Time-dependent picture of the charge-transfer contributions to surface enhanced Raman spectroscopy

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We reexamine the Herzberg-Teller theory of charge-transfer contributions to the theory of surface enhanced Raman scattering (SERS). In previous work, the Kramers-Heisenberg-Dirac framework was utilized to explain many of the observed features in SERS. However, recent experimental and theoretical developments suggest that we revise the theory to take advantage of the time-dependent picture of Raman scattering. Results are obtained for molecular adsorption on nanoparticles in both the strong confinement limit and the weak confinement limit. We show that the Herzberg-Teller contributions to the charge-transfer effect in SERS display a resonance at the molecule-to-metal or metal-to-molecule transition while retaining the selection rules associated with normal Raman spectroscopy (i.e., harmonic oscillator, as opposed to Franck-Condon overlaps). The charge-transfer contribution to the enhancement factor scales as $\Gamma^{-4}$, where $\Gamma$ is the homogeneous linewidth of the charge-transfer transition, and thus is extremely sensitive to the magnitude of this parameter. We show that the Herzberg-Teller coupling term may be associated with the polaron-coupling constant of the surface phonon-electron interaction. A time-dependent expression for the Raman amplitude is developed, and we discuss the implications of these results for both metal and semiconductor nanoparticle surfaces. © 2007 American Institute of Physics. [DOI: 10.1063/1.2748386]

INTRODUCTION

The phenomenon of surface enhanced Raman scattering1–3 (SERS) has become an important tool of considerable utility in understanding nanotechnology as well as leading to numerous possible practical applications. In the early days of this endeavor, it was quickly realized that since the effect was largest when using the noble metals as the enhancing surface, plasmon resonances must play an important part in the observed enhancement (usually described as on the order of $10^6$). These resonances resulted in strong enhancements of the electric field near the metal surface both for the incoming and scattered radiation. Realistic enhancement ratios up to $10^4$ could easily be explained by this theory.

However, as more research was carried out, it became clear that the plasmon theory alone could not explain all the observations. It was not possible to explain why only molecules with the ability to be chemically adsorbed on the silver surface (such as pyridine, thiols, and carboxylic acids) displayed the largest enhancements, while those which could only be physisorbed (such as benzene and hydrocarbons) had small, if measurable effects. This is true even for pairs of molecules with similar Raman cross sections, such as CO versus N$_2$. Observations on electrode surfaces showed resonance-shaped intensity profiles as a function of applied potential. It was further found that different vibrational modes showed slight shifts in this resonance and that the resonance maximum shifted linearly with excitation wavelength. It soon became clear that an additional cause was operative, and simultaneously several investigators4–7 proposed that these phenomena could be explained by a charge-transfer mechanism. It was suggested that the conduction band orbitals of the metal lay between the highest molecular filled level (highest unoccupied molecular orbital) and its first excited unfilled level (lowest unoccupied molecular orbital), and that transitions take place from the molecular filled level to empty levels above the Fermi level or, alternatively, from the filled metal levels below the Fermi level to unfilled orbitals in the molecule. These ideas received impetus by the experiments of Demuth and Sanda,8 who observed low-lying, energy-transfer bands in pyridine and pyrazine on silver by high-resolution electron energy loss experiments. However, early attempts to explain these observations using the standard theory of resonance Raman spectroscopy also ran into difficulties. Although there was no problem with the additional enhancement (10–100), which, together with the plasmon resonance, readily accounted for the total observed enhancement, it could not be adequately explained why no overtones were observed, nor why nontotally symmetric modes were prominent in the spectra.9 The normal resonance Raman theory predicts both strong overtones and only totally symmetric modes. Furthermore, the resonance potential intensity profile could not be adequately fitted with either the usual Lorentzian or Gaussian line shape functions.

