PHYSICAL REVIEW B VOLUME 29, NUMBER 6 15 MARCH 1984

Ground-state charge transfer as a mechanism for surface-enhanced Raman scattering

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(Received 2 August 1983)

A model is presented for the contribution of ground-state charge transfer between a metal and adsorbate to surface-enhanced Raman scattering (SERS). It is shown that this contribution can be understood using the vibronic theory for calculating Raman intensities. The enhancement is due to vibronic coupling of the molecular ground state to the metal states, the coupling mechanism being a modulation of the ground-state charge-transfer energy by the molecular vibrations. An analysis of the coupling operator gives the selection rules for this process, which turn out to be dependent on the overall symmetry of the adsorbate-metal system, even if the charge transfer is small enough for the symmetry of the adsorbate to remain the same as that of the free molecule. It is shown that the model can yield predictions on the properties of SERS, e.g., specificity to adsorption geometry, appearance of forbidden bands, dependence on the applied potential, and dependence on the excitation wavelength. The predictions are in good agreement with experimental results. It is also deduced from this model that in many cases atomic-scale roughness is a prerequisite for the observation of SERS. A result on the magnitude of the enhancement can only be given in a crude approximation. Although in most cases an additional electromagnetic enhancement seems to be necessary to give an observable signal, this charge-transfer mechanism should be important in many SERS systems.

I. INTRODUCTION

Since the first observation of surface-enhanced Raman scattering (SERS) a couple of years ago[1-3] extensive investigations on this topic have been performed (for recent reviews, see Refs. 4 and 5). Enhanced Raman scattering has been reported for nearly 100 adsorbates (ranging from simple diatomics to highly complex biomolecules), on about 10 substrates (from silver, which works best, through various noble and transition metals to even polydiacetylene), and in different environments (from electrolyte solutions to ultrahigh vacuums). In addition to the enhancement, the appearance of forbidden Raman bands[6] as well as overtones and combination modes, though rarely,[7] have been claimed. Although not all of these observations could be confirmed by other investigators, there exists a great bulk of reliable experimental material which should give a sound basis for explaining the effect theoretically.

Despite this fact, the different theoretical models proposed up to now have not led to an unequivocally accepted model. Theories have been reviewed in Refs. 4,5, and 8. Roughly, they can be divided into two groups: (i) "classical" or "electromagnetic models," and (ii) "nonclassical" or "chemical" models. The first group explains the enhancement as due to an enhanced electromagnetic field near the surface of a metal when light is acting on it. Especially when the surface is not ideally flat, the field of the incoming light may be enhanced by the "lightning-rod" effect at surface regions of high curvature, as well as by resonantly excited charge-density vibrations in the metal (conduction resonances and surface-plasmon polaritons). For the incoming as well as for the outgoing (scattered) light the surface protrusions may constitute "antennas," which are matched to the radiation field much better than is an individual molecule. Thus, an enhanced coupling of the scattering molecule via the metal surface to the radiation field is achieved, yielding an enhancement of up to 10^{11} in the Raman intensity for special situations.[9] In general, there seems to be widespread agreement now that a substantial part of the enhancement is caused by this electromagnetic mechanism.

On the other hand, a number of arguments have been set forth for an additional enhancement based on a more specific interaction of the adsorbed molecule with the metal substrate (for an exhaustive compilation, see Ref. 5). The main points are the different behavior of different molecules, the different enhancement of different Raman bands in the same molecule, the dependence on adsorption geometry, and the influence of experimental parameters to which the electromagnetic mechanism should be insensitive. The existence and the mechanism of a chemical enhancement, which has been postulated to explain these points, is still much in debate. Nevertheless, it has turned out that the best candidates for enhancement models of this type are those involving some kind of charge transfer between the molecule and the substrate. This is corroborated by the fact that virtually all the molecules examined successfully in SERS experiments are able and show the tendency to form charge-transfer complexes with noble and transition metals, since all possess lone-pair and/or π orbitals. There is not any conclusive result on saturated hydrocarbons, for example. So it seems justified to assume that charge transfer is an indispensable prerequisite for the chemical-enhancement mechanism.

Charge-transfer models for SERS can be divided into ground-state and excited-state mechanisms. In the excited-state models it is assumed that there exists a charge-transfer transition, where an electron is excited from a filled state located at one of the charge-transfer

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partners to an empty state located at the other one. The surface enhancement is attributed to the resonance encountered when the energy of the exciting photon matches the charge-transfer transition energy. In this sense the surface enhancement is viewed as a kind of resonance Raman scattering. Ground-state models, on the other hand, rely on the fact that even in the ground state there exists a (though weak) charge transfer between the partners. This transfer is modulated by molecular vibrations and thus gives rise to Raman bands. The enhancement in these models is attributed to the high-scattering cross section of the metal, which "lends" intensity to otherwise weak Raman bands from the adsorbate. While the theory of the excited-states mechanism has been developed to a considerable extent,[10–12] the ground-state mechanism has been established only in rather general terms.[13–15] The purpose of this paper is to fill this gap.

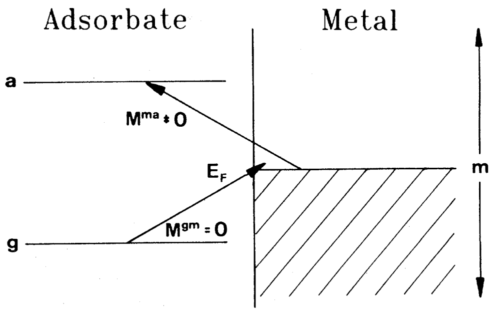

FIG. 1. Schematic state diagram used in this model. g and a, adsorbate ground and excited states; m, metal states; E_F, Fermi energy; $M^{ma}$and M^{gm}, charge-transfer transition moments $m \rightarrow a$ and $g \rightarrow m$.

