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# Charge transfer effects in surface-enhanced Raman scattering<sup>a)</sup>

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Surface-enhanced Raman scattering (SERS) due to charge-transfer interactions between the adsorbed molecule and the metal surface is analyzed using the semiempirical Wolfsberg-Helmholz method to relate the molecule-surface interactions and the resulting charge-transfer states to the overlap integrals between the metal conduction-band orbitals and an acceptor or donor molecular orbital of the molecule. Calculations for the model system of ethylene adsorbed on silver, with charge-transfer excitation of an electron from the metal to the antibonding ethylene  $\pi$  orbital, show that charge-transfer Raman enhancements of the order of 10 to 1000 are possible if the charge-transfer band is partially resonant with the exciting radiation. Symmetric vibrations usually will be enhanced substantially more than nonsymmetric ones by this mechanism because the vibrational coupling is primarily Franck-Condon rather than Herzberg-Teller. The presence of overtone and combination bands in charge-transfer-enhanced Raman spectra is also possible.

## I. INTRODUCTION

Extensive experimental and theoretical investigations of the phenomenon of surface enhanced Raman scattering (SERS) have made very substantial progress in identifying possible mechanisms of this striking effect.<sup>1-3</sup> A less well resolved problem, however, is the relative importance of the different mechanisms, and various experiments designed to resolve this question have yielded widely varying answers. Much of the controversy centers around two models, one electromagnetic and the other involving charge transfer between the adsorbed molecule and the metal surface.

This electrodynamic model, in which small irregularly shaped metal particles or surface irregularities support optical-frequency surface plasmon resonances with consequent strong local enhancement of both the electric field of the Raman-exciting radiation and the radiation-induced dipole moment of the adsorbed molecule, undoubtedly plays an important if not predominant role in SERS.<sup>2</sup> It explains the need for surface roughness,<sup>4</sup> which metals are most favorable, the existence of SERS beyond the first monolayer,<sup>5</sup> SERS in colloidal metal solutions,<sup>2(b)</sup> and a correlation between excitation frequency and very low frequency vibrations of the metal particles.<sup>6</sup> Recently, additional detailed corroboration has been provided by two elegant investigations, one using silver particles of known size and shape on a lithographically prepared substrate,<sup>7</sup> the other using controlled deposition techniques to separate the metal surface and the adsorbed molecules by varying thicknesses of aluminum oxide.<sup>8</sup>

Despite the successes of this electrodynamic model, however, a number of investigations have indicated SERS contributions from other mechanisms, especially those involving a charge-transfer interaction between the surface and molecules in the first adsorbed monolayer. These investigations include: (1) Experiments

in which the SERS gain of the first monolayer was found to be considerably larger than that of succeeding monolayers.<sup>9</sup> (2) The failure of the frequency dependence of the SERS gain to conform to light scattering and/or absorption measurements of the plasmon resonance frequency.<sup>3(f),10</sup> (3) Very recently, there has been a report of SERS for benzene adsorbed on small platinum particles,<sup>11</sup> which is suggestive of some mechanism other than electrodynamic enhancement because the field-enhancing plasmon resonances are strongly damped in platinum.<sup>2(e)</sup> (4) Finally, high resolution electron energy loss experiments have revealed low-energy charge-transfer bands associated with the absorption of such molecules as pyridine and pyrazine on silver.<sup>12</sup>

Two distinct charge-transfer mechanisms have been suggested. The first proposes that the transferred charge affects the surface plasmon modes and modulation of this charge transfer by molecular vibrations yields a corresponding change in the surface plasmon contribution to light scattering by the metal surface.<sup>3(c),3(e),3(f)</sup> The resultant amplitude modulation of the scattered radiation is proposed to yield strongly enhanced Raman sidebands. The second proposes that virtual excitations to the charge transfer state, which can be partially resonant with the exciting radiation even at visible wavelengths, yield large contributions to the Raman-scattering polarizability tensor of the combined metal-molecule system.<sup>3(b),3(d),3(g),12(b)</sup>

In this paper we consider the second of these charge-transfer mechanisms of SERS, and attempt a rough quantitative estimate of its importance. It will be assumed, as is probably the case in most experimental systems, that the metal-molecule interaction is a weak one in which the molecular energy levels do not partially overlap the metal conduction band. For this model the degree of charge-transfer mixing, and the resulting matrix elements for virtual excitation of the charge-transfer state (and also real excitation yielding fluorescence if desired), can be estimated from a perturbation theory solution of a semiempirical electronic Hamiltonian

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whose matrix elements are determined by overlap integrals between the metal conduction band orbitals and the donor or acceptor orbitals of the adsorbed molecules.

Results for ethylene adsorbed on silver, which is a model for the typical SERS system of an unsaturated or conjugated molecule on a metal surface, will strongly suggest that charge-transfer effects can be important in SERS, even though they usually cannot fully account for the observed enhancements, and thus probably operate in conjunction with the aforementioned electrodynamic mechanism. It will also be found that the charge transfer SERS can have a rather complicated dependence on such factors as excitation frequency, vibrational mode, absorbing site, etc. One source of this complexity is that the charge-transfer band will usually have to be partially resonant with the exciting radiation to yield a significant SERS contribution, in which case the Raman vibrational transition may acquire intensity from both the Franck-Condon (FC) and Herzberg-Teller (HT) mechanisms.<sup>13,14</sup> FC vibrational coupling results from overlap of different vibrational substates of the ground and excited electronic states, which are nonvanishing if the electronic states have different equilibrium nuclear configurations. HT vibrational coupling results from mixing of different vibrational states by vibrationally induced changes in the electronic wave functions. The FC term can be considerably larger than the HT term for low-lying electronic excitations, but it usually is effective only for totally symmetric vibrations.<sup>14</sup> Another complicating factor is the strong dependence of the charge-transfer mechanism on the nature of the absorbing site insofar as this determines the overlap between the wave functions of the metal and the molecule. Finally, an apparent charge transfer contribution to SERS is possible if the interaction orients the adsorbed molecules so that the optical electric field, which must be locally perpendicular to the microscopically roughened surface, is along a minimum of the anisotropic intramolecular transition-polarizability tensor. Understanding these effects of charge transfer on SERS, at least qualitatively, is of obvious importance in interpreting SERS spectra.

## II. THEORY

### A. Molecule-surface model

We concentrate on the case where the charge-transfer band is due to electron excitation from the metal to the adsorbed molecule. The case where the molecule is the donor is less likely because of the relatively high ionization potential of most molecules investigated by SERS as compared with the work function of metals. However, extension of the theory to this case would be straightforward.

The problem of an electronic transition between a conduction band orbital and an acceptor (or donor) molecular orbital (MO) of an adsorbed molecule, although similar in principle to a charge-transfer transition involving two small molecules, presents considerable additional practical difficulties which will be treated here by introducing a highly simplified model. The difficul-

ties arise because the conduction band orbitals, unlike ordinary MOs, are highly degenerate in the sense that there are many such orbitals within a range of energies comparable to the charge-transfer transition energy. Consequently, the conduction band orbitals will be strongly perturbed in the excited charge-transfer state and, therefore, considerably different from the corresponding ground state orbitals. Formal treatment of this problem would require an intractable configuration interaction calculation in a very highly dimensioned orbital space. The fact that in the excited state the conduction band orbitals will rearrange so that the metal charge is localized in the metal surface near the molecule suggests the following approximate model: Details of the molecule-metal interaction such as charge-transfer mixing of the metal and molecule orbitals, and the resulting charge-transfer matrix elements, are calculated for a molecule interacting with a small number of surface metal atoms, while the underlying band nature of the metal orbitals is used to estimate the shape of the charge-transfer band and certain details of the metal-molecule interaction which depend on the band structure. Clearly, contributions to SERS from this charge-transfer mechanism will be further enhanced by the aforementioned electrodynamic mechanism, because the surface-plasmon-enhanced optical electric fields are present in the region between these surface metal atoms and the adsorbed molecule. Finally, this model, with appropriate changes in the metal band structure, will also apply to charge-transfer interactions involving the adsorbed molecule and one or more metal adatoms located on but separate from the bulk metal surface or surface irregularity.

For this model the transition energy from the top of the 0 K Fermi distribution of the metal to an acceptor orbital of the molecule (cf. Fig. 1) may be estimated by a slight modification of a formula used for charge-transfer transition energies in molecular pairs.<sup>15</sup> The result is

$$E_{CT}(k_F) = W_M - E_A - E_C ; \quad E_C = (\epsilon_M - \epsilon) e^2 / [2\epsilon(\epsilon + \epsilon_M)R] , \quad (1)$$

where  $W_M$  is the work function of the metal,  $E_A$  is the electron affinity of the molecule, and  $-E_C$  is the Coulomb interaction energy between the molecular anion and the positively charged metal surface in the charge-transfer state. The second equation above is the image model<sup>16</sup> estimate of  $E_C$ , with the molecular anion approximated as a point charge. Here,  $\epsilon$  is the dielectric constant of the medium outside the metal,  $\epsilon_M$  is the dielectric constant of the metal, and  $R$  is the distance of the molecule from the metal surface.

