that classical chemists have been working on catalysis, electrochemistry and general surface chemistry for a long time. However, the problem of understanding the physical mechanisms responsible for these surface reactions is still largely unsolved. As we know, usual chemistry and physics seemed to be completely different fields till 1928, when quantum basis was established for the physical mechanism responsible for chemical reactions. After that, of course, the boundary between these two fields disappeared. Similarly, the problem for a physicist in this area today is to develop the microscopic physical understanding of surface reactions to the extent that it removes the boundary between surface physics and the traditional surface chemistry.

As a simple example, let us consider briefly the chemical reactivity of metals and its usefulness in catalytic processes due to their ability to break chemical bonds. In a Lennard-Jones type of theoretical model, this problem is studied by comparing the potential energy curves involving interaction between the molecular complex AB and the metal with the bonding of individual complexes A and B and the metal (figure 1). The theoretical problem is to obtain explicit and detailed results for the electronic structure and the total energy in a model which treats the interaction of molecular clusters with an extended, semiinfinite metal (electron system) in a realistic way. It is only then that we can understand the role of a given metal as a catalyst for a given dissociative or associative chemical reaction. At present, available calculations of this type[5] are too crude, but there are very encouraging signs. Nevertheless, we will still need a lot of experimental data on controlled surfaces and surface

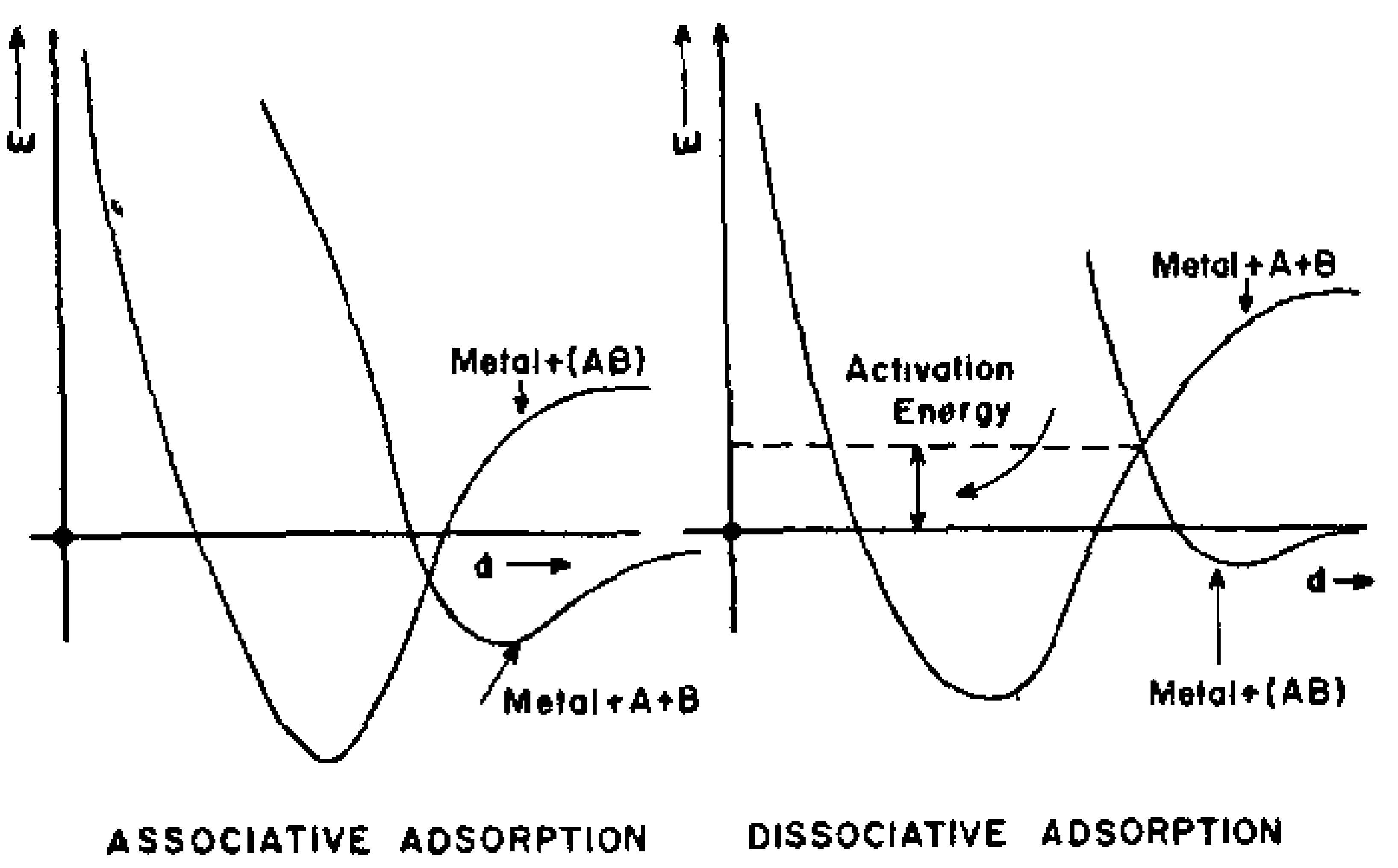

Figure 1. The possible Lennard-Jones potential-energy diagrams for the dissociative and associative adsorptions of a molecule AB on a metal. The molecule-metal potential energy curve (metal + AB) is compared with that for widely separated fragments A and B interacting with the metal. Associative chemisorption can occur when the minimum of the curve for the separated fragments A and B lies above the minimum of the molecule-metal curve, or when the activation energy in the right hand side plot is too high.

reactions in order that we may attack these basic problems in a meaningful way.