II. THEORY

When a molecule is adsorbed to a metal surface, in order to calculate the Raman intensity the adsorbate-surface system has to be considered as a whole. Thus, strictly speaking, one has only eigenstates of the system and cannot separate the adsorbate and substrate states. This fact will be taken into account in this theory, but for convenience nevertheless those states, whose wave functions resemble those of the free molecule, will be termed the (perturbed) adsorbate states, while those resembling the states of the bare metal will be called the (perturbed) metal states. Experimental investigations[16,17] have shown that in usual SERS systems there exist charge-transfer transitions from the metal conduction band to unoccupied states of the adsorbate, while charge-transfer transitions from the adsorbate ground state to unoccupied states of the metal have not been observed. This is expected from the properties of molecule-metal complexes as known from coordination compounds. So as a basis for this analysis a schematic state diagram for the adsorbate-metal system as shown in Fig. 1 will be considered. Transition moments M_{ma} from metal to excited adsorbate states are assumed to be finite, while the moments M_{gm} from the adsorbate ground state to metal states are assumed to be zero.

The quantity responsible for the scattered radiation is, in a semiclassical approximation, the induced dipole moment $M = \alpha E$ (α polarizability, E field strength of the exciting electromagnetic field). The polarizability involved in a Raman transition $k \rightarrow 1$ is known from second-order perturbation theory to be

$$(\alpha_{\rho\sigma})_{mn} = \sum_{e \neq k,l} \left[\frac{\langle k \mid M_\sigma \mid e \rangle \langle e \mid M_\rho \mid l \rangle}{E_e - E_k - E_0} + \frac{\langle k \mid M_\rho \mid e \rangle \langle e \mid M_\sigma \mid l \rangle}{E_e - E_k + E_0} \right] . \qquad (1)$$

Here $M_{\rho,\sigma}$ are the dipole-transition-moment operators for the polarization directions ρ and σ, E_0 is the energy of the exciting photon, E_e is the energy eigenvalue of a so-called intermediate state, and E_k and E_l are the energies of the initial and final state of the transition. Intermediate states have to be considered all eigenstates except the initial and the final one, the summation extending over all intermediates.

It has been shown in the so-called vibronic theory by Albrecht[18,19] that by applying the Born-Oppenheimer approximation and using a Herzberg-Teller expansion, the polarizability may be expressed as a sum over three terms:

$$(\alpha_{\rho\sigma})_{gi,gj} = A + B + C . \qquad (2)$$

The three contributions to the polarizability are given by

$$A = \sum_{e \neq g} \sum_{v} \left[\frac{M_{ge}^{(\rho)} M_{eg}^{(\sigma)}}{E_{ev} - E_{gi} - E_0} + \frac{M_{ge}^{(\sigma)} M_{eg}^{(\rho)}}{E_{ev} - E_{gj} + E_0} \right] \langle i \mid v \rangle \langle v \mid j \rangle , \qquad (3a)$$

$$B = \sum_{e \neq g} \sum_{v} \sum_{s \neq e} \left[\left[\frac{M_{eg}^{(\rho)} M_{gs}^{(\sigma)} h_{se}}{E_{ev} - E_{gi} - E_0} + \frac{M_{eg}^{(\sigma)} M_{gs}^{(\rho)} h_{es}}{E_{ev} - E_{gj} + E_0} \right] \frac{\langle i \mid v \rangle \langle v \mid Q \mid j \rangle}{E_e - E_s} + \left[\frac{M_{ge}^{(\rho)} M_{sg}^{(\sigma)} h_{es}}{E_{ev} - E_{gi} - E_0} + \frac{M_{ge}^{(\sigma)} M_{sg}^{(\rho)} h_{es}}{E_{ev} - E_{gj} + E_0} \right] \frac{\langle i \mid Q \mid v \rangle \langle v \mid j \rangle}{E_e - E_s} \right] , \qquad (3b)$$

$$C = \sum_{e \neq g} \sum_{t \neq g} \sum_{v} \left[\left[\frac{M_{ge}^{(\rho)} M_{et}^{(\sigma)} h_{tg}}{E_{ev} - E_{gi} - E_0} + \frac{M_{ge}^{(\sigma)} M_{et}^{(\rho)} h_{tg}}{E_{ev} - E_{gi} + E_0} \right] \frac{\langle i \mid v \rangle \langle v \mid Q \mid j \rangle}{E_g - E_t} + \left[\frac{M_{eg}^{(\rho)} M_{te}^{(\sigma)} h_{gt}}{E_{ev} - E_{gi} - E_0} + \frac{M_{eg}^{(\sigma)} M_{te}^{(\rho)} h_{gt}}{E_{ev} - E_{gj} + E_0} \right] \frac{\langle i \mid Q \mid v \rangle \langle v \mid j \rangle}{E_g - E_t} \right] . \qquad (3c)$$

Q is the normal coordinate of the vibration under consideration, the M_{eg}, etc., are the transition matrix elements $\langle e \mid M \mid g \rangle$, etc., the superscripts $(\rho),(\sigma)$ denote polarization, g denotes the electronic ground state, e, s, and t denote different intermediate electronic states, i, j, and v refer to the initial, final, and intermediate vibrational states, respectively, and h_{se}, etc., are the Herzberg-Teller expansion coefficients, which are given by $h_{ab} = \langle a \mid \partial H/\partial Q \mid b \rangle$, where H is the total electronic Hamiltonian of the system. The summations in e, s, and t go over all electronic eigenstates except those indicated, and the summation over v extends over all vibrational states of the respective electronic states.