For a test of Eq. (1) one may estimate  $E_{CT}(k_F)$  for pyridine on silver as follows.  $W_{Ag} = 4.7$  eV *in vacuo*,<sup>17</sup> and  $E_A = 0$  to 1 eV is typical of the electron affinity of many molecules exhibiting SERS.<sup>18</sup> Since many charge-transfer interactions involve  $\pi$  orbitals of conjugated or aromatic molecules,  $R = 6a_0$  is estimated as half the sum of the van der Waals thickness of an aromatic ring ( $3.2a_0$ )<sup>19</sup> and the covalent radius of tetrahedrally bonded Ag ( $2.8a_0$ ).<sup>20</sup> Finally, for *in vacuo* adsorption of the molecule  $\epsilon = 1 \ll \epsilon_{Ag}$ .<sup>21</sup> Thus,  $E_{CT}(k_F) = 1.4$  to 2.4 eV

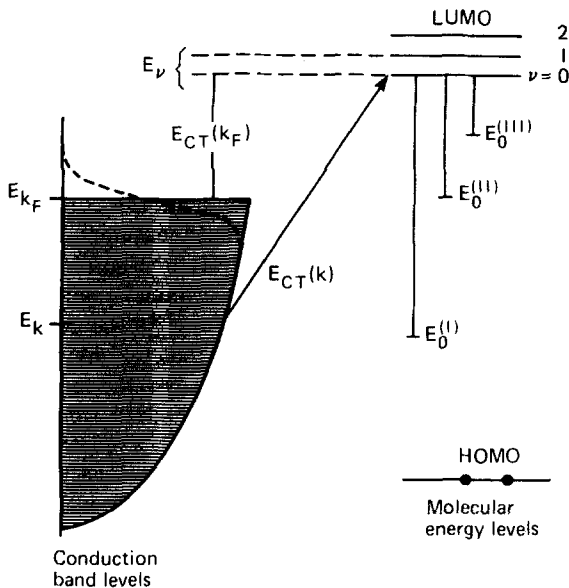


FIG. 1. Illustration of a charge-transfer transition from a metal conduction-band state to the lowest unoccupied molecular orbital (LUMO) of an adsorbed molecule. Conduction-band state distribution shown for  $T=0$  (solid line) and  $T>0$  (dashed line). Vibrational levels of molecule characterized by energy ( $E_\nu$ ) and excitation ( $\nu$ ). Cases where the excitation energy is greater than, equal to, or less than the minimum charge-transfer energy are denoted by  $E_0^{(I)}$ ,  $E_0^{(II)}$ , and  $E_0^{(III)}$ , respectively.

in reasonable agreement with the recently observed values.<sup>12</sup> Figure 1 shows that this and similar charge-transfer bands will be quite broad with the lowest energy portions corresponding to excitation of electrons from the top of the Fermi distribution and progressing to higher energy as electrons from successively lower levels of the conduction band are excited.

We approximate the metal conduction-band orbitals as those of a monovalent metal with a simple cubic lattice. The more complicated lattices and Fermi surfaces of actual metals are a refinement whose inclusion would be inconsistent with the approximate nature of the calculation and our very limited knowledge of the metal-molecule interactions. Furthermore, we shall describe the metal wave functions by a tight-binding approximation, even though this gives a rather poor description of the wave functions in the bulk of the metal where the electrons move in the field of many positive atomic cores, because it gives a reasonable description of the wave functions in the vicinity of the surface atoms which are of greatest importance here, particularly that part of the metallic wave function in the region between the surface and the adsorbed molecule. If  $a$  is the interatomic distance and the lattice contains  $N^3$  atoms, the tight-binding approximation to the  $k$ th conduction band orbital is<sup>22</sup>

$$\phi_{\mathbf{k}}^{(0)} = N^{-3/2} \sum_{\mathbf{L}} \psi(\mathbf{r} - \mathbf{r}_{\mathbf{L}}) \exp(i\mathbf{k} \cdot \mathbf{r}_{\mathbf{L}}), \quad (2)$$

where  $\mathbf{L}$  denotes a particular lattice site and  $\psi(\mathbf{r} - \mathbf{r}_{\mathbf{L}})$  is the metal valence orbital at that site. Here, the periodic boundary conditions specify:

$$\mathbf{k} = (k_x, k_y, k_z) = (2\pi/aN)(n_x, n_y, n_z), \quad (3)$$

where  $n_x, n_y, n_z$  are integers between  $-N/2$  and  $N/2$ .

The free electron part of the energies of these orbitals is<sup>23</sup>

$$E_{\mathbf{k}} = \hbar^2 k^2 / 2m, \quad (4)$$

where  $m$  is the electron mass. At 0 K the fraction of occupied states in the interval  $\mathbf{k}$  to  $\mathbf{k} + d\mathbf{k}$  is<sup>23</sup>

$$dF_{\mathbf{k}} = 2(a/2\pi)^3 k^2 \sin \theta_k dk d\theta_k d\varphi_k; \quad k \leq k_F = (3/\pi)^{1/3} \pi/a, \quad (5)$$

where  $k$ ,  $\theta_k$ , and  $\varphi_k$  are the polar coordinates of  $\mathbf{k}$  and  $\hbar k_F$  is the momentum of an electron at the Fermi surface.

According to our model the metal-molecule charge-transfer interaction will involve the acceptor or lowest unoccupied MO of the molecule, denoted  $\phi_A^{(0)}$ , and a group of surface metal atoms which have nonzero electronic interactions, as measured by their overlap integrals, with  $\phi_A^{(0)}$ . Following Eq. (2) this component of the  $k$ th conduction band orbital will be denoted as

$$\phi_{\mathbf{k},\Gamma}^{(0)} = \sum_{\mathbf{r}} \psi(\mathbf{r} - \mathbf{r}_{\Gamma}) \exp(i\mathbf{k} \cdot \mathbf{r}_{\Gamma}), \quad (6)$$

where  $\Gamma$  denotes an appropriate surface site. Note that  $\phi_{\mathbf{k},\Gamma}^{(0)}$  is unnormalized; the normalization will subsequently be taken care of by averaging over the density of conduction band states expressed as a fraction of the total number of such states by Eq. (5).

## B. Charge-transfer mixing

We estimate the mixing of the overlapping orbitals  $\phi_{\mathbf{k},\Gamma}^{(0)}$  and  $\phi_A^{(0)}$  by the electronic Hamiltonian using a semiempirical method introduced by Wolfsburg and Helmholtz<sup>24</sup> and employed extensively by others.<sup>25</sup> This method involves solving an electronic eigenvalue equation:  $\mathbf{H}\Psi = E\mathbf{S}\Psi$ , where  $\mathbf{H}$  is the electronic Hamiltonian matrix, whose diagonal elements are estimated semiempirically from experimental or calculated atomic orbital energies, and whose off-diagonal elements are estimated from the diagonal elements and the off-diagonal elements of the overlap matrix  $\mathbf{S}$ . Since the mixing of the conduction orbitals  $\phi_{\mathbf{k},\Gamma}^{(0)}$  and the acceptor orbital  $\phi_A^{(0)}$  is small we can use first order perturbation theory to estimate separately the mixing of each  $\phi_{\mathbf{k},\Gamma}^{(0)}$  with  $\phi_A^{(0)}$  and vice versa. The result for  $\phi_{\mathbf{k},\Gamma}$  is

$$\phi_{\mathbf{k},\Gamma} = \phi_{\mathbf{k},\Gamma}^{(0)} - [(H_{A\mathbf{k}} - S_{A\mathbf{k}} H_{\mathbf{k}\mathbf{k}}) / (H_{AA} - H_{\mathbf{k}\mathbf{k}})] \phi_A^{(0)}, \quad (7)$$

where

$$H_{AA} - H_{\mathbf{k}\mathbf{k}} = E_{CT}(\mathbf{k}) = E_{CT}(\mathbf{k}_F) + (\hbar^2/2m)(k_F^2 - k^2), \quad (8a)$$

and

$$H_{\mathbf{k}\mathbf{k}} = -W_M - E_F + E_{\mathbf{k}} = -W_M - (\hbar^2/2m)(k_F^2 - k^2). \quad (8b)$$

Here, the expressions on the far right sides of these equations are obtained by noting that  $E_{\mathbf{k}}$  is given by Eq. (4) and  $E_F$  is the Fermi energy given by Eq. (4) with Eq. (5) for  $k_F$ . The off diagonal matrix elements are

$$H_{A\mathbf{k}} = H_{\mathbf{k}A}^* = \frac{1}{2} \kappa (H_{\mathbf{k}\mathbf{k}} + H_{AA}) S_{A\mathbf{k}}; \quad S_{A\mathbf{k}} = S_{\mathbf{k}A}^* = \langle \phi_A^{(0)} | \phi_{\mathbf{k},\Gamma}^{(0)} \rangle, \quad (9)$$

where estimates of  $\kappa$  range from 1.6 to 2. Taking  $\kappa = 2$  simplifies the formulas, yielding

$$\phi_{\mathbf{k},\Gamma} = \phi_{\mathbf{k},\Gamma}^{(0)} - [(H_{\mathbf{k}\mathbf{k}} + E_{CT}(\mathbf{k})) S_{A\mathbf{k}} / E_{CT}(\mathbf{k})] \phi_A^{(0)}. \quad (10a)$$

Similarly, it can be shown that

$$\phi_A = \phi_A^{(0)} + [H_{\mathbf{k}A} S_{\mathbf{k}A} / E_{CT}(\mathbf{k})] \phi_{\mathbf{k},\Gamma}^{(0)}. \quad (10b)$$

As shown in Fig. 1, the charge transfer transition is excitation of an electron from the doubly occupied  $\phi_{k,T}$  orbital to the acceptor orbital  $\phi_A$ .

### C. Charge-transfer contribution to Raman transition

The intensity of the light scattered in a Raman transition  $|K''\rangle \rightarrow |K'\rangle$  is<sup>14</sup>

$$I_R(K'' \rightarrow K') = I_0 \omega_0^4 \langle |\alpha_{\omega}(K'' \rightarrow K')|^2 \rangle_{av}, \quad (11)$$

where  $I_0$  is the incident light intensity at frequency  $\omega_0$  and photon energy  $E_0$ ,  $\alpha(K'' \rightarrow K')$  is the polarizability tensor for the transition  $|K''\rangle \rightarrow |K'\rangle$ , and the average is over appropriate geometrical parameters to evaluate  $|\mathbf{e}_0 \cdot \alpha \cdot \mathbf{e}_0|^2$  where  $\mathbf{e}_0$  is a unit vector in the direction of the optical electric field. For  $|K''\rangle$  and  $|K'\rangle$  both ground electronic states, the components of  $\alpha_{\omega}$  are

$$\alpha_{\rho\sigma}(K'' \rightarrow K') = e^2 \sum_K \frac{\langle K'' | x_\rho | K \rangle \langle K | x_\sigma | K' \rangle}{E_K - E_{K''} - E_0 - i\delta E_K}, \quad (12)$$

where,  $\delta E_K$  is the Lorentzian linewidth associated with the finite lifetime of the intermediate excited state  $|K\rangle$ , and  $x_\sigma$  and  $x_\rho$  are components of the dipole operator  $\mathbf{x}$ .