AVAILABLE SURFACE ANALYTICAL TECHNIQUES

The oldest methods for surface analysis of adsorbed molecules involved optical absorption technique (spectrophotometer), flame spectrometry and polarography, all of which are destructive. Many of the modern techniques are nondestructive, and are based on the interaction of incident photons or particles like electrons, ions, etc., with the surface phase, and subsequent detection of emitted photons or charged particles. These techniques are classified below, using the notation, (*incident probe: emitted particles*) to distinguish them meaningfully. For more details on each of these techniques the recent review article by Higatsberger[6] and original references given there may be consulted.

(*Electrons Incident: Electrons Emitted*) The most important analytical techniques involving electrons incident to the surface and detection of electrons emitted from it relate to Auger electron spectroscopy (AES), electron energy loss spectroscopy (ELS), low energy electron diffraction (LEED), scanning and transmission electron microscopy and respective extension of these techniques. In AES, the incident electron ionizes an atomic core level which is followed by radiationless Auger transition of an outer electron to the core level and the escape of an Auger electron. Experimentally, the number of Auger electrons N(E) and the derivative dN/dE are obtained as a function energy to identify the surface atoms. In ELS, one studies the energy loss of electrons reflected from the surface due to electronic or vibrational excitations in the surace region. Since low energy electrons of energy 5 eV to 500 eV have usually very small penetration depth, LEED is a powerful technique to determine surface structure of atoms and molecules. In fact, in a modern laboratory, techniques of AES, ELS and LEED are normally combined in a single experimental set-up. One of the major drawbacks in these techniques is the requirement of ultrahigh vacuum for defining and detecting the electrons as a function of its true energy.

(*Electrons Incident: Ions or Neutral Particles or Photons Emitted*). In this class of techniques, one has electron-impact ion desorption, surface desorption molecule microscopy and soft x-ray appearance potential spectroscopy, etc.

(*Ions Incident: Electrons or other Particles Emitted*). In this class, most important techniques relate to ion neutralization spectroscopy, ion scattering spectroscopy, sputtering and ion-induced x-ray-analysis.

(*Neutral Particles Incident: Photons or Other Particles Emitted*). Neutron activation analysis in which atoms become radioactive due to neutron irradiation with subsequent emission of γ-ray photons is a widely used method in this class, along with the method of sputtering, etc.

(*Photons Incident: Electrons Emitted*). Apart from the powerful techniques involving the (*electrons*: electrons) class, the (*photons: electrons*) class is the most sensitive and important in modern surface analysis. The x-ray photoelectron spectroscopy (XPS) and the angle resolved ultraviolet photo-electron spectroscoy (UPS) give most of the information about the elementary composition of the surface layers, since the emitted electron energy can be measured quite accurately. The method is based on the well known principle of the photoelectric effect and the fact that the energy of the atomic and molecular levels and the corresponding photo-electron energy threshold are element and complex specific. With the availability of powerful synchroton excitation sources which give well collimated intense monoeneretic photons from infrared to x-ray regions, the photo-electron spectroscopy is now one of the best methods to study surfaces. However, once again high vacuum is necessary to energy analyse the emitted electrons.

(*Photons Incident: Photons Emitted*). This includes the class of techniques involving optical and x-ray fluorescence, ellipsometry, Mossbauer spectroscopy and laser surface Raman spectroscopy. Except for the surface Raman spectroscopy, many of the other processes are not surface specific and thus cannot be used widely. In what follows, our aim for this article is to show that in years to come, the surface Raman spectroscopy requiring no vacuum, etc., is destined to become a very important technique for surface analysis. It is capable of giving important information on surface reactions and atomic diffusion in natural conditions of the physical system.

There are various other probes, like acoustic surface waves, electric and magnetic fields (NMR, EPR) and thermal heat which may be used for surface studies in very special cases.

RAMAN SCATTERING CROSS-SECTION

For an isolated molecule at the position $\vec{r}_0\omega$, an incident light wave of frequency ω and amplitude $\vec{E}_{\rm inc}(\vec{r}, \omega)$ induces an electric polarization in the molecule of the form

$$\vec{P}(\vec{r},\omega) = \vec{\alpha}(\omega) \cdot \vec{E}_{\rm inc}(\vec{r}_0,\omega)\delta(\vec{r}-\vec{r}_0) \qquad (1)$$

where $\vec{\alpha}(\omega)$ is the electronic polarizability tensor of the molecule. Because of ionic vibrations in the molecule, $\vec{\alpha}$ is a function of the normal coordinates $\vec{Q}(\omega_v)$ oscillating with the vibrational mode frequencies ω_v. For a given vibration mode, this leads to the Raman electric polarization

$$\vec{P}_{\rm Raman}(\vec{r},\omega_s=\omega-\omega_v) = \left[\delta\vec{Q}(\omega_v)\cdot\frac{\partial\vec{\alpha}}{\partial\vec{Q}}\right] \cdot\vec{E}_{\rm inc}(\vec{r}_0,\omega)\delta(\vec{r}-\vec{r}_0) \qquad (2)$$

at the Stokes frequency $\omega_s = \omega - \omega_v$. The Stokes power scattered per unit solid angle, with polarization unit vector $\hat{e}_s$, is then given by the elementary expression (figure 2)

$$\frac{\mathrm{d}\,(\text{Stokes Power})}{\mathrm{d}\Omega} \simeq \frac{\omega_s^{\,4}}{8\pi c^3}\left|\left[\delta\vec{Q}(\omega_v)\cdot\frac{\partial}{\partial\vec{Q}}\right] \hat{e}_s\cdot\vec{\alpha}(\omega)\cdot\vec{E}_{\rm inc}(\vec{r}_0,\omega)\right|^2 \qquad (3)$$