We deal with Raman scattering starting from the molecular ground state as opposed to excited-state mechanism starting from metal states. Moreover, only off-resonance cases will be considered, which means that the exciting energy does not match any of the allowed transitions. Following Ref. 18 it is assumed that the resonance denominators in (3) are nearly independent of the quantum number v. Then the closure-of-the-sum rule can be applied and the products of vibrational matrix elements in B and C reduce to the form $\langle i \mid Q \mid j \rangle$. The energy denominators become $E_e \pm E_0$. In addition, $M_{ab}^{(\xi)} = M_{ba}^{(\xi)}$ is assumed. With these simplifications and following Ref. 19 in the treatment of the A term, one gets

$$A = 2 \sum_{e \neq g} \frac{h_{ee}[(E_e - E_g)^2 + E_0^2]}{[(E_e - E_g)^2 - E_0^2]^2} M_{ge}^{(\rho)} M_{ge}^{(\sigma)} \langle i \mid Q \mid j \rangle \ , \tag{4a}$$

$$B = -2 \sum_{e \neq g} \sum_{s > e} \frac{h_{es}[(E_e - E_g)(E_s - E_g) + E_0^2]}{[(E_e - E_g)^2 - E_0^2][(E_s - E_g)^2 - E_0^2]} \times (M_{ge}^{(\rho)} M_{sg}^{(\sigma)} + M_{ge}^{(\sigma)} M_{sg}^{(\rho)}) \langle i \mid Q \mid j \rangle \ , \tag{4b}$$

$$C = -2 \sum_{e \neq g} \sum_{t \neq e} \frac{h_{gt}(E_e - E_g)}{(E_t - E_g)[(E_e - E_g)^2 - E_0^2]} \times (M_{ge}^{(\rho)} M_{et}^{(\sigma)} + M_{ge}^{(\sigma)} M_{et}^{(\rho)}) \langle i \mid Q \mid j \rangle \ . \tag{4c}$$

For this problem the summations have to be extended over adsorbate as well as metal states. In these sums then there are terms containing only adsorbate or metal states, yielding Raman scattering from the compounds without specific interactions, and mixed terms, representing the adsorbate-substrate interaction. Since the states in this problem are perturbed ones and not exactly those of the noninteracting species, the first group of terms will give a slight modification in the Raman intensity also, which will be neglected in the following. A much higher influence is expected from the interaction terms, however. In writing these terms, metal states are denoted with the index m and excited adsorbate states with the index a. One then gets

$$A = 2 \sum_{m} \frac{h_{mm}[(E_m - E_g)^2 + E_0^2]}{[(E_m - E_g)^2 - E_0^2]^2} M_{gm}^{(\rho)} M_{gm}^{(\sigma)} \langle i \mid Q \mid j \rangle \ , \tag{5a}$$

$$B = -2 \sum_{a} \sum_{m < a} \frac{h_{am}[(E_m - E_g)(E_a - E_g) + E_0^2]}{[(E_m - E_g)^2 - E_0^2][(E_a - E_g)^2 - E_0^2]} \times (M_{gm}^{(\rho)} M_{ga}^{(\sigma)} + M_{gm}^{(\sigma)} M_{ga}^{(\rho)}) \langle i \mid Q \mid j \rangle \ , \tag{5b}$$

$$C = -2 \sum_{a} \sum_{m} \frac{h_{gm}(E_a - E_g)}{(E_m - E_g)[(E_a - E_g)^2 - E_0^2]} \times (M_{ga}^{(\rho)} M_{ma}^{(\sigma)} + M_{ga}^{(\sigma)} M_{ma}^{(\rho)}) \langle i \mid Q \mid j \rangle \ . \tag{5c}$$

The A and B terms both contain dipole moments M_{gm}. The (experimentally justified) supposition has been made, however, that these moments are zero. So it is found that A and B vanish, and the interaction between the adsorbate and the metal shows up in the Raman intensity only via the C term. This term describes vibronic coupling between the ground state and other states nearby. Usually, this term is neglected, since there are no other states near the gound state. In this case, however, the substrate states provide the opportunity for the ground state to couple. Since the substrate states are very closely spaced, forming an energy band in the metal, many of these states can interact with the adsorbate ground state. Moreover, the energy difference between these states and the ground state can be very small, thus yielding a very large C term. So, in this model the surface enhancement is caused by C-term Raman scattering based on vibronic coupling of the adsorbate ground state to close-by metal states. The condition for this mechanism to work is, apart from nonvanishing expansion coefficients h_{gm}, a finite transition probability for a charge-transfer transition from metal states m to excited states a of the adsorbate, which for their part have to be connected to the ground state by allowed transitions. Thus, also in this model charge-transfer transitions are necessary, but the enhancement is caused by ground-state coupling to the metal state and does not involve any resonance of the exciting light with the charge-transfer transition.

To evaluate the contribution of C-term scattering to the surface enhancement, one has to take into account the perturbation of the states g and m by adsorption. A simple expression for the perturbed states can be used, assuming linear mixing, since the perturbation is assumed to be small. Then one has

$$\Phi_g = \Phi_g^{(0)} + \sum_{m} F_{gm} \Phi_m^{(0)} \ , \tag{6a}$$

$$\Phi_m = \Phi_m^{(0)} + \sum_{a} F_{ma} \Phi_a^{(0)} \tag{6b}$$

with Φ_m,Φ_g,Φ_a the wave functions of the perturbed states, $\Phi_m^{(0)},\Phi_g^{(0)},\Phi_a^{(0)}$ those of the unperturbed ones, and $F_{gm} = \langle m^{(0)} \mid g^{(0)} \rangle E_g / \Delta E_{gm}$, $F_{ma} = \langle a^{(0)} \mid m^{(0)} \rangle E_m / E_{ma}$ the mixing coefficients. Mixing of the ground state with the metal states is assumed to be small compared to excited-state mixing and has been omitted therefore in (6b).

In a harmonic-oscillator approximation one has $\langle i \mid Q \mid j \rangle = (\hbar^2/2E_{ij})^{1/2} \equiv b_{ij}$ for Stokes-shifted first-order Raman scattering with vibrational energy E_{ij}. Thus,

$$C=-2b_{ij}\sum_a\sum_m \alpha'_{am}\langle m\,|\,h_Q\,|\,g\rangle/(E_m-E_g) \tag{7}$$

with

$$\alpha'_{am}=(M^{(\rho)}_{ga}M^{(\sigma)}_{ma}+M^{(\sigma)}_{ga}M^{(\rho)}_{ma})(E_a-E_g)/[(E_a-E_g)^2-E_0^2]$$

and $h_Q=\partial H/\partial Q$. For weak coupling, as is usually the case in SERS systems, α'_{am} may be approximated by the unperturbed value, so that the perturbation shows up only in the energies E_m, E_g and the matrix element $\langle m\,|\,h_Q\,|\,g\rangle$. In a better approximation, the perturbed states should also be considered in α'_{am}. This refinement will not be undertaken in this paper, however. By introducing the perturbed states into (7) one gets

$$C=-2b_{ij}\sum_a\sum_m \frac{\alpha'_{am}}{E_m-E_g}\left[\langle m^{(0)}\,|\,h_Q\,|\,g^{(0)}\rangle+\left\langle \sum_m F_{gm}m^{(0)}\,|\,h_Q\,|\,m^{(0)}\right\rangle+\left\langle g^{(0)}\,|\,h_Q\,|\,\sum_a F_{ma}a^{(0)}\right\rangle\right] . \tag{8}$$

A second-order term has been neglected in (8).