Here,  $|K''\rangle$  is the electronic and vibrational ground state of the metal-molecule system, which is written as a Born-Oppenheimer product of electron and vibrational wave functions, i.e.,  $|K''\rangle = |0\rangle |v_{0,0}\rangle$ . Similarly,  $|K'\rangle$  is the electronic ground state with  $\nu'$  quanta in the  $v$ th vibrational mode, i.e.,  $|K'\rangle = |0\rangle |v_{0,\nu'}\rangle$ , and  $|K\rangle$  denotes the  $k$ th electronically excited state with  $\nu$  quanta in the vibrational mode, i.e.,  $|K\rangle = |k\rangle |v_{k,\nu}\rangle$ . For a surface enhanced Raman transition the electro-dynamically enhanced optical electric field is locally perpendicular to the metal surface, i.e., perpendicular to the microscopic surface at the site of the molecule which direction is not necessarily perpendicular to the bulk surface.<sup>2</sup> Defining this direction as  $z$  we need find only  $\alpha_{zz}$ . Finally, our interest is in the contribution of the charge-transfer states produced by exciting an electron from one of the filled conduction band orbitals to the lowest acceptor state of the adsorbed molecule. The corresponding ground and excited states may be written respectively as:  $|0\rangle = \mathcal{A} \phi_k \bar{\phi}_k$  and  $|k\rangle = 2^{-1/2} \mathcal{A} (\phi_k \bar{\phi}_A - \bar{\phi}_k \phi_A)$ , where  $\mathcal{A}$  denotes the operation of antisymmetrization and renormalization, and the barred and unbarred orbitals have "up" and "down" electron spins, respectively. Therefore, the Raman scattering polarizability due to charge transfer is

$$\alpha_{CT}(v_{0,0} \rightarrow v_{0,\nu'}) = 2e^2 \sum_\nu \sum_k \frac{\langle v_{0,0} | \langle \phi_{k,T} | z | \phi_A \rangle | v_{k,\nu} \rangle \langle v_{k,\nu} | \langle \phi_A | z | \phi_{k,T} \rangle | v_{0,\nu'} \rangle}{E_{CT}(k) + E_\nu - E_0 - i\delta E}, \quad (13)$$

where we have introduced our approximate model in which only the surface-orbital component of  $\phi_k$ , given by Eqs. (10) and (6), is used in calculating the charge transfer matrix elements, the angle and round brackets denote, respectively, averages over electronic and vibrational coordinates, and  $E_\nu = \hbar\omega_\nu$  is the vibrational energy. Furthermore, it has been assumed that the lifetime and width of the excited state will be independent of  $k$ .

Using Eq. (10) and taking the origin for the operator  $z$  to be halfway between the adsorbed molecule and the metal surface gives for the transition matrix elements:

$$\langle \phi_{k,T} | z | \phi_A \rangle = [H_{kA} + \frac{1}{2} E_{CT}(k)] R S_{kA} / E_{CT}(k), \quad (14)$$

where we have neglected terms of order  $|S_{kA}|^2$  and also the term  $\langle \phi_{k,T}^{(0)} | z | \phi_A^{(0)} \rangle$  which is small because our choice of origin gives  $z \approx 0$  in the region midway between the surface and the molecule where the orbital overlap is greatest. From Eqs. (6) and (9),

$$S_{kA} = \sum_{\mathbf{r}} \exp(i\mathbf{k} \cdot \mathbf{r}_T) \langle \phi_A^{(0)} | \psi(\mathbf{r} - \mathbf{r}_T) \rangle. \quad (15)$$

Equation (13), with Eq. (14) for the dipole matrix elements, is revised as follows to obtain an expression in which the sum over charge-transfer states, i.e., the sum over  $k$ , is approximated by an integral. First, we use Eq. (8b) for  $H_{kA}$ , Eq. (8a) for  $E_{CT}(k)$ , and Eq. (1) for  $E_{CT}(k_F)$ . Next, we introduce the scaled energies and overlap integrals defined by the equations:

$$\bar{E}_i = E_i / E_F; \quad \bar{S}_{kA} = S_{kA} / S_{FA}. \quad (16a)$$

Here,  $E_F = (\hbar^2 / 2m) k_F^2$  is the Fermi energy and

$$S_{FA} = [\langle \langle S_{kFA}(R_0) |^2 \rangle \rangle_{\Omega(k)}]^{1/2}, \quad (16b)$$

where  $R_0$  is the equilibrium metal-molecule distance and  $\langle \langle \rangle \rangle_{\Omega(k)}$  denotes the average over  $\theta_k$  and  $\varphi_k$ , i.e.,

$$\langle \langle F(R, k) \rangle \rangle_{\Omega(k)} = \frac{1}{4\pi} \int_0^{2\pi} d\varphi_k \int_0^\pi d\theta_k \sin \theta_k F(R, k). \quad (17)$$

Finally, the sum over  $k$  in Eq. (13) is carried out by converting it to an integral using the distribution of states given by Eq. (5). Using Eq. (5) to replace  $a$  by  $k_F$  and introducing the new variable  $x = k/k_F$  gives the result

$$\alpha_{CT}(v_{0,0} \rightarrow v_{0,\nu'}) = (6e^2 R_0^2 S_{FA}^2 / E_F) \times \sum_\nu \int_0^1 dx x^2 \frac{V(x, R_0; 0, \nu, \nu')}{\bar{E}_{CT}(k_F) + 1 - x^2 + \bar{E}_\nu - \bar{E}_0 - i\delta \bar{E}}, \quad (18a)$$

where

$$V(x, R_0; 0, \nu, \nu') = \langle \langle (v_{0,0} | f(R, k) | v_{k,\nu}) (v_{k,\nu} | f^*(R, k) | v_{0,\nu'}) \rangle \rangle_{\Omega(k)}, \quad (18b)$$

$$f(R, k) = -(R/R_0) \bar{S}_{kA}(R) \left[ \frac{1}{2} + \frac{\bar{E}_A + \bar{E}_C}{\bar{E}_{CT}(k_F) + 1 - x^2} \right], \quad (18c)$$

and the angle averages are defined in Eq. (17).

Several approximations will be introduced to simplify the evaluation of the vibrational matrix elements in Eq. (18).

The first is that the electronic part of the charge transfer transition dipole moment, given by  $f(R, k)$  in Eq. (18c), depends only on  $R$  and  $k$ , and not on vibrationally induced changes in other quantities in this expression. Consequently, the HT contribution to the vibrational transition depends only on vibrationally induced changes in the molecule-metal separation  $R$ , since  $k$  is a state parameter which is unaffected by nuclear motions. It is possible, of course, for the molecular vibrations to produce other changes in the electronic

wave functions, but the large effect in a charge-transfer type transition should be changes in the separation of the interacting species.

Second, we assume that the vibrational wave functions for the electronically excited states, i. e.,  $|k, \nu\rangle$ , are independent of  $k$ , which is expected for the molecular vibrations of interest here. It is also assumed that the only difference between these vibrational functions and the corresponding functions in the ground electronic state is due to a difference in the equilibrium nuclear configurations of the ground and excited states, which should be substantial for a charge-transfer state. Differences in vibrational frequency between the ground and excited state vibrational functions are neglected because they cannot contribute to the  $\Delta\nu = 1$  transitions of importance in the Raman effect.<sup>14</sup>

With these approximations, expanding  $f(R, k)$  in vibrationally induced changes in  $R$  decomposes  $\alpha_{CT}(v_{0,0} \rightarrow v_{0,\nu})$  into its FC and HT components, according to the equations:

$$V(x, R_0; 0, \nu, \nu') = V^{(FC)}(x, R_0; 0, \nu, \nu') + V^{(HT)}(x, R_0; 0, \nu, \nu'), \quad (19a)$$

where

$$V^{(FC)}(x, R_0; 0, \nu, \nu') = \langle\langle f(R_0, k) |^2 \rangle\rangle_{\Omega(k)} \times (v_{0,0} | v_{e,\nu}) (v_{e,\nu} | v_{0,\nu'}) \quad (19b)$$

and

$$V^{(HT)}(x, R_0; 0, \nu, \nu') = \langle\langle f(R_0, k) (\partial f^* / \partial R)_0 \rangle\rangle_{\Omega(k)} (\partial R / \partial Q_\nu) \times (v_{0,0} | v_{e,\nu}) (v_{e,\nu} | Q_\nu | v_{0,\nu'}) + \langle\langle f^*(R_0, k) (\partial f / \partial R)_0 \rangle\rangle_{\Omega(k)} \times (\partial R / \partial Q_\nu) (v_{0,0} | Q_\nu | v_{e,\nu}) (v_{e,\nu} | v_{0,\nu'}). \quad (19c)$$

Here,  $Q_\nu$  is the vibrational displacement (from the ground state equilibrium position) in the  $\nu$ th mode, and  $v_{e,\nu}$  denotes the vibrational wave functions in the excited charge-transfer state.