These problems impelled us10 to explore the possibilities of contributions from the Herzberg-Teller theory, which come from a mixing of zero-order Born-Oppenheimer electronic states by means of vibronic interaction terms in the Hamiltonian. This concept was pioneered by Albrecht11 to explain the observed intensities of Raman spectra. Our contribution was to explicitly include the continuum of charge-transfer states. This work (hereafter referred to as I) was able to explain in a single theory both the molecule-to-metal and metal-to-molecule charge transfer. Furthermore, we were
able to explain correctly the dependence of the voltage maximum on the exciting wavelength, the absence of overtones, and the presence of non-totally symmetric modes. Resonant charge-transfer enhancements of 10–100 were predicted, and furthermore, we were able to show that a logarithmic singularity led to an excellent fit to the line shape.

In the intervening years, it is safe to say that thousands of articles, both experimental and theoretical, have appeared, vastly extending our understanding of SERS and providing new insights, as well as raising new questions to be answered. It is not possible here to review all of these developments, but we would like to mention several new experiments and theoretical developments, which suggest that we revisit our earlier work. Perhaps it would be clearer to list them.

(1) There have been remarkable extensions of SERS observations to smaller and smaller sample sizes, eventually down to the single-molecule level. These were observed with single molecules adsorbed on one or between two Ag nanoparticles. Such observations can only be explained by resorting to enhancement factors as large as $10^{14}$. Despite initial attempts to explain these enhancements solely on the basis of plasmon resonance theory, enhancements this large would require extremely high electric fields on the molecule. These fields might be sufficiently high to ionize or dissociate the molecule, or at least cause serious distortion to the vibrational modes. However, none of these effects are observed. Instead, the Raman frequencies are negligibly shifted from those observed with considerably lower enhancements. Further indications of the importance of charge transfer come from observations of the blinking effect, which arises from time-dependent interruptions of the electronic coupling between molecule and nanoparticle. The observation of anti-Stokes intensity, which is considerably greater than expected, indicates a resonance enhancement due to silver-molecule charge-transfer states. Michaels et al. found a lack of correlation between resonant Rayleigh scattering and single-molecule SERS intensity. They interpreted this to indicate that effects other than plasmon resonances are important in SERS. Brolo et al. examined the potential dependence of the anti-Stokes/Stokes ratio on a silver electrode and the importance of charge-transfer contributions to the enhancements. Their potential excitation profiles are quite similar to those used previously by us (I) to test the Herzberg-Teller influences on the charge-transfer contributions. From these observations, it is clear that the charge-transfer mechanism must make important contributions to the single-particle enhancement factor. Michaels et al. suggested that the dipolar plasmon resonance $P(\omega)$ as well as its sideband $P(\omega - \omega_{vb})$, created by a strong interaction with the chemisorbed molecular vibration $(\omega_{vb})$, are strongly coupled to the molecule by electron exchange, resulting in an enormous effective cross section.

Note also that these single-molecule experiments suggest the possibility that a large part of the normally observed SERS enhancement can be explained by a relatively smaller number of molecules (measured by $10^6/10^{14}$ or $10^{-8}$ fewer molecules). These molecules are presumed to be located at a special "hot spot" between two nanoparticles or perhaps some other special site, with the rest of the molecules in the sample contributing little if anything to the enhancement. In fact, this possibility was suggested long ago by experiments using underpotential deposition of Pb and Tl (Refs. 27–29) to poison certain sites on the silver surface. A mere underpotential surface coverage of 3% was sufficient to completely quench the SERS signal. In addition, Hildebrandt and Stockburger showed that for rhodamine 6G adsorbed on silver colloid, anion activated specific sites are formed at extremely low surface coverage, and that these sites are responsible for a large portion of the enhancement.