While the C term is responsible for surface Raman scattering, the Raman intensity in the free molecule is dominated by A (Franck-Condon) and B (Herzberg-Teller) scattering. The surface-enhancement factor is then given by

$$\beta=\frac{I_{\text{absorbed}}}{I_{\text{free}}}=\left[\frac{C}{A_{\text{free}}+B_{\text{free}}}\right]^2 . \tag{9}$$

This enhancement factor can only be estimated using crude approximations. Assuming only two excited states a and a' in the molecule, $h_{mg}\approx h_{aa'}\approx h_{aa}$ and $M_{ga}\gg M_{ma}$, one finds

$$\beta\approx\sum_m\left[\frac{E_a-E_g}{E_m-E_g+i\Gamma_{mg}}\right]^2 , \tag{10}$$

where a damping term Γ_{mg} corresponding to the homogeneous width of the states m and g has been introduced to avoid a singularity in the energy denominator. Taking the free-electron lifetime for h/Γ_{mg} (h being Planck's constant) and assuming a reasonable distribution of the states m around g one gets a value of $\sim 100-1000$ for β. Of course, because of the extreme approximations used in finding this value, it is of no quantitative significance. Nevertheless, Eq. (10) can give a feeling of how β will qualitatively be influenced by the position of the energy levels involved, and in what range or orders of magnitude it can be expected to find the surface-enhancement factor. In a better approximation, β will depend on various other parameters, as for example (at least for some cases as will be discussed later), on the excitation wavelength, and above all, on the matrix elements in (8). Obviously these matrix elements are determined by the operator h_Q. Therefore, it will be necessary to investigate the properties of this operator more closely.

After Mulliken[20] the wave function ψ_{CT} of an adsorbate-metal charge-transfer complex in the ground state can be expressed by

$$\psi_{\text{CT}}=a\psi_{a,m}+b\psi_{a^-m^+} . \tag{11}$$

Here $\psi_{a,m}$ is the wave function of the interacting species without charge transfer, and $\psi_{a^-m^+}$ is the wave function corresponding to the transfer of an electron from the metal to the adsorbate. The coefficients a and b denote the relative contributions of the neutral and the ionic structure. In weak complexes $a\approx 1$ and $b\ll 1$ always. Formally, the complex can be viewed as a supermolecule with a fractional charge Δq shifted from the metal to the adsorbate. The fractional charge is given by (taking into account the normalization $a^2+2abS+b^2=1$)

$$\Delta q=e(b^2+abS)\approx 6eS^2 \tag{12}$$

with e the elementary charge and $S=\langle\psi_{a,m}\,|\,\psi_{a^-m^+}\rangle$.

The Hamiltonian H_{CT} for the complex can now be written

$$H_{\text{CT}}=H_{a,m}+H_1 , \tag{13}$$

where $H_{a,m}$ is the Hamiltonian for the interacting species without charge transfer and H_1 contains the charge-transfer contribution. $\psi_{a^-m^+}$ consists of a half-filled metal orbital $m^{(0)}$ and the lowest, previously unoccupied molecular orbital $a_L^{(0)}$, now also filled with one electron. H_1 is thus the potential energy caused by the Coulomb field of the ionic species. One gets

$$H_1=-e\Delta q\left[\frac{1}{r_m}-\frac{1}{r_{aL}}\right] \tag{14}$$

with $r_m=|(\vec{r}-\langle m^{(0)}\,|\,r\,|\,m^{(0)}\rangle)|$ and $r_{aL}=|(\vec{r}-\langle a_L^{(0)}\,|\,r\,|\,a_L^{(0)}\rangle)|$ distances from the "centers of charge" of the orbitals $m^{(0)}$ and $a_L^{(0)}$. To find the operator h_Q (12) and (14) are inserted into (13) and derived with respect to Q. Neglecting a term $\partial H_{a,m}/\partial Q$, which describes vibronic coupling by processes other than charge transfer, one finds

$$h_Q=-6e^2\left\{2S\left[\frac{\partial S}{\partial Q}\right]_0\left[\frac{1}{r_m}-\frac{1}{r_{aL}}\right]\right.$$
$$\left.-S^2\left[\frac{1}{r_m^2}\left[\frac{\partial r_m}{\partial Q}\right]_0-\frac{1}{r_{aL}^2}\left[\frac{\partial r_{aL}}{\partial Q}\right]_0\right]\right\} . \tag{15}$$

The subscript 0 denotes the derivative to be taken at $Q=0$.