To evaluate the vibrational matrix elements we use the creation-destruction operator formulation of the harmonic oscillator problem, which facilitates expanding the displaced vibrational wave functions of the excited state in terms of the vibrational wave functions of the ground electronic state and the subsequent matrix element calculations.<sup>28</sup> The results for the Raman fundamental  $\Delta\nu' = 1$  and first overtone  $\Delta\nu' = 2$  are

$$(v_{0,0} | v_{e,\nu}) (v_{e,\nu} | v_{0,1}) = e^{-\gamma^2} (\gamma^2 - \nu) \gamma^{2\nu-1} / \nu! , \quad (20a)$$

$$(v_{0,0} | v_{e,\nu}) (v_{e,\nu} | v_{0,2}) = e^{-\gamma^2} [\gamma^4 - 2\nu\gamma^2 + \nu(\nu-1)] \gamma^{2\nu-2} / \sqrt{2}\nu! , \quad (20b)$$

$$(v_{0,0} | Q_\nu | v_{e,\nu}) (v_{e,\nu} | v_{0,1}) = e^{-\gamma^2} (\gamma^2 - \nu)^2 \gamma^{2\nu-2} \langle Q_\nu \rangle / \nu! , \quad (20c)$$

$$(v_{0,0} | v_{e,\nu}) (v_{e,\nu} | Q_\nu | v_{0,1}) = e^{-\gamma^2} [\gamma^4 - (2\nu-1)\gamma^2 + \nu(\nu-1)] \gamma^{2\nu-2} \langle Q_\nu \rangle / \nu! , \quad (20d)$$

$$(v_{0,0} | Q_\nu | v_{e,\nu}) (v_{e,\nu} | v_{0,2}) = e^{-\gamma^2} (\gamma^2 - \nu) [\gamma^4 - 2\nu\gamma^2 + \nu(\nu-1)] \gamma^{2\nu-3} \langle Q_\nu \rangle / \sqrt{2}\nu! , \quad (20e)$$

$$(v_{0,0} | v_{e,\nu}) (v_{e,\nu} | Q_\nu | v_{0,2}) = e^{-\gamma^2} [\gamma^6 - (3\nu-2)\gamma^4 + \nu(3\nu-5)\gamma^2 - \nu(\nu-1)(\nu-2)] \gamma^{2\nu-3} \langle Q_\nu \rangle / \sqrt{2}\nu! . \quad (20f)$$

where

$$\gamma = \delta Q_\nu / 2 \langle Q_\nu \rangle ; \quad \langle Q_\nu \rangle = (\hbar / 2\mu_\nu \omega_\nu)^{1/2} . \quad (21)$$

TABLE I. Approximate vibrational transition matrix elements to terms of second order in the small parameters  $\langle Q_\nu \rangle$  and  $\gamma$ . Dashed line indicates quantity is zero to terms of this order.

$\nu$	0	1	2
$(v_{0,0}   v_{e,\nu}) (v_{e,\nu}   v_{0,1})$	$\gamma$	$-\gamma$	$\dots$
$(v_{0,0}   v_{e,\nu}) (v_{e,\nu}   v_{0,2})$	$\gamma^2 / \sqrt{2}$	$-\sqrt{2}\gamma^2$	$\gamma^2 / \sqrt{2}$
$(v_{0,0}   Q_\nu   v_{e,\nu}) (v_{e,\nu}   v_{0,1})$	$\dots$	$\langle Q_\nu \rangle$	$\dots$
$(v_{0,0}   v_{e,\nu}) (v_{e,\nu}   Q_\nu   v_{0,1})$	$\langle Q_\nu \rangle$	$\dots$	$\dots$
$(v_{0,0}   Q_\nu   v_{e,\nu}) (v_{e,\nu}   v_{0,2})$	$\dots$	$\sqrt{2}\gamma \langle Q_\nu \rangle$	$-\sqrt{2}\gamma \langle Q_\nu \rangle$
$(v_{0,0}   v_{e,\nu}) (v_{e,\nu}   Q_\nu   v_{0,2})$	$\sqrt{2}\gamma \langle Q_\nu \rangle$	$-\sqrt{2}\gamma \langle Q_\nu \rangle$	$\dots$

Here,  $\delta Q_\nu$  is the change in the origin of  $\nu$ th vibrational mode due to the change in nuclear equilibrium position on going from the ground to the excited electronic state, and  $\langle Q_\nu \rangle$  is the root-mean-square vibrational displacement of the  $\nu$ th mode in the ground state, where  $\mu_\nu$  and  $\omega_\nu$  are, respectively, the reduced mass and frequency for the  $\nu$ th mode.<sup>28</sup> It will be helpful for a qualitative understanding of the theory to have approximations to the foregoing vibrational matrix elements for small  $\langle Q_\nu \rangle$ , which is invariably the case, and small  $\gamma$ , which may or may not represent the actual situation. These approximations up to second order in the small quantities are given in Table I.

This completes the formal development of the theory, but, unfortunately, the resulting formulas do not yield a very satisfactory picture of the physical and chemical factors involved in charge-transfer contributions to SERS. The complexity is not in the basic concepts, but rather in the number of concepts involved, and the correspondingly large number of parameters. Analytic estimates of the integral in Eq. (18a) are best for obtaining a physical picture of the mechanism, and the next section will present a highly approximate analytic model which does give the magnitude of the charge transfer contribution to SERS, and illustrates some of the physically important factors. Unfortunately, the approximations required are too crude even to be fully consistent with the already quite approximate model, so the analytic formulas will have to be augmented by numerical evaluations of Eq. (18).

### III. RESULTS AND DISCUSSION

#### A. Approximate analytic model

A general overview of the theory and a rough estimate of the SERS gain due to charge transfer (denoted  $G_{CT}$ ) can be obtained from an approximate analytic estimate of the integrals in Eq. (18a) for the case of partial Raman resonance. For this case, which is realized when the real part of the denominator of the integrand vanishes somewhere in the integration interval, and  $\delta$  sufficiently small, Appendix A shows that, the real part of the integral is approximately zero, and the imaginary part is given by a relatively simple formula. Applied to Eq. (18) this approximation gives

$$\alpha_{CT}(v_{0,0} \rightarrow v_{0,\nu}) = (3\pi e^2 R_0^2 S_{FA}^2 / E_F) \times \sum_{\nu} [\sqrt{\Delta E_{\nu}} V(\sqrt{\Delta E_{\nu}}, R_0; 0, \nu, \nu')] ; \quad 0 \leq \Delta E_{\nu} \leq 1, \quad (22a)$$

where

$$\Delta E_{\nu} = \bar{E}_{CT}(k_F) + 1 + \bar{E}_{\nu} \nu - \bar{E}_0. \quad (22b)$$

Although this model will realize the objective of a rough estimate of  $G_{CT}$  and a physical picture, it is a very crude one. A particular difficulty is that because of the sign differences among the vibrational matrix elements (cf. Table I) we need differences between the integrals for different  $\nu$ . These differences are less accurately estimated by our approximation than are the integrals themselves, particularly for the real part of Eq. (18a).

The following additional approximations simplify the treatment without substantially affecting the already qualitative results and conclusions. First, we assume the overlap integral and other terms in  $f(R, k)$  [cf. Eq. (18c)] are independent of the orientation of  $k$ , which approximation is exact if the molecule interacts with only one metal atom. Second, we shall consider only the FC contribution to the vibrational transition, as given by  $V^{(FC)}$  in Eq. (19b). This approximation is exact if the molecular vibration does not change the metal-molecule separation. Finally, we consider only first order terms in  $\gamma$  which, by Table I, limits the sum over  $\nu$  to 0 and 1. With these approximations Eq. (22) becomes, to terms of first order in the ratios of the vibrational energy  $E_{\nu}$  to the electronic energies  $\Delta E_0$  and  $E_0$ ,

$$\alpha_{CT}(v_{0,0} \rightarrow v_{0,1}) = - (3\pi e^2 R_0^2 S_{FA}^2 / E_F) \sqrt{\Delta E_0} \left( \frac{1}{2} + \frac{\bar{E}_A + \bar{E}_C}{\bar{E}_0} \right) \times \left[ \left( \frac{1}{2} + \frac{\bar{E}_A + \bar{E}_C}{\bar{E}_0} \right) \frac{\bar{E}_{\nu}}{2\Delta E_0} + 2 \left( \frac{\bar{E}_A + \bar{E}_C}{\bar{E}_0} \right) \frac{\bar{E}_{\nu}}{\bar{E}_0} \right] \gamma. \quad (23)$$

The small ratio of vibrational to electronic energy appears in the foregoing equation because, as noted previously, the result involves differences between contributions from charge-transfer transitions to the  $\nu=0$  and 1 vibrational substates of the excited charge-transfer state. This difference is nonzero, first because of differences in the density of  $k$  states available for these transitions and, second, because the electronic part of the charge-transfer excitation energy differs in the two cases [these effects are given by the  $\bar{E}_{\nu}/\Delta E_0$  and the  $\bar{E}_{\nu}/\bar{E}_0$  terms, respectively, in Eq. (23)]. Since the charge-transfer excitation energy can be relatively small compared to typical intramolecular excitation energies the FC vibrational contribution becomes an important and often the dominant contribution in the charge transfer mechanism of SERS. This effect combined with the generally large oscillator strengths of charge-transfer transitions and the partially Raman-resonant character of this transition can yield substantial charge-transfer enhancements.

Equation (23) will be used to estimate  $G_{CT}$  for the C=C stretching vibration of ethylene adsorbed on silver. Taking  $a = 5.46a_0$ , which is the nearest neighbor distance

in the Ag crystal lattice,<sup>27</sup> yields from Eqs. (4) and (5) the Fermi energy  $E_F = 4.4$  eV, which model value is reasonably close to the actual value of 5.48 eV.<sup>28</sup> Taking  $R_0 = 6a_0$  and  $\epsilon = 1$  yields by Eq. (1)  $E_C = 2.3$  eV ( $\bar{E}_C = 0.52$ ). Taking  $E_A = 0.4$  eV ( $\bar{E}_A = 0.091$ ), gives, by Eq. (1),  $E_{CT}(k_F) = 2.0$  eV [ $\bar{E}_{CT}(k_F) = 0.45$ ]. For the C=C stretching vibration at  $1600 \text{ cm}^{-1}$ ,  $E_{\nu} = 0.2$  eV ( $\bar{E}_{\nu} = 0.045$ ). Taking  $E_0 = 2.5$  eV ( $\bar{E}_0 = 0.57$ ), which corresponds to excitation at 500 nm, assures that the resonant Raman condition will occur substantially below the top of the metal conduction band for the  $\nu=0, 1$  vibrational sublevels of the excited charge-transfer state, as is required for the present approximation to be valid (region  $E_0^{(1)}$  in Fig. 1). The overlap integral is calculated assuming interaction between a single carbon  $2p$  atomic orbital (AO) directed toward a single Ag  $5s$  AO [a more realistic basis for this calculation will be discussed when numerical methods are used to evaluate Eq. (18a)]. For carbon a Hartree-Fock  $C^- 2p$  AO<sup>29</sup> will be used since the site of the accepted electron will be a carbanion, as can be seen by writing out the antisymmetrized many-electron wave function for a C=C bond containing two bonding and one antibonding  $\pi$  electrons. Then, using a Hartree-Fock  $5s$  AO for Ag,<sup>29</sup> gives  $S_{FA} = 0.26$ . These values in Eq. (23), with the aid of Eq. (22b), gives  $\alpha_{CT}(v_{0,0} \rightarrow v_{0,1}) = 43.8\gamma a_0^3$ .