(2) SERS measurements have been extended to systems in which plasmon resonance contributions should be small. Campion and co-workers have found an enhancement on an atomically flat Cu surface. In another study, on silver nanoparticles, enhancement has been observed at 1064 nm, far from the silver plasmon resonance. Single-molecule anti-Stokes Raman signals have been observed from silver clusters too small (Ag$_n$) to support a plasmon. Enhancements have also been observed by Tian and co-workers on many metals other than the noble metals such as transition elements. SERS enhancements up to $10^4$ have recently been observed on semiconductor quantum dots, both on molecular beam epitaxial (MBE) grown surfaces such as InAs/GaAs (Ref. 39) and CdSe/CdMgZnSe, as well as in colloidal suspensions such as CdS, ZnS, ZnO, and CdTe. These results are surprising in that for semiconductors, plasmon resonances lie far in the infrared, so that there is no possibility of plasmon contributions in the visible region. Such systems are of considerable interest since when the particle diameter is less than the exciton Bohr radius, the conduction band shows quantum effects, replacing a continuum with narrow bands resembling atomic energy levels. Both the bandwidth and the energy levels are functions of the particle diameter, which may be controlled by the synthetic process. This quantum confinement can be further modified by a capping layer of a substance with a band gap larger than the quantum dot. This holds out the prospect of tuning a quantum dot resonance by controlling either particle size or capping layer properties. Improvements in synthetic tools also enable increasing the degree of monodispersity in these systems, allowing reduction of the inhomogeneity in the observed optical bandwidths. All these effects are of importance for device manufacture, but we shall also see that they may enable us to improve our understanding of the SERS enhancement in these systems.

(3) There have been considerable advances in our ability to determine accurate molecular properties using quantum mechanical calculations. Of special interest is the ad-
vent of convenient and fast density functional theory (DFT) calculations. We may now routinely predict the IR and Raman spectrum of rather large molecules with DFT, enabling accurate and reliable normal mode assignments. This development has also had its impact on SERS. Schatz and co-workers, for example, have studied a pyridine-Ag_{20} cluster,\textsuperscript{45} as well as a pyridine molecule at the junction between two Ag_{20} clusters.\textsuperscript{46} These calculations enable the authors to separate clearly the various contributions to the SERS enhancement and estimate the relative contribution of each. Calculations by Zhou et al.\textsuperscript{47} on the interaction of CO with small silver particles also show indications of the importance of charge transfer on binding and C=O vibrational frequencies.

Another line of research, which has had a large impact on our understanding of Raman spectroscopy, is the development of time-dependent theories of spectroscopy. These techniques have been pioneered by Heller and co-workers,\textsuperscript{48–51} and Lee\textsuperscript{52,53} who have recast the Raman theory described by Kramers, Heisenberg, and Dirac\textsuperscript{54,55} (KHD) in terms of the time evolution of wave packets. Such studies have led to considerable insight into the nature of the Raman process and have further simplified the calculations, showing that the rather impractical sum over all molecular states inherent in the KHD approach could be replaced by reference to a single excited state. It has the further advantage of allowing density functional calculations, which had been restricted to ground state properties, to be extended to excited states. This has been incorporated into DFT calculation packages (Amsterdam density functional, ADF).\textsuperscript{56,57} It is these developments which enabled the calculations of Schatz and co-workers described in the previous paragraph.

With these considerations in mind, we decided to revisit our previous work on the Herzberg-Teller contributions to the CT theory of SERS (I). In the next section, we provide a brief review of the earlier work and introduce some of the notation to be used. In the following section, we apply the principles of time-dependent theory to our previous results, casting it in a form suitable for modern time-dependent density functional theory calculations. Results are obtained for molecular adsorption on nanoparticles in both the strong confinement limit and the weak confinement limit. We also examine more carefully the Herzberg-Teller vibronic coupling term and show the connection to electron-phonon (polaron) interactions in solid-state theory. We further interpret the implications of the results for SERS in metallic systems and for semiconductors.

\textbf{REVIEW OF CHARGE-TRANSFER THEORY OF SERS (I)}

The intensity of a Raman transition may be obtained from the polarizability tensor by the expression

\[ I = [8\pi(\omega \pm \omega_{12})^4|I_L|^2/9e^4] \sum \alpha_{\nu\nu}^2, \]

where \( I_L \) is the incident laser intensity at \( \omega \), and \( \omega_{12} \) is a molecular transition frequency between states \( I \) and \( I' \) (presumably two different vibronic levels of the ground electronic state \( I_L \)). Using second-order perturbation theory, it may be shown that

\[ \alpha_{\nu\nu} = \sum_{K=1}^{N} \left\{ \langle I|M_{\nu}\rangle[K] \langle K|M_{\nu}\rangle[I'] \right\} E_I - E_K - \hbar \omega, \]