From (15) it is possible to establish the conditions for h_Q to be nonvanishing. For convenience the origin of h_Q is chosen in the center of mass of the adsorbed molecule, because with this choice the usual definition of the normal coordinate Q can be retained and the symmetry of the vibrations remains the same as in the free molecule. Then it is seen immediately that $(\partial r_m/\partial Q)_0$ is zero if the distance between the adsorbate and the metal atom to which it is attached is independent of Q. For weak bonding this is fulfilled to a good approximation for all intramolecular vibrations of the adsorbate. So $(\partial r_m/\partial Q)_0$ has only to be considered for a vibration of the entire adsorbate against the metal. $(\partial r_{aL}/\partial Q)_0 \neq 0$ means that the center of charge of the a_L orbital is dependent on the normal coordinate, i.e., the vibration must be infrared active. If the adsorbate has inversion symmetry, due to this term Raman bands forbidden in the free molecule by the mutual exclusion rule will become allowed, a fact that has been observed experimentally in SERS.[21]

Because of (12) the term $(\partial S/\partial Q)_0$ represents a modulation of the charge transfer Δq by the adsorbate vibration. This corresponds to the electron-hopping term (also called electron-tunneling integral) considered in the standard Newns-Andersson theory[22] and the excited-state charge-transfer models of SERS.[10,11] The existence of this modulation has been proven and its magnitude estimated by quantum-chemical calculations for simple molecular complexes.[23] The charge-transfer modulation does not depend explicitly on the symmetry of the vibration with respect to the symmetry elements of the free molecule, but the symmetry elements of the entire adsorbate-metal system have to be considered. It is thus dependent on the adsorption geometry. Only vibrations symmetric with respect to the symmetry elements of the system can give a charge-transfer modulation.

Having established the conditions for h_Q to be nonvanishing, one is able to state selection rules for the ground-state charge-transfer model of surface-enhanced Raman scattering. If one assumes all the $m^{(0)}$ contributing significantly to C belong to the same energy band in the metal and hence have the same symmetry, then it is obvious from (8) that, to give a nonvanishing matrix element, $\langle \sum_m F_{gm} m^{(0)} | h_Q | m^{(0)} \rangle$ has to have the same symmetry as the states $m^{(0)}$ (with respect to the symmetry elements of the whole system). Since S is not a function of the space coordinates, and the distances r_m and r_{aL} are absolute values and hence always positive, the only symmetry in h_Q is that of the normal coordinate Q. So one gets the selection rule that only vibrations give a contribution to this matrix element that have the symmetry of the states $m^{(0)}$.

For the matrix element $\langle m^{(0)} | h_Q | g^{(0)} \rangle$ to be nonvanishing, h_Q and hence Q have to be symmetric if both $m^{(0)}$ and $g^{(0)}$ are of the same symmetry, and antisymmetric if $m^{(0)}$ and $g^{(0)}$ are of opposite symmetry.

In the third matrix element there is a sum over the excited states of the adsorbate. Since these states may be of different symmetry, no general selection rule can be given. Assuming, however, only one state $a^{(0)}$ to give a finite mixing coefficient (or, in other words, assuming a single charge-transfer transition), then the matrix element reduces to $\langle g^{(0)} | h_Q | F_{ma} a^{(0)} \rangle$ and one can give a selection rule in analogy to that given for $\langle m^{(0)} | h_Q | g^{(0)} \rangle$.

The selection rules developed above are collected in Table I. It should be pointed out, however, that the magnitude of the matrix elements is determined by the mixing coefficients, and hence, because of $F_{ab} \propto \langle a | b \rangle$, by the overlap integral between the states concerned. This is, though not explicitly expressed, even true for the matrix element $\langle m^{(0)} | h_Q | g^{(0)} \rangle$ because the operator h_Q does not change very much the spatial distribution of the wave function of $g^{(0)}$. So for making predictions on the surface enhancement one has to consider not only symmetries, but also the overlap integrals.

III. RESULTS AND DISCUSSION

The theory developed above can yield quantitative results on the surface enhancement by ground-state charge transfer only, if the wave functions of the adsorbate and metal states involved are explicitly known. This is generally not the case. Therefore, the following treatment will be confined to qualitative discussions of some real SERS systems known from experiments. This should allow, by comparison of this theory with published data, one to estimate the relative importance of the mechanism just described compared to others.

The system pyridine-silver is the one most extensively

TABLE I. General selection rules for the various terms contributing to C.

Term	Condition to be nonvanishing
$(\partial S/Q)_0$	Q symmetric with respect to all symmetry elements of the system
$(\partial r_{aL}/\partial Q)_0$	Q infrared active
$(\partial r_m/\partial Q)_0$	Whole adsorbate vibrating against the metal
$\langle m^{(0)} \| h_Q \| g^{(0)} \rangle$	Q symmetric with respect to all symmetry elements of the system for which $g^{(0)}$ and $m^{(0)}$ have the same symmetry Q antisymmetric with respect to all others
$\left\langle \sum_m F_{gm} m^{(0)} \| h_Q \| m^{0} \right\rangle$	h_Q symmetric with respect to all symmetry elements of the system
$\langle g^{(0)} \| h_Q \| F_{ma} a^{(0)} \rangle$	If only one state a: analogous to $\langle m^{(0)} \| h_Q \| g^{(0)} \rangle$
F_{gm}	$\langle M^{(0)} \| g^{(0)} \rangle \neq 0, \quad \Delta E_{gm} \ll E_g$
F_{am}	$\langle a^{(0)} \| m^{(0)} \rangle \neq 0, \quad \Delta E_{ma} \ll E_m$

studied in SERS experiments. So it is suited best to examine the ability of this model to correctly describe some of the experimental results. However, since the mechanism proposed in this paper is certainly not the only one at work in surface-enhanced Raman scattering, the conclusions will certainly not be unambiguous. The situation is even deteriorated by the fact that most experiments were performed on rather ill-defined surfaces.