In the excited charge-transfer state the ethylene molecule has a substantial anion character, with the transferred electron occupying an antibonding  $\pi$  orbital. Since there also two electrons in bonding  $\pi$  orbitals, the ethylene anion has roughly 50% double bond character, so its C=C bond distance should be roughly  $2.72a_0$ , intermediate between the single and double bond distances of  $2.91$  and  $2.53a_0$ , respectively.<sup>30</sup> Thus,  $\delta Q_{\nu} = 0.19a_0$  which combined in Eq. (21) with  $\langle Q_{\nu} \rangle = 0.079a_0$  for the  $1600 \text{ cm}^{-1}$  C=C stretching vibration yields  $\gamma = 1.2$ . This value almost certainly overestimates  $\gamma$  in the actual charge transfer state for several reasons including: (1) complete charge transfer is unlikely; (2) not all the transferred charge will be localized in the C=C bond, especially for larger molecules such as butene which actually have been investigated experimentally<sup>9</sup> and (3) the vibrations will not be pure C=C stretches. It seems reasonable to take  $0.5 < \gamma < 1$  in actual systems.

This range of  $\gamma$  values gives  $\alpha_{CT} = 22$  to  $44a_0^3$ . Eq. (B3) of Appendix B estimates the polarizability for this Raman transition in the isolated molecule as  $\alpha_{\parallel} = 0.83\gamma + 1.7a_0^3$ , where  $\parallel$  denotes the C=C bond direction. Since the transition intensity is proportional to  $|\alpha|^2$ , the charge-transfer transition provides significant enhancements of the order:  $G_{CT} = 100$  to  $300$ , for  $0.5 \leq \gamma \leq 1$ . Somewhat larger enhancements are possible if we compare  $\alpha_{CT}$  with the orientationally averaged free molecule polarizability. From Eq. (B4) of Appendix B,  $\alpha_{\perp} = 0.31\gamma + 0.63a_0^3$  and  $\alpha_{av} = 0.48\gamma + 0.99a_0^3$ , yielding an enhancement of  $300$  to  $900$  for  $0.5 \leq \gamma \leq 1$ . Nonetheless, these enhancements are too small to account for the very large observed SERS gains of the order  $10^6$ , indicating that the charge-transfer mechanism usually operates in conjunction with the electrodynamic mechanism.<sup>1,2</sup>



Furthermore, if charge-transfer plays the dominant role in molecule-surface bonding and thereby determines the surface orientation of the first monolayer (and possibly succeeding monolayers if there is any tendency toward crystalline ordering), then it may produce an additional apparent charge-transfer enhancement by ordering the adsorbed molecules so that the isolated-molecule transition polarizability is minimized. In ethylene, for example, achieving maximum overlap between the acceptor  $\pi$  orbital and the metal orbitals requires that the molecule be oriented with the C=C bond parallel to the surface and hence perpendicular to the electrostatically enhanced optical electric field which must be perpendicular to the surface. The intramolecular transition polarizability is minimized by this orientation.

This point may have important implications for the much studied pyridine-metal systems, because adsorbed pyridine apparently orients either parallel or perpendicular to the surface depending on the degree of surface coverage.<sup>12(a)</sup> A significant pyridine-metal charge-transfer interaction is unlikely if the molecular plane is perpendicular to the surface because this precludes interaction between the pyridine  $\pi$  MO and the metal orbitals and leaves donation of a nitrogen lone-pair electron to the metal as the most likely charge-transfer process. Despite the weak basicity of pyridine, the metal is unlikely to be a sufficiently good acceptor for this process to be significant. This perpendicular orientation, however, yields the maximum intramolecular contribution to the Raman transition because pyridine, like other conjugated planar molecules, is most polarizable when the electric field lies in the molecular plane. Consequently, SERS experiments on pyridine-Ag and similar systems could give both positive and negative indications of charge-transfer effects depending on experimental conditions and the consequent molecular orientation.

Inspection of Eq. (23) suggests that  $\alpha_{CT}$  and the Raman intensity will increase as  $E_0$  decreases until  $E_0$  falls below the lower limit of the charge-transfer band (region  $E_0^{(III)}$  in Fig. 1), at which point the Raman intensity will decrease rapidly. The reason for this is twofold. First, as can be seen from Eqs. (10) and (14), decreasing  $E_0$  increases the charge-transfer mixing and the resulting transition oscillator strength in the Raman resonant region which makes the dominant contribution to the polarizability. Second, as Eq. (5) and Fig. 1 show, there is an increase in the number of donor conduction band states as the Raman resonant region approaches the top of the conduction band. Calculations using Eq. (23) show that  $\alpha_{CT} = 28\gamma$  and  $80\gamma$  for  $E_0 = 3$  and  $2$  eV, respectively, which corresponds to an increase of roughly eight in the Raman intensity over this energy range. [Although, the approximation used to obtain Eqs. (22) and (23) is not strictly inapplicable when the excitation energy is at the lower end of the charge transfer band where the density of states is changing rapidly (region  $E_0^{(III)}$  in Fig. 1), the foregoing reasoning will be supported by numerical calculations to be discussed in the next section.] This rather anomalous behavior has been ob-

served in some systems exhibiting SERS,<sup>10</sup> and it is possible, but by no means certain, that charge transfer effects such as the ones described here may be the cause.

## B. Numerical estimates

Here we use numerical methods to analyze the model of ethylene adsorbed on a silver surface in more detail than was possible using the crude analytic approximations presented in the previous section. This analysis requires a more detailed consideration of two important parameters: the overlap integral and lifetime of the excited charge-transfer state which determines  $\delta E$ .

### 1. Overlap integral

The conduction band and molecular donor-acceptor orbitals involved in the overlap integral [cf. Eq. (15)] are weakly bonding or antibonding orbitals with considerable sign variation among the coefficients of their constituent atomic orbitals. Consequently, the magnitude of the overlap, and hence  $G_{CT}$ , will vary greatly with the nature of the molecule and various features of the metal surface such as which crystal plane is exposed, disorder, etc. For example, the ethylene acceptor orbital is an antibonding antisymmetrical  $\pi$  MO which yields zero overlap with a single metal atom located symmetrically with respect to the two olefinic C atoms. Thus, the interaction must either be an unsymmetrical one in which a single metal atom interacts more strongly with one C atom than the other, or the interaction involves two or more metal atoms. The latter interaction, with the plane of the molecule parallel to the surface, seems more likely for ethylene. The former interaction would probably require that the molecular plane be tilted with respect to the surface resulting in unfavorable steric interactions between the surface and H atoms or other groups bonded to the C=C moiety. The former interaction could occur in other cases, however, such as pyridine which could be tilted and interact with the surface via its nitrogen  $\pi$  orbital without the aforementioned steric problems.

Two possible modes of interaction of ethylene with the metals atoms in a [100] plane of the simple cubic model Ag lattice are shown in Fig. 2. If all nonzero overlaps are considered (practically, only the overlap of each carbon with the two nearest metal atoms need be considered) it turns out that orienting the C=C bond along the (110) crystal axis yields a larger overlap than does the (100) orientation even though the individual C-Ag distances are greater in the former case for a given (molecular plane)-(metal surface) separation. Taking the nearest neighbor Ag distance as  $5.46a_0$ , the C=C bond distance as  $2.53a_0$  and the molecule-surface separation as  $6a_0$ , makes the nearest and next nearest C-Ag distances  $6.54$  and  $7.89a_0$ , respectively, for the (110) orientation of the  $C_2H_4$  molecule. Calculating the individual overlap integrals as described previously, yields the overlap integrals:

$$S_{kA}(R_0 = 6.00a_0) = (0.094/\sqrt{2}) \times \{ \exp[\frac{1}{2}ia(k_x + k_y)] - \exp[-\frac{1}{2}ia(k_x + k_y)] \} . \quad (25)$$



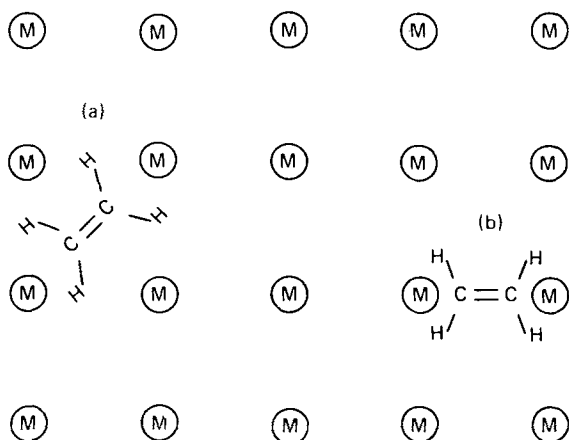


FIG. 2. Two possible orientations of an ethylene molecule on the [100] surface of a simple cubic metal lattice: (a) C=C bond parallel the (110) axis and (b) C=C bond parallel the (100) axis. The molecular plane is parallel to the surface in each case.

A similar calculation for the molecule oriented along the (100) crystal axis gave  $(0.085/\sqrt{2})[\exp(\frac{1}{2}iak_x) - \exp(-\frac{1}{2}iak_x)]$  for the overlap integral. To average  $|S_{kA}|^2$  over the orientations of  $k$  following Eq. (17) we expand the exponential obtaining several terms of which only the integral of  $\cos(ak_x)\cos(ak_y)$  is nontrivial. Using Eq. (5) for  $a$ , setting  $k_x = k \cos \theta_k$ ,  $k_y = k \sin \theta_k \cos \varphi_k$ , and remembering that  $x = k/k_F$ , this integrand can be rewritten as  $\cos(px \cos \theta_k) \cos(px \sin \theta_k \cos \varphi_k)$ , where  $p = (3/\pi)^{1/3} \pi$ . The integration over  $\varphi_k$  yields the Bessel function<sup>31</sup>  $J_0(px \sin \theta_k)$  and the integration over  $\theta_k$  then yields the result<sup>32</sup>

$$\langle |S_{kA}(R_0)|^2 \rangle_{\Omega(k)} = 8.8(10)^{-3} [1 - \sin(\sqrt{2}px)/(\sqrt{2}px)]. \quad (26)$$

Therefore, by Eq. (16b),  $S_{FA}^2 = 0.011$ .