(2)

where \( K \) represents all the other states of the molecule, \( \mu \) is the dipole moment operator, and \( \sigma \) and \( \rho \) are the scattered and incident polarization directions. This is the standard KHD expression and, using the zero-order Born-Oppenheimer approximation, we may write all the vibronic states \( (I, I', K) \) as products of the electronic and vibrational wave functions: \( |I\rangle = |I_e\rangle |I_v\rangle \), \( |I'\rangle = |I^\prime_e\rangle |I^\prime_v\rangle \), and \( |K\rangle = |K_e\rangle |K_v\rangle \), where the subscript \( e \) indicates a purely electronic state, and lower case letters represent vibrational functions. Albrecht\textsuperscript{41} utilized the Herzberg-Teller mixing of vibronic functions,

\[ |K\rangle = |K_e\rangle + \sum \lambda_{KM} |M_{\nu}\rangle, \]

(3)

\[ \lambda_{KM} = \hbar h_{KM} (E_{K}^{0} - E_{M}^{0}), \]

(4)

\[ h_{KM} = \langle K_e\rangle \langle \partial V_{CNC} \partial \mathcal{Q}_{0} \rangle |M_{\nu}\rangle, \]

(5)

to derive an expression for \( \alpha_{\nu\nu} \) which involves three terms, usually called A, B, and C. \( V_{CNC} \) is the electron-nuclear attraction term in the Hamiltonian, evaluated at the equilibrium nuclear positions (0). For the purely electronic transition moment between states, we write

\[ M_{\nu}^{c} = (\langle I_{e}| \mu_{\nu}| I_{e} \rangle), \quad \mu_{M}^{c} = (\langle M_{\nu}| \mu_{\nu}| I_{e} \rangle), \quad \mu_{M}^{c} = (\langle K_{e}| \mu_{\nu}| M_{\nu} \rangle). \]

In (I) we assumed that the molecule was bound to the metal surface through a weak covalent bond and that the molecule-metal system may be considered together for purposes of calculations. Thus the charge-transfer states obtained by molecule-to-metal (or metal-to-molecule) charge transfer must be included in the A, B, and C terms derived by Albrecht. In the original theory of Albrecht, the states labeled \( M \) run over all the states of the molecule-metal system. We instead restrict ourselves to the molecular ground state \( I_e \) and the first excited state \( K_e \) (to which an allowed transition from the ground state exists), while \( M \) denotes only the charge-transfer (molecule-metal) states.

We should point out that there are actually two types of molecule-metal coupling, which contribute to the charge-transfer part of the enhancement (sometimes called the chemical enhancement). The first is due to the weak chemical bond between the molecule and metal. This contributes by increasing the effective volume of the molecule, increasing the ground state polarizability. The second is due to second-order breakdowns in the Born-Oppenheimer approximation via the Herzberg-Teller coupling, and it is this contribution we are mainly concerned with here. When the molecule is not coupled to the metal, charge-transfer transitions between the molecule and metal are forbidden. On coupling, charge-transfer intensity is borrowed from the allowed mo-
lular transition \( \mu_{KM} \) by the molecule-to-metal transition \( \mu_{IM} \) through the Herzberg-Teller coupling term \( h_{KM} \) or by the metal-to-molecule transition \( \mu_{MK} \) through the Herzberg-
Teller coupling term \( h_{IM} \). We then obtain analogs of the Albrecht \( A, B, \) and \( C \) terms for the molecular-metal system. These are two \( A \) terms, \( A_I \) and \( A_K \), \( A_I \) and \( B \) correspond to molecule-to-molecule transitions, while \( A_I \) and \( C \) correspond to metal-to-molecule transitions. The full expressions for each term have been given,\textsuperscript{10,58} but since both pairs of terms are symmetric and may be derived from one another by a simple interchange of letters, for brevity we will only present the molecule-to-metal equations here.

\[
A_I = (2\hbar) \sum_M \mu_{M}^\alpha \mu_{M}^\beta \delta(\mathbf{k}) \delta(\mathbf{f}) \frac{\omega_{MI} + \omega_f}{(\omega_{MI} + \omega_f)^2 - \omega_f^2}, \tag{6}
\]

\[
B = - \frac{1}{2 \hbar^2} \sum_{K+1} \sum_{M<K} \left[ \mu_{M}^\alpha \mu_{M}^\beta + \mu_{M}^\gamma \mu_{M}^\gamma \right] \frac{(\omega_{KI} + \omega_{MI} + \omega_f) \hbar_{KM} \delta(\mathbf{k})}{(\omega_{KI}^2 - \omega_f^2) (\omega_{MI}^2 - \omega_f^2)} \tag{7}
\]