Raman scattering of pyridine adsorbed to a single-crystal Ag(111) surface in different positions will be discussed. This plane has been chosen because for it the best experimental results are available.[24–27] From desorption studies[26] it can be concluded that pyridine is weakly chemisorbed. By electron-energy-loss spectroscopy (EELS) measurements[26] it has been shown that there exist at least two different adsorption geometries for pyridine on an Ag(111) surface: a flat-lying one and an inclined one. The observed weak chemisorption can be caused in this system by a very weak covalent interaction of the lone-pair orbital of pyridine with the conduction band of silver as well as of the *d* orbitals of silver with the two lowest unfilled π orbitals of pyridine. Then for the flat-lying geometry there are two possible chemisorption sites with different orientations (Fig. 2). All other geometries can be excluded for a chemisorbed species. While the symmetry of the free pyridine molecule is C_{2v}, the adsorbate-metal system has only the symmetry C_S. When *yz* is chosen as the plane of the molecule (Fig. 3), then the mirror plane σ_{xy} is the only symmetry element retained in the system. The $11A_1$ nonbonding orbital of pyridine[28] is assumed to be the $g^{(0)}$ state and the $3B_1\pi_5^*$ orbital to be the only contributing $a^{(0)}$.[24] The *sp* states of Ag are symmetric with respect to σ_{xy} for both orientations. For orientation 1 (Fig. 2) the t_{2g} orbitals are symmetric, and the e_g antisymmetric, while orientation 2 (Fig. 2) gives the reverse. It is found that A_1 and B_2 vibrations become enhanced only, if the ground state is close to the energy range of the *sp* or t_{2g} states, while A_2 and B_2 vibrations are enhanced, if it is situated near the e_g states. However, in both orientations the overlap of $g^{(0)}$ with any metal state is very small, since the $11A_1n$ orbital has its extension mainly in the *y*-*z* plane. The overlap of $a^{(0)}$ with the *sp* states is negligible, while the energy difference between $a^{(0)}$ and any *d* state is too large to yield considerable F_{ma}. So it is concluded that for both flat-adsorption geometries no surface enhancement by the gound-state charge-transfer mechanism is to be expected.

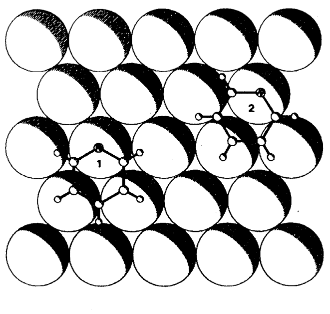

FIG. 2. Pyridine chemisorbed on Ag(111), flat-lying configurations. Size of balls has no significance (also in the following figures).

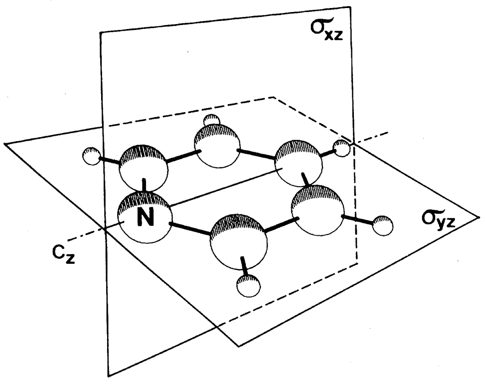

FIG. 3. Symmetry elements in free pyridine.

In the inclined geometry one can distinguish three cases favorable for chemisorption (Fig. 4). The first has the *y*-*z* plane of the molecule perpendicular to Ag(111) and the C_{2v} axis and the *x*-*z* plane inclined by ~55°, the e_g orbitals of the metal overlapping the unfilled π_5^* orbital of pyridine. The ground state can overlap the conduction-band states of the metal. The second possible geometry has the *x*-*z* plane perpendicular to the surface and the C_{2v} axis and the *y*-*z* plane inclined by ~55° to the surface. Now the t_{2g} orbitals overlap the π_5^* orbital, and again the ground-state orbital can overlap the conduction-band states. The third geometry has the *y*-*z* plane inclined by an angle of ~55°, while the *x*-*z* plane and the C_{2v} axis are inclined by ~35° to the surface (possibly the angles are slightly modified by steric hindrance). This last geometry comes closest to the values inferred from EELS measurements for the inclined case[29] (~55° and ~30°). In this case exists the most favorable overlap, namely the π_5^* orbital with the t_{2g} orbitals of two nearest-neighbor atoms, and the ground-state *n* orbital with the *sp* orbitals. So this geometry is expected to have the highest binding energy and hence to be the most probable among the inclined ones.

The contributions to this surface-enhancement mechanism can be summarized as follows: The first two cases obey the same selection rules for the terms in h_Q and the matrix elements as the flat-lying geometry. The third case retains none of the former symmetry elements, and hence all contributions become allowed [with the exception of $(\partial r_m/\partial Q)_0$]. But there is an important difference between the inclined and the flat-lying geometry: In the inclined case F_{gm} as well as F_{ma} are nonvanishing due to the considerable overlap of $g^{(0)}$ and $a^{(0)}$ with the *sp* as well as *d* states. Thus, for the most probable inclined adsorption geometry, a surface enhancement is expected for all vibrations, irrespective of symmetry.

The results given above are in remarkable agreement with experimental values.[27] For the flat-lying geometry no surface enhancement could be observed, while the inclined phase showed an enhancement. The fact that in this experiment an additional electromagnetic enhance-

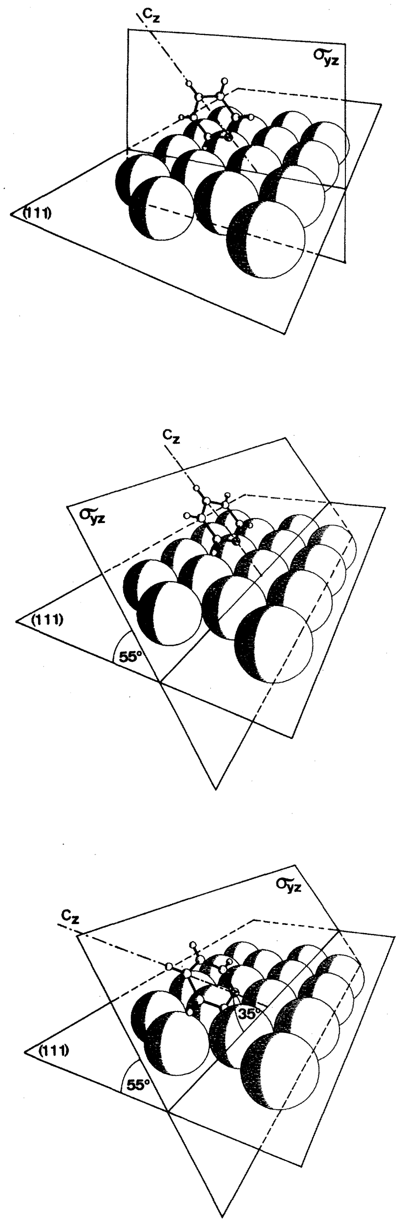

FIG. 4. Pyridine chemisorbed on Ag(111), inclined configurations.

ment was necessary to observe SERS is not unexpected in view of the estimated enhancement factor of ~100—1000 (see above).