## 2. Lifetime broadening of the excited state

Rapid electron scattering among the conduction-band states of the metal, which changes the vacant metal orbital in the excited charge-transfer state, and radiative decay of this excited state are both lifetime-limiting processes which contribute to  $\delta E$ . The former process gives  $\delta E = \hbar/\tau_{AE} = 0.021$  eV where  $\tau_{AE} = 3.1(10)^{-14}$  s is the electron scattering relaxation time in Ag.<sup>21</sup> Calculation of the dipole moment for the transition between the ground and excited charge-transfer state, using the formalism in Secs. IIB and IIC and the parameters used in the analytic calculation of  $G_{CT}$  with  $k = k_F$  and  $S_{FA} = 0.105$  for the overlap integral, yields a radiative lifetime<sup>33</sup> of  $5(10)^{-8}$  s for the excited charge-transfer state in the absence of field enhancing effects of the metal surface. If the interaction with the metal surface enhances the transition rate by the same amount it enhances the Raman transition, i.e., by  $10^5$  to  $10^6$ , the lifetime becomes  $5(10)^{-13}$  to  $5(10)^{-14}$  s with corresponding  $\delta E$  values of 0.001 to 0.01 eV. Thus, the estimate of 0.02 eV based on conduction electron scattering is reasonable and will be used in most of the calculations.

We shall, however, examine the effect of a considerably larger  $\delta E$  of 0.2 eV.

## 3. Numerical results for $G_{CT}$

We can now proceed with the numerical evaluation of Eq. (18a), using Eq. (19) and related equations for  $V$ , Eq. (18c) for  $f(R, k)$ , and Eq. (20) for the vibrational matrix elements as functions of the nuclear displacement accompanying the charge-transfer transition. The sum over  $\nu$  will cover  $0 \leq \nu \leq 10$ . The energy and other parameters will be the same as used in the previous rough analytic calculation.

For the ethylene-Ag system the HT contribution to the Raman transition, given by  $V^{(HT)}$  in Eq. (19c), is zero because the C=C stretching vibration does not significantly change the metal-molecule separation, i.e.,  $(\partial R/\partial Q_{C=C}) = 0$  in Eq. (19c). Even if the vibrations did change  $R$ , such that  $(\partial R/\partial Q_{C=C}) = 1$ , the calculations for this case will show that the HT term is small compared to the FC term, given by  $V^{(FC)}$  in Eq. (19b), for those values of  $E_0$  and  $\gamma$  which yield significant charge transfer contributions to SERS. Thus, the present results are based on the FC term alone. It is convenient to write the transition polarizability of the Raman fundamental as

$$\alpha_{CT}^{(1)} = \alpha_{CT}(v_{0,0} \rightarrow v_{0,1}) = (6e^2 R_0^2 S_{FA}^2 / E_F) (J_{R\bullet}^{(1)} + iJ_{Im}^{(1)}) \gamma, \quad (27)$$

where  $J_{R\bullet}^{(1)}$  and  $J_{Im}^{(1)}$  are plotted vs  $\gamma$  for various  $E_0$  values in Fig. 3. Clearly, it is incorrect to assume that real part of Eq. (18a) will be small compared to the imaginary part if the charge-transfer band is partially resonant with the exciting radiation. Despite this difficulty, however, the numerical results will generally confirm the physical picture given by the previous analytic treatment which necessarily used this assumption.

Figure 4 gives the charge-transfer contribution to the SERS gain of the C=C stretching fundamental as a function of excitation energy for various values of  $\gamma$ . This gain is:  $G_{CT}^{(1)} = |\alpha_{CT}^{(1)} / \alpha_{av}|^2$ , where  $\alpha_{av}$  is the orientationally averaged free-molecule polarizability given by Eq. (B4) of Appendix B. The jaggedness of these plots is due to the sensitivity of  $G_{CT}$  to the exact position of the excitation energy relative to the conduction band edge and the corresponding minimum transition energy  $E_{CT}(k_F)$ ; it is artificially exaggerated since these plots are calculated only at 0.125 eV intervals in the range  $1.5 \leq E_0 \leq 3$  eV with straight lines drawn between the points. This structure of resonant Raman spectra as a function of excitation energy is well known and is a useful method for investigating vibrational structure.<sup>14</sup> Such methods may be useful in SERS, at least to identify and separate charge-transfer and electrodynamic contributions to the SERS gain. It is unlikely, however, that the structure observed in Raman resonance spectra of homogeneous systems<sup>14</sup> and suggested by Fig. 4 will be observed in SERS, because of substantial broadening of the charge-transfer band by inhomogeneities in the metal-adsorbed molecule system. For example, if these inhomogeneities were to cause  $E_{CT}(k_F)$ , which is 2 eV in the present calculation, to be binomially dis-

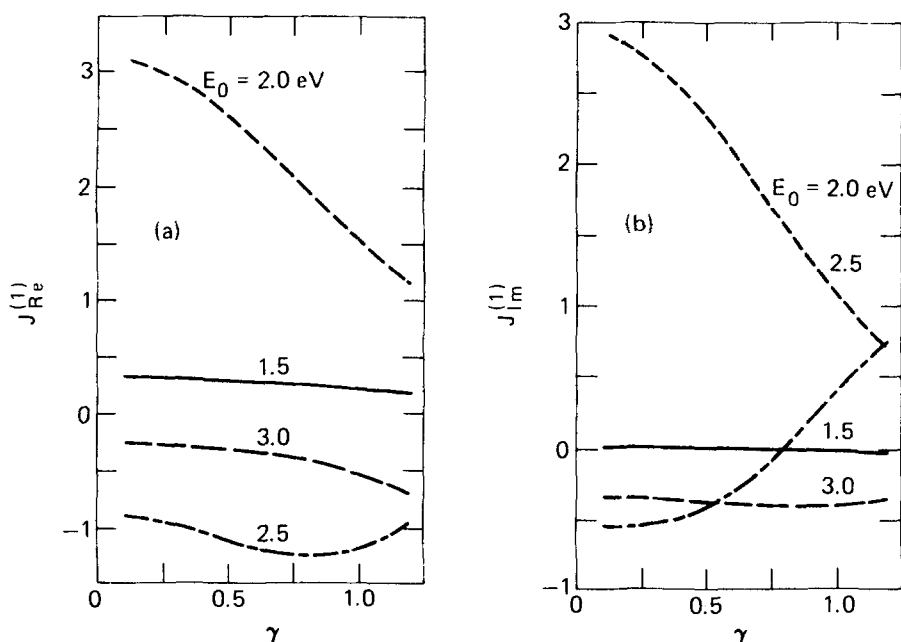


FIG. 3. Coefficients describing the charge-transfer contribution to the complex Raman transition polarizability of the C=C stretching vibration of ethylene adsorbed on silver: (a) real part; (b) imaginary part. Results given as functions of the nuclear displacement parameter  $\gamma$  for various values of the excitation energy  $E_0$ . Other parameters are:  $E_0 = 6 a_0$ ,  $|S_{FA}|^2 = 0.011$ , and energies  $E_C = 2.3$ ,  $E_A = 0.4$ ,  $E_{CT}(k_F) = 2.0$ ,  $E_v = 0.21$ , and  $\delta E = 0.02$  eV.

tributed at 0.125 eV intervals about 2 eV (this is affected by adjusting the metal work function parameter and roughly approximates a Gaussian distribution of width 0.3 eV at half-intensity), then the results for  $G_{CT}^{(1)}$  are shown in Fig. 5. There is still a strong dependence on excitation frequency but the detailed structure is gone.

Homogeneous broadening due to a shorter lifetime for the intermediate charge-transfer state could also obliterate the structure observed in Fig. 4. Taking  $\delta E = 0.2$  eV and otherwise repeating the calculations which yielded Fig. 4 gave a set of broadened gain vs excitation energy curves quite similar to those in Fig. 5 except that the maximum gains in Fig. 5 were reduced by factors of roughly 7.0, 5.6, 4.4, and 3.1 for  $\gamma = 0.3, 0.6, 0.9$ , and 1.2, respectively.

Calculations of  $G_{CT}$  vs  $E_0$  for different charge transfer

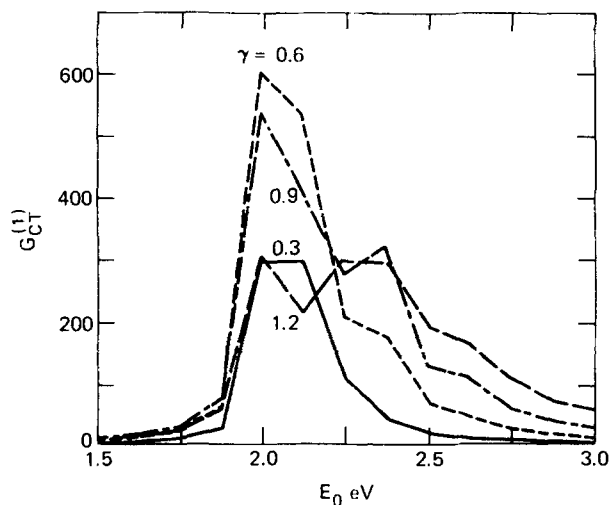


FIG. 4. Charge-transfer contribution to the Raman gain of the C=C stretching fundamental of ethylene adsorbed on silver. Parameters are given in the caption of Fig. 3.

excitation energies show that the curves retain the general shape shown in Figs. 4 and 5 but the maxima shift so as to occur for  $E_0$  near  $E_{CT}(k_F)$ . Also, and in accordance with Eq. (23), the maximum gain decreases as  $E_{CT}(k_F)$  increases.