We then replaced the sum over charge-transfer states \( M \) in these terms with an integral over \( \omega_{MI} \). We used a step function at the Fermi energy \( \omega_f \) and a constant density of states. This had the effect of replacing every \( \omega_{MI} \) in the above equations with \( \omega_f \).

The results of Eqs. (6) and (7) now may easily be interpreted. We focus on the Fermi energy rather than the band-edge resonances here since they are of interest for understanding the potential dependence of SERS. \( A_I \) is the analog of the resonance Raman term in the normal Raman theory. It predicts that at resonance only totally symmetric transitions will be observed and overtones should be routinely observed. The denominator has a potential-dependent resonance at \( \omega_f + \omega = \omega_f \), but there are no Herzberg-Teller contributions. Since these predictions are not in accord with observations (except where there is already a molecular resonance Raman spectrum, sometimes denoted SERRS), we conclude that this term contributes at best marginally to the SERS effect. Any contribution from the \( A_I \) term is solely to the totally symmetric modes.

The \( B \) (and \( C \)) term is the most interesting. It is unusual in that the numerator looks like the normal nonresonant \( (B \) and \( C \)) term derived by Albrecht, but the denominator indicates a resonance. The numerator contains the factor \( \delta(\mathbf{k}) \delta(\mathbf{f}) \), which indicates the existence of a nonresonant transition, as well as the absence of overtones in the harmonic approximation (i.e., the harmonic oscillator selection rules \( f = \pm 1 \) hold). However, unlike the normal Raman \( B \) term, it contains a denominator, which is resonant under the assumptions made here. It predicts a resonance at \( \omega = \omega_f \) and necessarily includes the Herzberg-Teller coupling. Note that this resonance comes about because we have explicitly included charge-transfer states in the derivation. This derivation predicts the correct linear relationship between the excitation frequency \( \omega \) and the applied potential. We may scan the resonance by varying either the excitation frequency or the applied potential.

The expression for \( B \) then predicts a negative slope for \( V_{\text{max}} \) (the applied voltage at resonance) against \( \omega \) for molecule-to-metal transfer, and the \( C \) term predicts the opposite slope for metal-to-molecule transfer (\( \hbar \omega = \hbar \omega_f = E_f(0) \pm \omega V_{\text{max}} \)). This is in accord with observations.

We also obtained, as a result of integration over the density of states, a resonance line shape, which provided an excellent fit to the observed Raman intensity profiles. \( \Gamma \) was inserted as the homogeneous linewidth caused by the finite lifetime of the excited charge-transfer state. It is an easy matter to show that with this line shape,\textsuperscript{10,60} the Raman polarization scales as \( \Gamma^{-2} \), and therefore the enhancement factor scales as \( \Gamma^{-4} \). We feel that this point was not made sufficiently clear in the previous work (I), but we would like to emphasize it here. Note the extreme sensitivity of the enhancement factor to linewidth. Since \( \Gamma \) represents the homogeneous linewidth, if the observed inhomogeneous linewidth is used, we are at best underestimating the CT contributions to the enhancement factor. Any careful determination of the enhancement factor requires an accurate value for \( \Gamma \).