An analysis for SERS on surfaces other than Ag(111) will be presented elsewhere.[39] It should be pointed out, however, that in any case the overlap integrals and the mixing coefficients play the important role. So the conclusion that a flat-lying geometry gives no surface enhancement in the pyridine-Ag system is valid also for the other low-index surfaces.

In many of the SERS experiments reported polycrystalline surfaces were used that show necessarily some degree of "atomic-scale roughness."[5] In this case, the symmetry selection rules may be strongly relaxed, and also the probability for an orbital overlap is much higher. Assuming the flat-lying geometry, which was found to dominate on Ag(111) for low coverage, also to be the most probable on a surface with atomic-scale roughness (steps, kinks, adatoms, etc.), then one expects to find an enhancement even for this geometry, which gives no enhancement on perfect-crystal faces. The experimental importance of these surface defects has been most convincingly proven by Otto.[5] In this context, also the results of Campion and Mullins[29,30] may be understood; they reported to observe no enhancement for pyridine adsorbed to perfect-crystal surfaces of Ag. It can be assumed that under the experimental conditions present in their work (adsorption of pyridine at temperatures of 100—150 K) only the flat-lying phase was present. Because of the smooth surface, neither electromagnetic nor charge-transfer enhancement occurred. With this assumption also the discrepancy to other observations[31,32] can be removed by assuming that different geometries were present. In the experiments of Refs 29 and 30 no shift of the Raman bands was observed with respect to the free molecule, which observation points to negligible overlap integrals, while a shift was found in the other works[31,32] indicating the ground state taking part in the chemisorption process.

The appearance of forbidden bands in SERS has been reported, for example, for ethylene on Ag.[6] This fact has been tentatively assigned to the action of a strong field gradient near the surface. It will be shown, however, that also this model is able to account for this observation.

Ethylene has the symmetry D_{2h}. The adsorption geometry is with certainty a flat one. As an example, adsorption on a Ag(100) plane, the C=C band being directed along the [101] axis will be discussed. The symmetry in this geometry is reduced to C_{2v}. The remaining symmetry elements are $C_{2(z)}$, $\sigma_{v(xz)}$, and $\sigma_{v(vz)}$ (following Herzberg,[33] the z axis is chosen to be perpendicular to the plane of the molecule and the x axis is along the C=C double bond). The ground state of ethylene (highest occupied orbital) overlaps the sp and t_{2g} states of the two nearest-neighbor metal atoms. The overlap provides the necessary prerequisite for a surface enhancement even for a flat-lying geometry in this case. The ground state $g^{(0)}$ is symmetric in all remaining elements, the excited state $a^{(0)}$ symmetric with respect to σ_{xz} and antisymmetric with respect to C_z and σ_{zy}. The energy difference ΔE_{ma} is rather large, however, so that the third term in Eq. (8) can be neglected. The selection rules are given in Table II. It turns out that the Raman-forbidden species A_u, B_{1u}, B_{2u}, and B_{3u} now become allowed. The experiments reported in Ref. 6 were performed on rough surfaces, so this result cannot be directly compared. To show how atomic-scale roughness can even further relax the selection rules, consider a molecule situated near a step on the Ag(100) surface. The overall symmetry now is reduced to C_S. The selection rules for this case are shown in Table III. It is found that now only B_{1g} and B_{2g} remain forbidden; all the other species become allowed in this enhancement mechanism, including all formerly forbidden vibrations of symmetry u. This model agrees with the experimental result that B_{1g} vibrations do not show a surface enhancement. That the B_{2g} vibration is observed in SERS[6] may be due to an

TABLE II. Selection rules for ethylene on Ag(100) (+ allowed, − forbidden) for vibrations of different symmetry species.

Term	A_g	B_{1g}	B_{2g}	B_{3g}^{a}	A_u	B_{1u}	B_{2u}	B_{3u}
$(\partial S/\partial Q)_0$	+	−	−	−	−	+	−	−
$(\partial r_{aL}/\partial Q)_0$	−	−	−	−	+	+	+	+
$(\partial r_m/\partial Q)_0$	−	−	−	−	−	−	−	−
$\langle m^{(0)} \mid h_Q \mid g^{(0)} \rangle$	+	−	−	−	−	+	−	−
$\left\langle \sum_m F_{gm} m^{(0)} \mid h_Q \mid m^{(0)} \right\rangle$	+	−	−	−	−	+	−	−
Total C term	+	−	−	−	+	+	+	+

[a]There is no B_{3g} vibration in ethylene.

electromagnetic enhancement of this (*a priori* allowed) vibration.

So it has been demonstrated that, due to the lowered overall symmetry of the system adsorbate metal, bands not allowed in usual Raman scattering may appear due to the ground-state charge-transfer mechanism. It should be pointed out that this occurs even in very weakly adsorbed systems, where the symmetry of the adsorbate remains the same as that of the free molecule. For this enhancement mechanism the overall symmetry of the system is decisive.

From the very beginning of SERS investigations it has been found[34] that the enhancement may be dependent on the electric potential of the surface with respect to its surroundings. This is one of the features of SERS the electromagnetic models cannot explain sufficiently. A change in potential may alter the adsorption, but in view of the expected long-range action of the electromagnetic effects this should give no considerable change in the SERS intensity. The charge-transfer transition models interpret the potential dependence as due to tuning the system in and out of resonance.[5] In the following the influence of an applied potential on the ground-state charge-transfer enhancement mechanism will be analyzed.