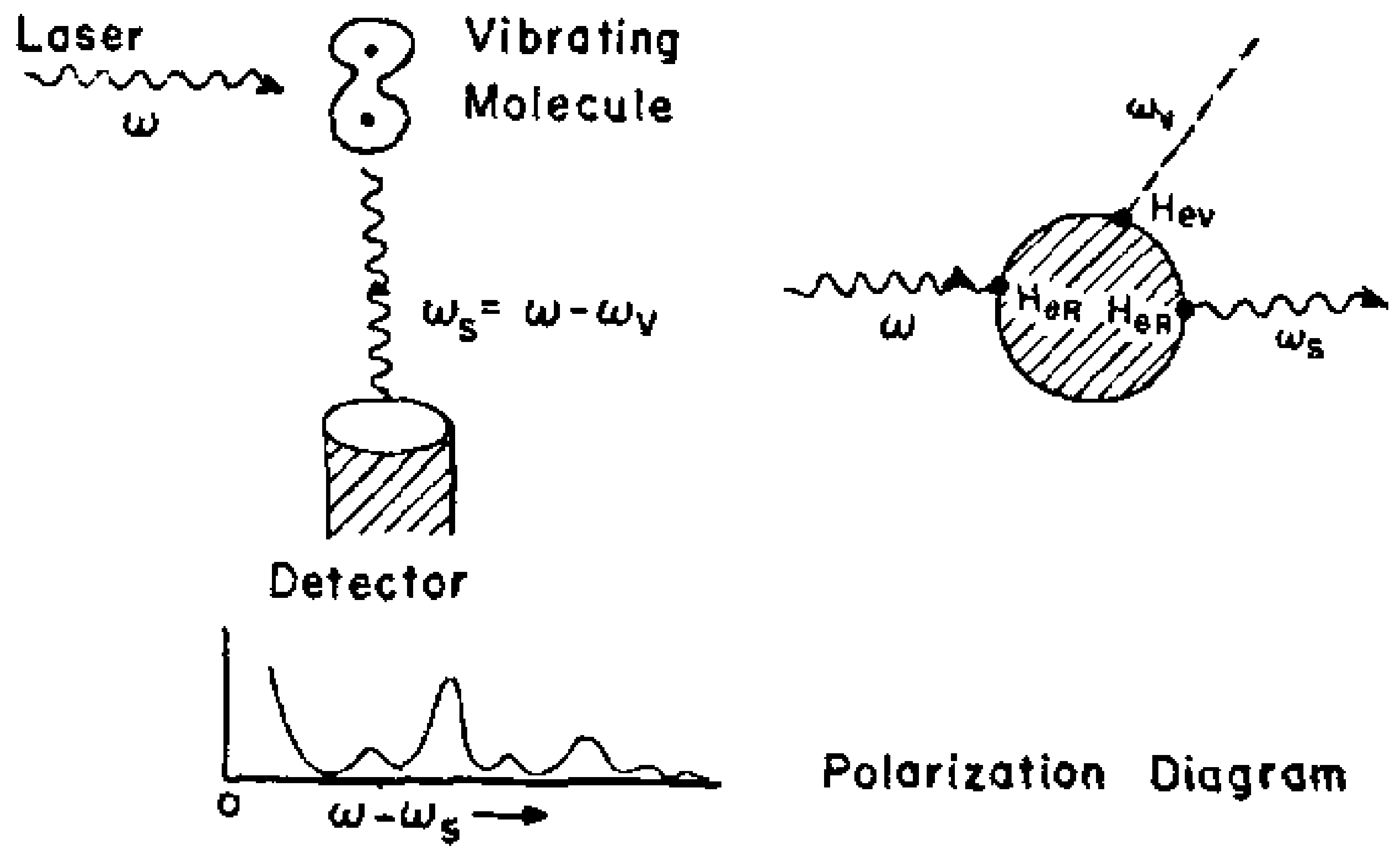

Figure 2. Raman scattering process from an isolated molecule, showing the modulation of induced optical polarizability due to the interaction between the electrons and the ionic vibration. H_{eR} represents the interaction of the electrons with the optical radiation.

For the spontaneous Stokes scattering, the square of zero-point vibrational amplitude for the normal mode of frequency ω_v is

$$\langle \delta Q^2 \rangle \simeq \frac{\hbar}{2M\omega_v} \simeq 10^{-18}\ \mathrm{cm}^2 \qquad (4)$$

where M is the effective ionic mass. Since the molecular polarizability α has the dimensions of (length)^3, it is of the order of $(10^{-8})^3$ cm^3, and $(\delta\alpha / \delta Q)$ is of the order of $(10^{-8})]^2$ cm^2, *i.e.* square of the atomic size. From (3) and (4), the Raman cross-section per molecule may thus estimated to be of the order of

$$(\mathrm{d}\sigma)_{\rm Raman}\ \text{per molecule} = \frac{4\pi\ \text{Power}}{C|E_{\rm inc}|^2}$$

$$\simeq \frac{|\langle \partial Q^2 \rangle|| \partial\alpha/\partial Q|^2}{\lambda_s^{\,4}} \simeq 10^{-30}\text{–}10^{-31}\ \mathrm{cm}^2 \qquad (5)$$

where ω_s is the wavelength of the scattered light.

For an incident laser flux of 10 mW/cm^2, which may be used safely and conveniently in surface experiments, there are approximately 10^{17} photons/sec cm^2, so that for a molecular monolayer adsorbed on a surface there may be about 10^{13} molecules in the beam region. The scattering rate is thus about 10^{1} to 10^{2} photons-sec only. Till very recently, such precision in highly (frequency) resolved optical photon counting techniques was out of question, and most researchers were not interested in using Raman scattering as a probe in surface science. However, by the middle of the seventies a few workers were brave enough to try it any way, and now we have a new technique! We will discuss this in the next section.