**TIME-DEPENDENT PICTURE OF SERS CHARGE TRANSFER**

We follow the procedure outlined by Lee and Heller,\textsuperscript{48} who showed that the Raman scattering intensity can be obtained by the second order, time-dependent amplitude, defined as

\[
(i \hbar)^2 \mathcal{C}_{i\rightarrow f}(2) = \int_0^T ds e^{i(\omega - \omega_f)s} f(s, \omega), \tag{8}
\]

where we have included the Herzberg-Teller contributions as well as the sum over charge-transfer states explicitly.

\[
f(s, \omega) = \sum_M \int_0^s ds' e^{i(\omega - \omega_f)s'} |\mu_{MI}| e^{-i(H_M - \omega_f) s'} \langle \mathbf{K} \rangle e^{iH_{KM}M} \delta(\mathbf{k}) \delta(\mathbf{f}) |\mu_{MI}| \langle \mathbf{K} \rangle. \tag{9}
\]

\( H_M \) is the excited state Hamiltonian. We have used the molecule-to-metal expression for \( B \), but it is an easy matter to extend this to the \( C \) term. We will not include this for brevity. We have made a few adjustments to the notation to more readily utilize the previous derivation (I). The relationship between the notation of Lee and ours is

\[
|\phi_i \rangle = \mu_{IM} |\chi_i \rangle, \tag{10}
\]

\[
|\phi_i \rangle = |\chi_i \rangle |\mu_{MI} \rangle \tag{11}
\]

We should now discuss in more detail the assumptions concerning the molecule-metal interaction. We assume that the Hamiltonian governing the normal vibrations in the free molecule may be written as \( H_{\text{mol}} \), while that for the metal surface phonon modes may be written as \( H_{\text{ph}} \). The molecule is adsorbed to the surface through a weak covalent bond, which couples the molecular modes with the metal modes. We assume that this coupling may be expressed by an interaction Hamiltonian \( H_{\text{int}} \), which is a function of the molecule-metal bond distance and force constant. The total vibrational Hamiltonian for the molecule-metal system is then

\[
H = H_{\text{mol}} + H_{\text{ph}} + H_{\text{int}}. \tag{12}
\]
If the coupling is weak, we expect the zero-order molecule and metal modes to be only slightly perturbed. The largest effect on the molecular modes would be expected to be those modes directly linked to the molecule-metal bond. These have been observed in the spectral region around 200–240 cm\(^{-1}\) for molecules such as pyridine on silver.\(^{61}\) It is further assumed that the surface phonon modes will also be somewhat perturbed. Although these modes are acoustic in metals, and therefore expected to appear at very low frequencies, sizable state densities as high as 180–200 cm\(^{-1}\) have been identified in silver nanoparticles or thin films both theoretically\(^{62}\) as well as experimentally.\(^{63}\) For many semiconductors there are optical phonon modes with sufficient energy to interact with the molecule-metal vibration. In any case a complete normal-mode analysis would involve detailed knowledge of the surface features, which is not feasible at this time. However, we will assume that this problem can, in principle, be solved and that a new set of normal modes may be obtained for the molecule-metal system using the correct form of the vibrational Hamiltonian above. It is assumed that the resulting molecule-metal normal modes are represented by the \(Q\) term above. Although we must, in fact, sum over all the modes, for simplicity in an already complex notation, we will just use one of the \(Q\) modes.

With these considerations in mind, we may now examine the Herzberg-Teller coupling term \(h_{KM}\). As defined in Eq. (5), it represents the coupling of the molecular state \(K\) with the charge-transfer states \(M\) through \(\partial V_{CS}/\partial Q\), which represents the change in the electronic energy with the vibrational normal mode \(Q\). The complete electronic Hamiltonian includes terms in the electron kinetic energy, the electron-electron repulsion, and the electron-nuclear attraction, but only the latter involves the nuclear positions. So, the term \(\partial V_{CS}/\partial Q\) involves the effect on the energy \(\varepsilon_{\text{def}}\) of distortions of the nuclear lattice. We make the further assumption that this deformation energy does not vary much with the charge-transfer state since for adjacent states the electronic wave function should be almost the same. The term \(\langle K|\partial V_{CS}/\partial Q|0\rangle M\) may be approximated by \(\delta \varepsilon_{\text{def}}/\Delta\), where \(\Delta\) is the lattice dilation.\(^{64}\)

\[
h_{KM} = \langle K|\partial V_{CS}/\partial Q|0\rangle M = \delta \varepsilon_{\text{def}}/\Delta. \tag{13}
\]

This term is often treated as resulting from scattering between electrons and lattice phonons. It usually involves only the longitudinal phonon modes and often shows up as an increase in the effective mass of the electron. The electron-phonon interaction is quite different in metals than in semiconductors. In metals, where the conduction band is partly filled, electrons move freely, and due to screening by other electrons, the phonon coupling tends to be weak. It shows up in increased resistivity\(^{65}\) and superconductivity\(^{66}\) as well as in the effects on the specific heat.\(^{67}\) In semiconductors, the interaction is often somewhat larger, appearing as a polaron-coupling term. With ionic crystals, where optical phonons are present, the polaron coupling is even larger. We will discuss these various effects in the following sections.