Calculations also show that in general the FC component of charge-transfer enhancement will increase strongly with increasing vibrational frequency. The reason, as Eq. (23) qualitatively shows, is that increasing the vibrational energy decreases the cancellation among the different vibrational sublevels of the excited charge-transfer state which contribute to this term. Thus, lower frequency vibrations, such as molecule-surface vibrations, along with nontotally symmetric vibrations which do not have a FC component,<sup>14</sup> and vibrations involving atoms whose orbitals are not in-

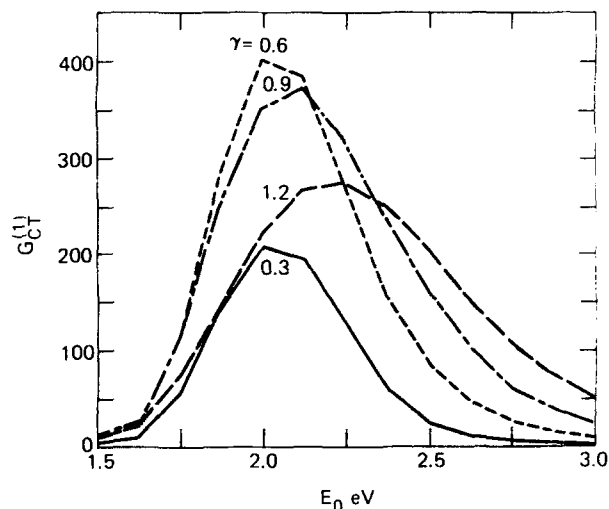


FIG. 5. Charge-transfer contribution to the Raman gain of the C=C stretching fundamental of ethylene adsorbed on silver. The parameters are the same as Fig. 4 except the charge-transfer band is inhomogeneously broadened with a half-intensity width of 0.3 eV.

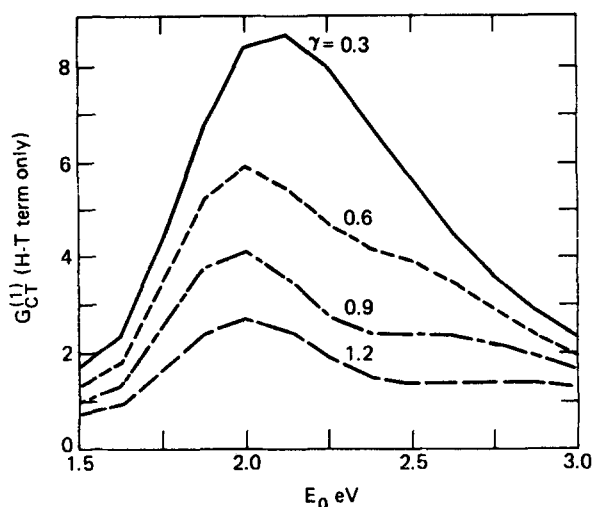


FIG. 6. Herzberg-Teller part of the charge-transfer Raman gain of the C=C stretching fundamental of ethylene adsorbed on silver. All other conditions are the same as in Fig. 5.

involved in the charge-transfer excitation and thus do not experience a substantial change in vibrational origin, are likely to be relatively unenhanced by the charge-transfer mechanism.

Charge-transfer enhancement of the foregoing types of vibrations by the HT mechanism is still possible, however, so it is instructive to calculate this term for comparison with the FC contribution to  $G_{CT}$ . The results given in Fig. 6 are for the same parameters used in the calculation of Fig. 5, with  $\langle Q_v \rangle = 0.079a_0$ , and  $(\partial R/\partial Q_v) = 1$  in Eq. (19c) which is used in the integrand of Eq. (18a) for this case. Clearly, the HT contribution to  $G_{CT}$  is at least an order of magnitude smaller than the FC term for this case. Unlike the FC term, the HT term is largest for small  $\gamma$ , which is to be expected since large differences in equilibrium nuclear configurations between the ground and excited states are not necessary for this term, but only introduce destructive interference between contributions from different vibrational sublevels of the charge-transfer state. Although these results were calculated for a specific case, the results are probably generally true, so that vibrations having a large FC term will be enhanced significantly more by charge transfer than those which do not.

In summary, the calculated results, in general agreement with the analytic formula of Eq. (23), predict charge-transfer enhancement factors of the order of several hundred over a wide range of likely experimental parameters. These values are consistent with experimental estimates, especially the investigation of SERS of various butenes adsorbed on silver.<sup>9</sup>

#### 4. Overtones in SERS

Many values of  $E_0$  and  $\gamma$  which yield large  $G_{CT}$  were also found to enhance the corresponding first overtone sufficiently to suggest it should be observable in the SERS spectrum. For example, a calculation using the conditions of Fig. 5 shows that at the maxima in the

$G_{CT}^{(1)}$  vs  $E_0$  curves the (overtone/fundamental intensities) are 0.06, 0.27, 0.35, and 0.42 for  $\gamma = 0.3, 0.6, 0.9$ , and 1.2, respectively. There have been few if any reports of overtone or combination bands in SERS spectra, however, including the aforementioned detailed investigation of charge transfer contributions to SERS in butene.<sup>9</sup> This problem needs to be investigated further by observing the excitation frequency dependence of systems in which charge-transfer contributions are suspected, since the overtone enhancement has a somewhat different dependence on  $E_0$  than does  $G_{CT}^{(1)}$ , particularly for small  $\gamma$ .

A possible obstacle to observing overtones in SERS is that the electrodynamic mechanism will usually enhance a given fundamental more than its overtones. It is not possible to satisfy simultaneously the plasmon resonance conditions for maximum enhancement of the optical field and the radiating molecular dipole because their frequencies differ by the vibrational frequency, and the reduction in electrodynamic gain due to this frequency mismatch is usually greater for an overtone or combination band than for the fundamental. This is illustrated in Fig. 7 which shows the maximum electrodynamic SERS gains (i.e., for molecules at the point of a prolate spheroidal roughness feature where the field enhancements are largest) for the 1600  $\text{cm}^{-1}$  C=C stretching fundamental ( $G_{EM}^{(1)}$ ), its first overtone, ( $G_{EM}^{(2)}$ ), and the ratio  $G_{EM}^{(1)}/G_{EM}^{(2)}$  as functions of the shape of the prolate spheroidal surface roughness element, defined as:  $f_s = \text{minor}/\text{major}$  semiaxis. Over most of the range of  $f_s$  the fundamental is enhanced more than the overtone, with the effect being especially large in the plasmon resonance region which makes the largest contribution to the gain. For very prolate roughness features ( $f_s < 0.2$ )  $G_{EM}^{(2)}$  becomes greater than  $G_{EM}^{(1)}$  but such highly needle-like roughness features are probably less numerous than the more nearly spherical ones. An average electrodynamic gain, calculated assuming

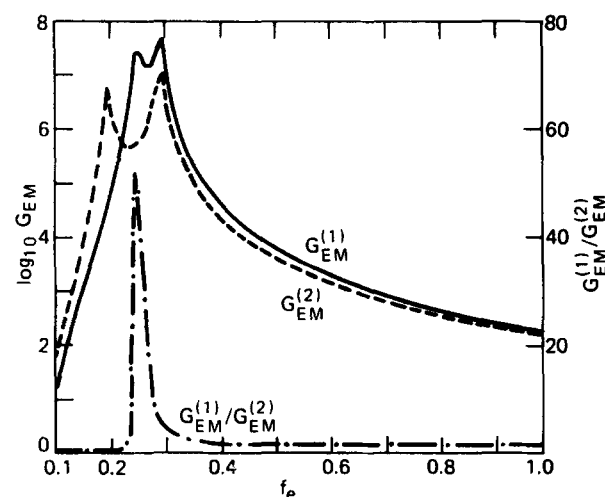


FIG. 7. Electrodynamic contributions to the Raman gains of the fundamental, first overtone, and their ratio, for the C=C stretching vibration of ethylene adsorbed on silver. Results given as functions of  $f_s = \text{minor}/\text{major}$  semiaxis ratio of the surface roughness element. Pure silver values used for  $\epsilon_{Ag}$  (Ref. 21) and  $\epsilon = 1$ .

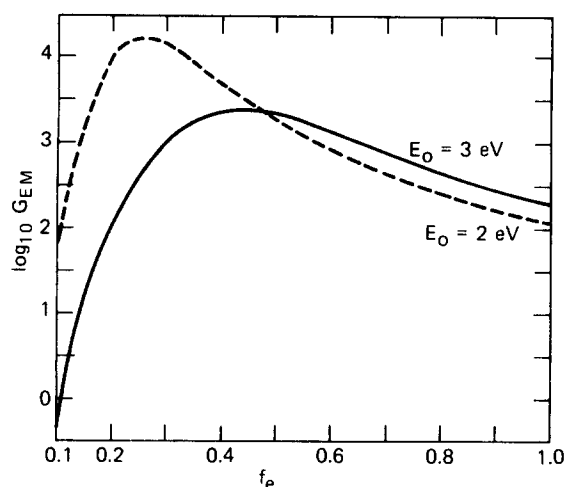


FIG. 8. Electrodynamic contributions to Raman gain on platinum.  $\epsilon_{pt}$  obtained by extrapolation of the results of Ref. 34.  $\epsilon = 1$ . Results for  $E_0 = 2$  (---) and 3 eV (—).

the effectiveness of a particular surface roughness feature, after weighting for distribution of particle shapes and available area in the region of maximum enhanced fields, is proportional to  $f_e^2$  over the range  $0.1 \leq f_e \leq 1.0$ , gave  $\langle G_{EM}^{(1)} \rangle = 7.8(10)^5$  and  $\langle G_{EM}^{(2)} \rangle = 1.5(10)^5$ , so  $\langle G_{EM}^{(1)} \rangle / \langle G_{EM}^{(2)} \rangle = 4.8$ . This result does not depend too strongly on the particle distribution, a linear dependence on  $f_e$  yields nearly the same result for  $\langle G_{EM}^{(1)} \rangle / \langle G_{EM}^{(2)} \rangle$ . In addition to limiting the intensities of high frequency overtones in SERS spectra, this may partially explain why high frequency vibrations such as C-H stretches are often weak or absent from SERS spectra. Although this electrodynamic discrimination against overtones will be less effective for low frequency vibrations, the FC mechanism which produces the overtones is, as previously noted, substantially less effective for low frequency vibrations.