RESONANCE RAMAN AND SURFACE-ENHANCED RAMAN SCATTERING

To overcome the small cross-sections for Raman scattering, one of the usual methods to detect small numbers of molecules, *e.g.*, in biological samples, is to use the technique of resonance Raman effect. As is well known, the electronic polarizability $\vec{\alpha}(\omega)$ has resonances with respect to the incident frequency ω. It is given by the second-order perturbation expression

$$\vec{\alpha}(\omega) = \sum_i f_i \sum_n \frac{\langle i|e\vec{r}|n\rangle\langle n|e\vec{r}|i\rangle}{(E_n-E_i-\hbar\omega-\Gamma_{ni})} + \frac{\langle i|e\vec{r}|n\rangle\langle n|e\vec{r}|i\rangle}{(E_n-E_i+\hbar\omega+i\Gamma_{ni})} \qquad (6)$$

where f_i are the occupation probabilities of the single-electron states $i\rangle$, with energy E_i in the molecule. Note that the polarizability has a resonance whenever any intermediate state electronic excitation energy $E_n - E_i = \hbar\omega$, the incident photon energy. The same resonance occurs for the Raman cross-section in a more elaborate theory which goes beyond the simple polarizability theory being used here for the sake of simplicity. The polarizability theory is of course correct in the limit[7] $\omega_s \to \omega$. The essential point is that one can indeed increase the cross-sections by several orders of magnitude in Resonance Raman scattering (by a factor $h^2\omega^2/\Gamma_{ni}^2$) if we can tune the incident frequency to one of the electronic excited states of the molecule. Indeed, this method is being used for several years now by Yamada[8] and others. However, the tunability requirements for different molecules are different for the incident frequency, and it is not very convenient to study solid surfaces with different kinds of adsorbed molecules by this method. The technique of the normal Raman spectroscopy, where it is not necessary to fine tune the incident photon energy has the obvious advantages. Of course, if one can use the broad excited states of the substrate solid to enhance the Raman signal from the adsorbed molecule, this problem may be solved partly. This, indeed, brings us to the next topic of surface-enhanced Raman spectroscopy.

In spite of severe handicaps, in 1974 Fleishmann *et al.*[4] were using laser Raman spectroscopy to detect adsorbed pyridine in the region of silver-electrolyte interface inside an electrochemical cell. They indeed observed a large signal compared to the one expected. However, because of the complexity of the electrochemical system they thought that the increased signal might be due to the increased surface area and correspondingly increased adsorbed molecules on the silver electrode, because of its roughening during the anodization process. It was not till 1978, when Jeanmaire and van Duyne showed that the enhanced signal is not due to the increase in the number of adsorbed molecules, but due to increase of Raman cross-sections by almost 10^6, for adsorbed molecules on anodized Ag surface. Since then there has been a large amount of activity[9], both theoretical and experimental, in this field of surface-enhanced Raman scattering (SERS). This is not the place to mention all the examples, but experimentally such enhancements ranging from a factor of 10^2 on a smooth surface to 10^7 on rough surfaces have been observed[9] for many types of organic as well as inorganic molecular complexes adsorbed on metals like Ag, Cu, Au, Pt, Ni, Hg, etc. and alloys like Ag-Pd, etc.

A general theoretical formulation for SERS, observed with a variety of substrate shapes and structures in different types of systems, had been hindered for several years by somewhat conflicting experimental results and because of the complex nonreproducible physical systems chosen in initial experiments. From the expression (3) for Raman intensity for an isolated molecule, it is obvious that due to the presence of the metal close to the molecule, the following changes may take place:

(1) The local field acting on the molecule is not the incident field $\vec{E}_{\rm inc}(\omega)$, but modified to $\vec{E}^{(0)}(\omega)$, due to the presence of the metal with a given dielectric function (see figure 3).