We are interested in examining two limits. In the first, we assume a strong confinement of our nanoparticles. In this case the exciton Bohr radius is larger than the particle radius, and we expect that the resonant charge-transfer state of the nanoparticle may be taken to be a discrete state, somewhat separate from adjacent states. Then, we need not require the sum over \(M\) in Eq. (9). We then have

\[
f(s,\omega) = \frac{\delta \varepsilon_{\text{def}}}{\Delta} \int_0^s d\nu e^{i\nu} \langle f|\mu_{KR}Q\langle M|e^{-i(\omega_M-\nu)\mu}|I_f\rangle i\rangle,
\]

and we may now recognize

\[
\langle M|e^{-i\omega_M\nu}\rangle = \langle M|e^{-i\omega_M\nu},
\]

so that

\[
f(s,\omega) = \frac{\delta \varepsilon_{\text{def}}}{\Delta} \int_0^s d\nu e^{i\nu} \langle f|\mu_{KR}Q\langle M|e^{-i(\omega_M-\nu)\mu}|I_f\rangle i\rangle. \tag{16}
\]

We have also further simplified the notation by measuring all frequencies from the ground state of the molecule, so that \(\omega_{MI} = \omega_M\), etc., and for the same reason we have suppressed the \(\sigma\rho\) subscripts in \(\mu\). In the spirit of Lee and Heller,\(^{48}\) it is now convenient to redefine the initial and final vibrational wave functions [see Eqs. (10) and (11)] as

\[
\langle f|\mu_{KR}Q = \langle f|I_f, \tag{10'}
\]

\[
|\mu_M|i\rangle, \tag{11'}
\]

\[
f(s,\omega) = \frac{\delta \varepsilon_{\text{def}}}{\Delta} \int_0^s d\nu e^{i\nu} \sum_M \langle f|\mu_{KR}Q\langle M|e^{-i(\omega_M-\nu)\mu}|I_f\rangle i\rangle. \tag{18}
\]

Replacing the sum over \(M\) with an integral over the metal density of states\(^{68,69}\) at the Fermi level,

\[
\rho_F = \int_{-\infty}^{\infty} d\omega_M \delta(\omega_M - \omega_F). \tag{19}
\]

We then have

\[
f(s,\omega) = \frac{\delta \varepsilon_{\text{def}}}{\Delta} \int_0^s d\nu e^{i\nu}\times \langle f|\mu_{KR}Q\int_{-\infty}^{\infty} d\omega_M \delta(\omega_M - \omega_F) e^{-i(\omega_M-\nu)\mu}|\mu_M|\rangle i\rangle. \tag{20}
\]

Using Eqs. (10'), (11'), and (15), we then obtain an expression for \(f(s,\omega)\) as follows:
\[ f(s, \omega) = \frac{\delta e_{\text{def}}}{\Delta} \rho_F \int_0^\tau \text{d}v \langle \phi_J' [ e^{-\text{i}(H_J - \hbar \omega - i \Gamma) t} ] \phi_J' \rangle, \]  

(21)