### C. SERS on platinum

There has been a very recent interesting report of SERS for benzene chemisorbed on small platinum clusters.<sup>11</sup> The Raman enhancement was observed to increase by a factor of 20 as  $E_0$  increased from 2.1 to 3.2 eV (i.e., 600 to 400 nm). The electrodynamic mechanism of SERS is not expected to be effective for platinum because the metal is very lossy, i.e., the imaginary part of  $\epsilon_{pt}$  is large at optical frequencies,<sup>34</sup> which greatly diminishes the field-enhancing effects of the plasmon resonances. This is illustrated by calculation of  $G_{EM}$  for Pt at  $E_0 = 2$  and 3 eV as shown in Fig. 8. Comparison of Fig. 8 with Fig. 7 shows that  $G_{EM}$  is so much larger for Ag than for Pt in their plasmon resonance regions that, considering the typical signal to noise ratio observed for SERS spectra of molecules adsorbed on Ag, it is questionable if the electrodynamic mechanism alone can yield observable Raman spectra on Pt. Also, the calculated  $G_{EM}$  indicate the SERS gain on Pt will be unchanged or even decreased as  $E_0$  goes from 2 to 3 eV, whereas the observed spectra show a large increase.<sup>11</sup> This result could be due, however, to enhancement by a charge-transfer transition begin-

ning around 3 eV. Such a relatively high charge-transfer energy is not unreasonable for a molecule adsorbed on Pt because its work function is about 1 eV higher than that of Ag.<sup>17</sup> Although the large  $E_{CT}$  is unfavorable for charge-transfer SERS, an offsetting favorable factor may be that the Pt  $d$  orbitals can overlap better with the unsymmetrical antibonding benzene acceptor orbital than could the symmetrical Ag  $5s$  orbital. Finally, since the lowest unoccupied MO of benzene is degenerate there may be exceptionally large, Jahn-Teller-type, vibrational couplings to further increase  $G_{CT}$  in this case.<sup>14</sup>

### D. Luminescence and SERS

It is possible, of course, to have real as well as virtual excitation of the charge-transfer state. This can result in luminescent emission as the excited electron returns to the metal. Luminescence frequently appears as a background to SERS spectra.<sup>3(b),35,36</sup> Its origin is controversial, however, in that some authors claim it is observed in the absence of adsorbed molecules and ascribe it to electron-hole pair excitation in the metal,<sup>3(b)</sup> whereas others claim it is observed only in the presence of adsorbed molecules and is, therefore, due to luminescence from an excited metal-molecule charge transfer state.<sup>35</sup> All mechanisms for this luminescence predict, in agreement with experiment, an anti-Stokes component due to excitation of electrons in thermally excited conduction-band states at energies above the Fermi energy followed by luminescent return of these electrons to unoccupied conduction-band levels below the Fermi energy. Thus all luminescence mechanisms predict the intensity distribution of the anti-Stokes radiation should follow a Fermi distribution, which prediction has been confirmed.<sup>35</sup> For the metal-adsorbed-molecule charge-transfer excitation mechanism, however, the anti-Stokes emission is likely to be greatest when the excitation energy ( $E_0$ ) is of the order of the energy required for charge-transfer excitation from the top of the conduction band [ $E_{CT}(k_F)$ ] (cf. Fig. 1) which also maximizes  $G_{CT}$ . The presence or absence of the indicated correspondence between the anti-Stokes luminescence and maximum charge transfer Raman enhancement could help decide between the competing luminescence mechanisms.

### IV. SUMMARY

The foregoing analysis suggests that charge-transfer effects will contribute a factor of 10 to 1000 to the observed Raman gain in at least some of the systems exhibiting SERS, with the remainder of the gain coming from the field-enhancing effects of plasmon resonances at surface roughness features. For SERS of molecules adsorbed on lossy metals such as platinum<sup>11</sup> or presumably smooth surfaces such as liquid mercury,<sup>37</sup> the charge-transfer contributions may be predominant.

The charge-transfer gain has a rather complicated dependence on a number of parameters of the metal-adsorbed molecule system. Among the important factors are the position of the charge-transfer band with respect to the excitation frequency and such properties of the observed molecular vibration as its symmetry,

its frequency, and the difference between its origins in the ground and the excited charge-transfer state. Also important, is the dependence of the excitation energy and transition moment of the charge transfer state on such factors as the surface absorption site, the orientation of the adsorbed molecule, and its overlap with the conduction band orbitals.

Consequently, it is not surprising that identification of charge-transfer effects in SERS has been an uncertain and controversial process, with one experiment yielding positive indications of charge transfer and another presumably similar experiment yielding negative results.

The present results suggest that useful approaches to identifying charge-transfer effects in SERS will be to investigate the SERS spectra of reasonably good electron acceptor (or donor) molecules at various excitation energies, and to compare symmetric and anti-symmetric vibrations involving atoms where the acceptor (or donor) MOs have the highest electron density. Studies of SERS spectra as functions of surface coverage<sup>5,9</sup> and in the presence of several monolayers of an inert spacer<sup>8</sup> should also be useful, since the charge-transfer contributions to SERS, unlike the electrodynamic contribution, is zero except for the first monolayer. Hopefully such methods can both resolve the question of charge transfer in SERS, and provide information on the structural and dynamical properties of the adsorbed molecules.

## APPENDIX A

Equation (18a) requires evaluation of integrals of the general type

$$I = \int_0^1 dx x^2 g(x) / (\Gamma - x^2 - i\delta) . \quad (\text{A1})$$

With the change of variable  $t = (x^2 - \Gamma)/\delta$  this integral becomes

$$I = -\frac{1}{2} \int_{-\Gamma/\delta}^{(1-\Gamma)/\delta} dt \sqrt{\delta t + \Gamma} g(\sqrt{\delta t + \Gamma}) (t - i) / (t^2 + 1) . \quad (\text{A2})$$

If  $0 \leq \Gamma \leq 1$  and  $\delta$  is small in the sense that  $|\delta| \ll [\Gamma \text{ and } (1 - \Gamma)]$  then  $I$  can be approximated by its  $\delta \rightarrow 0$  limit, which is

$$\lim_{\delta \rightarrow 0} I = (\pi i / 2) \sqrt{\Gamma} g(\sqrt{\Gamma}) , \quad (\text{A3})$$

where the real part of  $I$  vanishes because its integrand in the  $\delta \rightarrow 0$  limit is an odd function of  $t$  over the limits.

## APPENDIX B

Here, we estimate the Raman transition polarizability for the C=C stretching fundamental in ethylene and similar molecules. It will be assumed that this polarizability is due to the two strong electronic transitions  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \sigma^*$  of the C=C bond. The dipole moment for the  $\pi \rightarrow \pi^*$  transition in the direction parallel to the C=C bond ( $z$  direction) is  $\langle \pi_+ \pi_- | z | (\pi_+ \pi_- - \pi_- \pi_+) / \sqrt{2} \rangle = \sqrt{2} \langle \pi_+ | z | \pi_- \rangle$ , where  $\pi_{\pm} = (\pi_1 \pm \pi_2) / \sqrt{2}$  are the bonding (+) and antibonding (−)  $\pi$  orbitals. Thus, the transition dipole moment is  $D/\sqrt{2}$  where  $D$  is the C=C bond dis-

tance. The  $\sigma \rightarrow \sigma^*$  transition is readily shown to have the same transition moment. Thus, from Eq. (12) the Raman transition polarizability may be estimated as

$$\alpha_{\parallel}(0 \rightarrow \nu') = e^2 \sum_{\nu} \frac{(v_{0,0} | D | v_{e,\nu})(v_{e,\nu} | D | v_{0,\nu'})}{\Delta E + E_{\nu} - E_0} , \quad (\text{B1})$$

where  $\Delta E$  is the average transition energy for the  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \sigma^*$  transitions and  $v_{e,\nu}$  is the vibrational wave function in the excited state.

We estimate  $\Delta E$  from the reported static C=C bond polarizability<sup>38</sup> of  $\alpha_{\parallel} = 19.30a_0^3$ , i. e.,  $E_0 = 0$ ,  $\nu = 0$ , obtaining  $\Delta E = 9.0$  eV. This estimate is reasonable since it is, as expected, somewhat greater than the  $\pi \rightarrow \pi^*$  transition energy of 7.6 eV.<sup>39</sup>

Following the procedures discussed for the charge-transfer contribution to the Raman transition polarizabilities [cf. Eqs. (18) and (19)] Eq. (B1) can be decomposed into the FC and HT contributions. Taking  $\nu' = 1$  and neglecting all terms of order  $\gamma^2$  and higher in Eq. (20) for the vibrational matrix elements gives

$$\alpha_{\parallel}(0 \rightarrow 1) = \frac{e^2 D^2 E_{\nu} \gamma}{(\Delta E - E_0)^2} + \frac{2e^2 D^2 (v_{0,0} | \delta D / D | v_{0,1})}{\Delta E - E_0} , \quad (\text{B2})$$

where the first term is the FC term, the second is the HT term, and  $\delta D$  is the vibrational displacement of the C=C bond. Inserting in Eq. (B2) the numerical values  $D = 2.53a_0$ ,  $\langle v_{0,0} | \delta D / D | v_{0,1} \rangle = 0.079a_0$  from Eq. (21) for the 1600  $\text{cm}^{-1}$  C=C stretching vibration and  $\Delta E = 9$  eV gives

$$\alpha_{\parallel}(0 \rightarrow 1) = [35\gamma / (9 - E_0)^2] + 11 / (9 - E_0) , \quad (\text{B3})$$

where  $\alpha$  is in  $a_0^3$  and  $E_0$  is in eV. We shall estimate  $\alpha_{\perp}$ , and thus the orientationally averaged polarizability, from the ratio of the static parallel and perpendicular polarizabilities.<sup>38</sup> The results are

$$\alpha_{\perp}(0 \rightarrow 1) = 0.37\alpha_{\parallel}(0 \rightarrow 1) ; \quad \alpha_{\text{av}}(0 \rightarrow 1) = 0.58\alpha_{\parallel}(0 \rightarrow 1) . \quad (\text{B4})$$

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