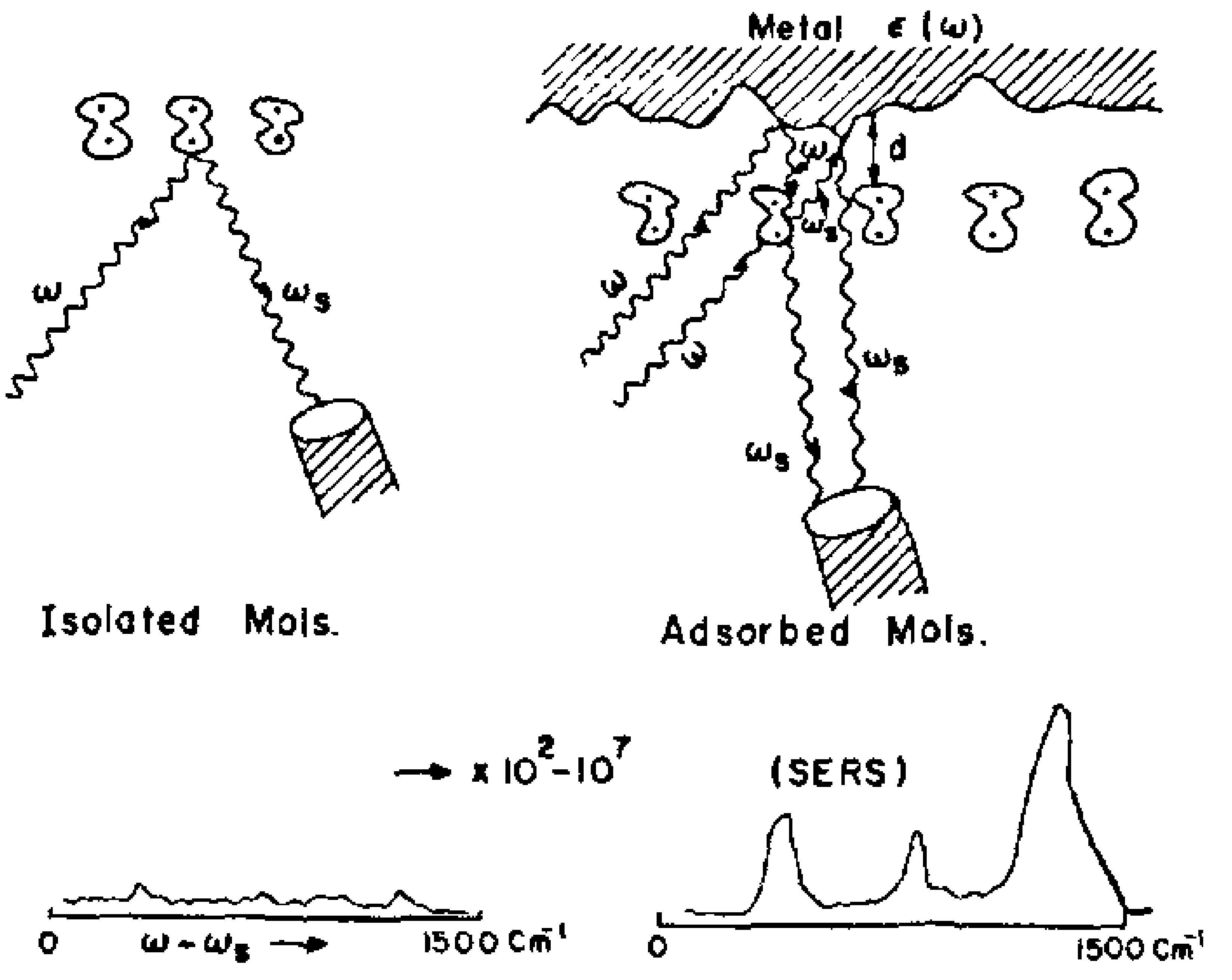

Figure 3. Comparison of Raman scattering from isolated molecules with that of molecules adsorbed on a metal surface. Note that the incident total field on a molecule as well as the total scattered field in the detector are modified due to the presence of the metal. In some cases, one has very large surface-enhanced Raman scattering (SERS).

(2) The emission from the Raman dipole polarization is now in the presence of the metal, and therefore the propagation properties of the Stokes scattered signal are changed. There may be additional signal in the detector (figure 3).

(3) The electronic polarizability $\vec{\alpha}$ of the isolated molecule gets changed because of the interaction and overlap of the electronic wave functions of the electrons in the molecule and the metal. This involves bonding and tunneling of metal electrons (figure 4). Of course, this will depend on the effective potential barrier for metal electrons and the nature of chemical bonding with adsorbed molecules.