The effect of an applied potential on the adsorption system is to shift the adsorbate states with respect to the metal states. This enters into expression (8) in two ways: one has to take into account the shift in the denominator $E_m - E_g$ and in the mixing coefficients F_{gm} and F_{ma}. To find the dependence of the enhancement on the applied potential, the sum over the metal states m in (8) has to be performed. This will be done for the pyridine-silver system under the assumption that $g^{(0)}$ couples to the d-band states of silver. For the metal states the following approximate wave function[35] is used:

$$\psi_m = u(\vec{r})e^{i\vec{k}_m \cdot \vec{r}} , \tag{16}$$

where the components of the wave vector $\vec{k}_m$ are given by $k_i = 2\pi/aN_i$ ($i = y,y,z$: a, lattice constant; N_i, number of lattice atoms along the direction i; and m, integers from $-N_i/2$ to $+N_i/2$). Because of the quasicontinuous distribution of the states over the energy band, the summation over m in (8) may be replaced by an integration over the density of states D_m.

Then a numerical integration has to be performed. In doing this, only one excited state $a^{(0)}$ has been considered. The adsorbate ground state has been chosen within the d band at 4.7 V below the Ag Fermi energy and the surface

TABLE III. Selection rules for ethylene near a step on the Ag(100) surface.

Term	A_g	B_{1g}	B_{2g}	B_{3g}^{a}	A_u	B_{1u}	B_{2u}	B_{3u}
$(\partial S/\partial Q)_0$	+	−	−	+	−	+	+	−
$(\partial r_{aL}/\partial Q)_0$	−	−	−	−	+	+	+	+
$(\partial r_m/\partial Q)_0$	−	−	−	−	−	−	−	−
$\langle m^{(0)} \mid h_Q \mid g^{(0)} \rangle$	+	−	−	+	−	+	+	−
$\left\langle \sum_m F_{gm} m^{(0)} \mid h_Q \mid m^{(0)} \right\rangle$	+	−	−	+	−	+	+	−
Total C term	+	−	−	+	+	+	+	+

[a]There is no B_{3g} vibration in ethylene.

density of d-band states has been taken from Ref. 36. Details concerning the calculation will be given elsewhere.[39] The result is shown in Fig. 5. For positive potential of the metal with respect to the surroundings the enhancement is small. Negative-going potential yields a growth of the enhancement, passing a maximum at ~ 0.9 V and falling rapidly for higher potential. This behavior is in very good agreement with experimental observations.[5]

The dependence of the SERS intensity on the excitation wavelength has been regarded as an important criterion to decide between various theoretical models. In most cases examined up to now the dependence expected for a pure electromagnetic mechanism has been found, which has led many authors to conclude that this is the only mechanism at work.

The excitation-wavelength dependence enters into this model via the denominator $(E_a - E_g)^2 - E_0^2$ in α'_{ma}. Obviously it is the same dependence usually encountered in Raman scattering. Hence, the surface enhancement due to this mechanism shows no dependence on excitation wavelength, as can also be seen from the (highly approximate) expression (10) for the enhancement factor. There is one exception, however, where this model predicts a different behavior, namely in the case of certain dye molecules as adsorbates.

The enhancement factor β has been defined above by $\beta = [C/(A_{\text{free}} + B_{\text{free}})]^2$. The excitation dependence in the free molecule is given by $[(E_a - E_g)^2 - E_0^2]^{-1}$ in the A_{free} term, and $\{[(E_a - E_g)^2 - E_0^2][(E_a^2 - E_g)^2 - E_0^2]\}^{-1}$ in the B_{free} term. For the adsorbate, following this model, the scattering is dominated by the C term, which has an $[(E_a - E_g)^2 - E_0^2]^{-1}$ dependence. Obviously, if Raman scattering in the free molecule is dominated by A_{free}, only a small excitation-wavelength dependence of β results, which is due to the fact that the adsorbate states are perturbed and hence differ slightly from those in the free molecule. If, however, B_{free} is dominating, β comes out to be proportional to $[(E_{a'} - E_g)^2 - E_0^2]^2$, thus showing (taking into account a damping term) a minimum near $(E_{a'} - E_g)^2 = E_0^2$. This fact might explain the different experimental results published on the surface enhancement in dye molecules.[34,37,38] A comparison of SERS excitation spectra of different dyes has shown[39,40] that indeed both cases predicted above can be observed: an enhancement independent of excitation wavelength as well as a dependence with a marked minimum within an absorption band. The latter has been predicted by none of the SERS models presented up to now.

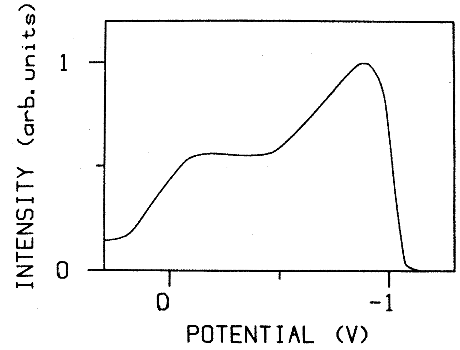

FIG. 5. Surface-enhanced Raman intensity vs applied potential for pyridine/Ag, calculated from this model.

IV. CONCLUSION

The mechanism developed above obviously can give a contribution to surface-enhanced Raman scattering. This mechanism seems to be important, as it allows one to account for a number of experimental facts which up to now have been attributed to several different causes or could not have been explained sufficiently at all. An advantage of this model is the explanation of the sensitivity of SERS to the adsorption geometry, and of the sometimes strange dependence on excitation wavelength. Another advantage is that due to this model SERS is largely determined by the metal states, despite the fact that it is based on a Raman-scattering mechanism involving mainly electrons located on the adsorbate. The enhancement is caused by an "energy-borrowing" mechanism from metal transitions to molecular transitions. Thus, the experimental fact can be understood that SERS for different adsorbates on the same metal shows a more or less uniform behavior. This model should be applicable in more cases than the models involving charge-transfer transitions, since in those it is necessary that the transition lies exactly within the (rather narrow) region accessible by usual laser sources, while for this model to give a considerable enhancement it is only necessary that the adsorbate ground state lies within one of the energy bands of the metal. That also this model is capable of describing features that have been attributed to charge-transfer transitions (e.g., dependence on applied potential) has been shown. It is unlikely, however, that there are many systems for which this mechanism alone can be invoked to explain SERS. In most (if not all) cases an additional electromagnetic enhancement is necessary to make SERS observable.

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