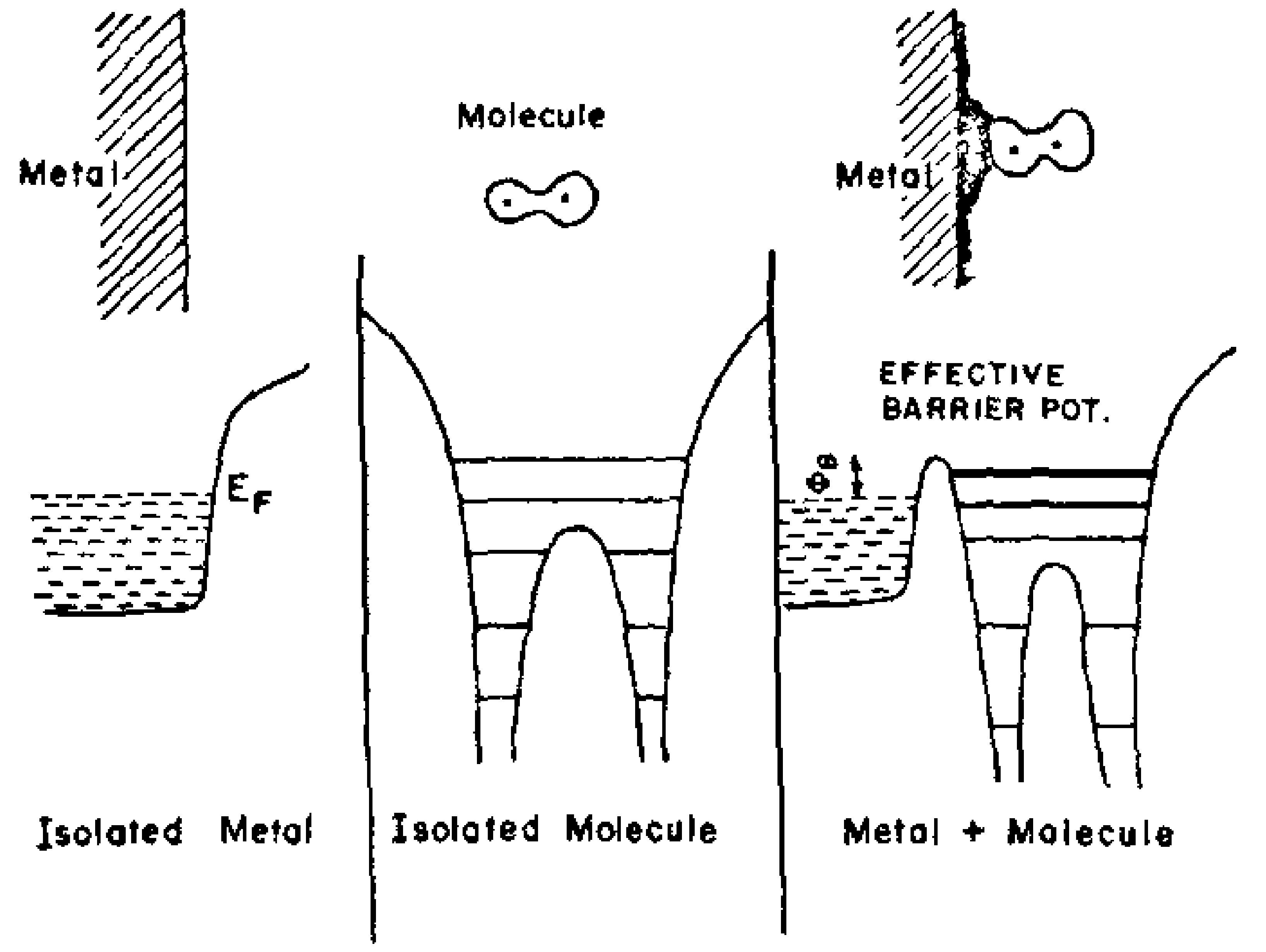

Figure 4. Schematic diagrams of one-electron potentials and energy levels in an isolated metal (free-electron like states filled upto the Fermi surface), in an isolated molecule (bound electronic states) and in a metal-molecule complex (broadened levels for the molecules, tunneling states and possible additional broad charge-transfer bound states). A change of molecular polarizability is possible for the first one or two layers, due to the quantum overlap. The language of induced surface-dipole moment[14] is, however, more appropriate in such a case. The change can be large for a small effective surface barrier potential Φ_B.

(4) The frequency of ionic vibrations and the fluctuation spectrum of $\langle \delta Q^2 \rangle$ may now be different than the case of vibrations in an isolated molecule. In most cases, the frequency shifts for various lines are found to be small, but line shapes and widths may be quite different.

There are three length scales in the problem under consideration: (i) wavelength of light λ, (ii) distance d of the molecule from the surface and (iii) the atomic size $a_0 \simeq 1$A°. Of course, there is no effect of the surface on Raman intensity if $d \gg \lambda$. We have to deal with only the case when the molecular distance $d \leq \lambda$. Again, as long as $d \gg a_0$, there can not be any overlap and the electronic polarizability change discussed as (3) above must be negligible. So is the change in linewidth discussed as (4). Thus in the long range limit ($d \gg a_0$, $d \lesssim \lambda$), only the local field at the molecule site and the Stokes propagation have to be accounted for. In the short range limit when $d \sim a_0$, all the four effects, including the change of $\vec{\alpha}$ to $\vec{\alpha}_s$, have to be included.

There is a class of theories[9,10] presented by Moskovits, Philpott, Metiu, Kerker, Gersten, Burstein and McCall *et al.* which deals with the case of classical long range enhancement by assigning SERS to the roughness or shape-induced local field enhancement. There is another class of theories by King *et al.*[11] and Otto[12] which considers the short range enhancement of $\vec{\alpha}$, due to the classical image dipole effect or strong "ad-atom" bond formation at the surface between the molecule and the metal. The classical image-dipole calculation, of course, can not be valid for $d \sim a_0$ where quantum overlap cannot be ignored. However, in a series of papers[13,14], Jha, Kirtley, Tsang and Agarwal have developed a comprehensive theory of SERS which takes into account, both the long range effect ($d > a_0$) and the short-range effect ($d \sim a_0$) in a tunneling model[13]. By performing controlled experiments on surfaces with known grating profiles, the major results of this model theory have been verified in a series of experiments[15,16] done by Tsang, Kirtley, Theis, Jha and Sanda *et al.* For detailed formulation and results, the original papers should be consulted.

In SERS, the local field $\vec{E}(\omega)$ acting on the adsorbed molecule can be enhanced by a factor of 10^2 or more as compared to the incident field $\vec{E}_{\mathrm{inc}}(\omega)$, because of resonant excitation of surface-plasmon-polaritons (SPP) or transverse conduction electron resonances in the metal substrate. SPP are nothing but the transverse surface electromagnetic excitations of the metal, with dielectric function $\epsilon(\omega) = \epsilon_1(\omega)$ $i\epsilon_2(\omega)$, $\epsilon_1(\omega)$ negative. For a plane surface, the dispersion relation for such excitation is

$$(K''_{sp})^2 = \mathrm{Re}\left[\frac{\varepsilon(\omega)}{\varepsilon(\omega)+1}\right]\frac{\omega^2}{c^2} > \frac{\omega^2}{c^2}, \qquad \mathrm{Re}\,\varepsilon(\omega) < -1 \tag{7}$$

where K''_{sp} is the wavevector of the SPP parallel to the surface. Note that maximum wave vector for an incident light wave ω is ω/c, implying that SPP on a plane surface cannot be excited by light (figure 5). However, if one has a rough surface on the scale of λ, the plane surface $z = 0$ is replaced by the surface

$$z = \sum_{g} \xi_{g} \exp[(i\vec{g}\,(x_{i} + y_{\hat{j}})] \tag{8}$$

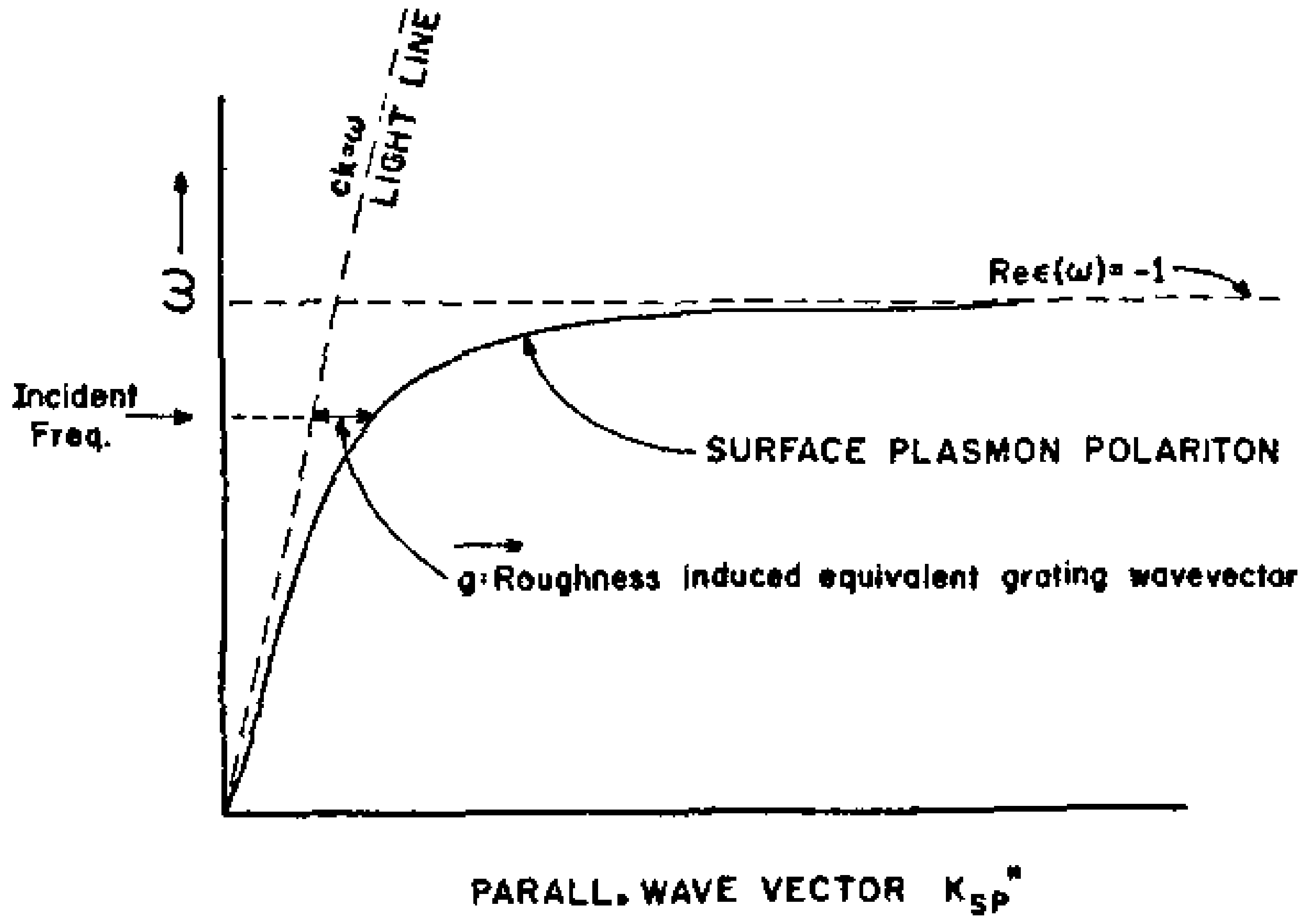

Figure 5. Surface-plasmon-polariton dispersion relation (ω *vs* the wave vector of SPP parallel to the surface), for a plane surface. Ordinary light ($\omega = ck$ can not excite SPP at a plane surface, because of wave vector (momentum) mismatch. Arbitrary surface roughness or a sinusoidal grating structure can provide the additional momentum for SPP excitation.

The equivalent two-dimensional grating vectors $\vec{g}$ (see figure 5) then allow the excitation of SPP on a plane surface. For a single sinusoidal grating and fix frequency ω, the resonance is possible for a fixed incident angle θ, so that $(\omega/c)\sin\theta \pm K''_{sp}(\omega)$. However, for an arbitrary rough surface, there can be a resonance at any angle. In that sense this type of SPP resonance on a metal surface is very broad in terms of the incident frequency ω; it is not possible only when Re $\epsilon(\omega)$ becomes greather than -1 at high frequencies. This is unlike the case of discrete molecular level resonances in the resonance Raman scattering discussed earlier.

As in the case of a rough surface, the local field can also be enhanced on the surface of metallic spheres, spheroids, etc., due to the corresponding SPP resonances. For a small sphere of radius R ($R \ll \lambda$), the lowest order dipolar resonance satisfies the dispersion relation

$$\mathrm{Re}\left[\varepsilon(\omega) + 2 + \frac{12}{5}\frac{\omega^2}{c^2}R^2\right] = 0 \tag{9}$$

As it is clear from the above discussions, on a plane surface (with no structure on it), there is no large enhancement of the local field, and only other reason for SERS can be the short range increase in the polarizability $\overleftrightarrow{\alpha}$. For $d \sim a_0$, because of tunneling of metal electrons to the molecular site and possible chemical bonding, there is a possibility of extra electronic oscillators and more tunneling-like or broad charge-transfer bound state like intermediate states. This can possibly increase $\overleftrightarrow{\alpha}$ for specific systems. However, in general, this is not expected to be more than a factor of 10^3 or so. But in the presence of SPP excitations due to roughness, the overall short-range enhancement for the first molecular monolayer can be as large as 10^6–10^7. The long range enhancement ($d \gtrsim a_0$) can be as high as 10^3–10^4 for Ag. Expected typical distance dependence of the combined enhancement in the so called modulated surface dipole model of Jha, Kirtley and Tsang[14] for the short range part is shown in figure 6. The experimental confirmation of this in Ref. 16 is the most crucial success for the theory of Jha, *et al.*

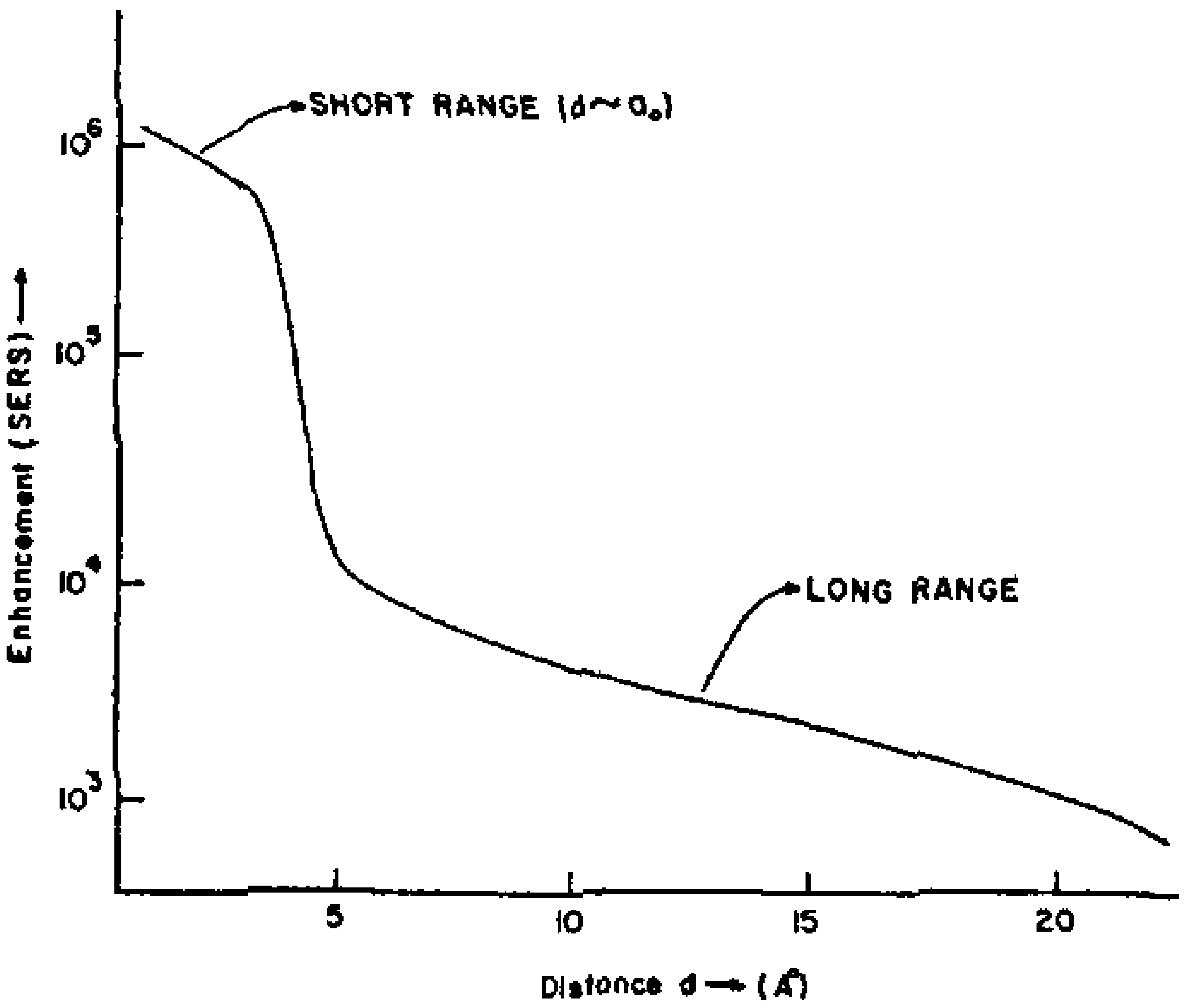

Figure 6. A sketch of the metal-molecule distance-dependence of long range as well as short range enhancements of Raman signal, in the modulated surface-dipole model of Jha *et al.*[14] including electromagnetic SPP excitation. The effective barrier potential for tunneling of the metal electrons to the molecular site, Φ_B, is assumed to be about 0.5 eV.

OUTLOOK FOR SURFACE RAMAN SCATTERING

From the preceding discussions of the resonance Raman scattering from adsorbed molecules and the surface-enhanced Raman scattering, it is quite clear that the surface Raman spectroscopy may be used in a wide variety of physical situations. However, both these techniques are not very universal. Although, highly tunable multiple frequency lasers are now available and although metals are an important class of substrates (catalytic agents, *e.g.*) in surface science, we still have to go a long way from the resonance Raman spectrosocpy and SERS. Insulators and semiconductors as substrate can not give very high enhancements in SERS for arbitrary incident frequencies, because of narrow surface exciton-polariton resonances in them. Similarly, for many molecules, unless the effective barrier potential for tunneling of metal electrons to the molecular site is small or there is a strong charge-transfer state and bonding, SERS is not very strong even for metals.

The most universal method for the surface analysis without any severe restrictions on vacuum, incident frequency, substrate, etc., is still the ordinary surface Raman spectroscopy, *without* expecting any substantial enhancement of the scattering crosssection. Thus in order to make the new technique of surface Raman spectroscopy the most important one, one must improve the optical photon counting techniques to detect very low frequency-resolved signals. This is, of course, the ongoing development of optical multi-channel analysers for use in Raman spectrosocpy. Already many laboratories throughout the world are involved in this, and it is possible now[17] to detect 10^{-1}–10^{-2} photons/sec without any problem, with the required frequency resolution. This has immediately opened up the possibility of detecting a monolayer of almost any molecule, on almost any reasonably nonabsorbing substrate. With further improvements in the counting rate, one should be able to study surface reactions using the surface Raman spectroscopy. Some day, we may even monitor real time fast surface reactions, with further improvements in optical photo-multiplier technology and associated electronics.

In summary, the future outlook for the new technique seems to be quite bright. It is not being claimed here that the surface Raman scattering technique is destined to solve immediately any specific problem of surface science which may have a great technical importance. What is being said here is that it would become a great analytical technique to study physical processes relevent to surface physics and chemistry, and it is the correct time for any one to enter this exciting field.

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