where \( \rho_F \) is the density of states at the Fermi energy. For Ag \( \rho_F \) is \( 0.24/\text{atom/eV}^7, \) for Au it is \( 0.27/\text{atom/eV}^7, \) while for Pt it is \( 2.20/\text{atom/eV}^8. \) Equations (21) and (17) are the results we are seeking. The operator in square brackets in each expression is the time evolution operator, which operates on the initial state wave function \( \phi_J' \), causing it to evolve in time, using the excited state energy surface (either \( H_M \) or \( H_F \)). The resulting time-evolved function is then projected on to the final wave function \( \langle \phi_J' \rangle \), and the resultant expression integrated over \( \nu \) gives \( f(s, \omega) \). For Raman spectroscopy, we take the short time approximation, so that the time variable \( s \) is chosen to be small.\(^48\) This is then inserted into Eq. (8), where we allow \( T \to \infty \) to take the half-Fourier transform, giving the Raman amplitude. The initial and final functions have been modified by the Herzberg-Teller coupling [see Eqs. (10) and (11)]. Note especially the factor \( Q \) in the final wave function \( \langle \phi_J' \rangle \). This ensures that the correct harmonic oscillator selection rules are maintained for the final expression. This, in addition to the predicted resonance Raman intensity at \( \omega = \omega_M \) or \( \omega_F \), is consistent with the previous results obtained by the application of the static theory of Raman spectroscopy (1).

### APPLICATIONS TO METAL NANOPARTICLES

Note that Eq. (21) indicates a resonance at the \( \omega = \omega_F \) Fermi energy. We are interested in this resonance for this is where most of the SERS observations have been made on electrode surfaces. It displays the same properties as found in the previous work in that we may scan either the potential or the excitation frequency through the resonance, and the signs of the slopes are determined by the direction of charge transfer. Thus, the time-dependent expression shows the same properties as the static approach of the previous work. Even though it has the numerator similar to the usually nonresonant \( B \) (and \( C \)) terms in the Herzberg-Teller expansion, it also displays a resonance at the Fermi level. This resonance is the source of the charge-transfer contributions to SERS in metals.

We have replaced the Herzberg-Teller coupling term \( \langle \partial V_{en}/\partial Q \rangle_0 \) with a measure of the effect of lattice deformation on the electron energies. For a metal, \( \delta e_{\text{def}} \) is \( C_1 \Delta \). For a free electron gas, \( C_1 = -2/3e_F \), where \( e_F \) is the Fermi energy. When phonon interactions are considered, there are several approaches that have been suggested. For a phonon-electron interaction we may introduce a coupling parameter \( \lambda \) such that \( C_1 = -2/3e_F \lambda \).

One approach has been recommended by Bardeen\(^22,67\) in which the deformation is shown to be

\[ \langle K | \partial V_{en}/\partial Q | M \rangle = \delta e_{\text{def}} \Delta \Delta = -\frac{2}{3}e_F(1 - \gamma_{\text{free}}/\gamma)/\Delta. \]  

(22)

Here, the free electron gas expression has been modified by a specific heat factor\(^23\) \( \lambda = (1 - \gamma_{\text{free}}/\gamma) \) which may be determined experimentally\(^65\) (\( \gamma_{\text{free}} \) is the specific heat for a free electron gas, while \( \gamma \) is the experimental specific heat). For copper, silver, and gold \( \gamma/\gamma_{\text{free}} \) is 1.44, 1.02, and 1.16, respectively.\(^67\) Note that despite the fact that \( e_F \) may be large [it is 5.49 eV in Ag (Ref. 69)], the specific heat factor tends to be small.

More recently, angle-resolved photoemission has found considerable use in determining more reliable values for the magnitude of the electron-phonon interaction in metals.\(^74,75\)

In these experiments, the coupling parameter \( \lambda \) is given by

\[ \lambda = \frac{1}{2\pi k_B} \frac{d\Delta E}{dT}. \]  

(23)

Here, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and \( \Delta E \) is the width of the photoemission band. Thus, measures of the bandwidth as a function of temperature yield values for \( \lambda \). The bulk value for \( \lambda \) in Ag is 0.29. However, in thin Ag layers it is found that this parameter is very large for extremely thin layers but decreases to the bulk value as 1/\( N \), where \( N \) is the number of Ag layers.\(^76\) These experiments suggest that quantum confinement as well as binding energy play an important role in determining the electron-phonon coupling strength. For states near the Fermi level it has been found useful to measure the deviation of the band dispersion from that of the noninteracting system.\(^77,78\) In this region, the electron mass is given by \( (1 + \lambda) \) times the effective mass \( (m^*) \). For the Be metal\(^78\) it is found that \( \lambda = 1.18 \), while for Cu it is 0.14. Comprehensive tables of the values of \( \lambda \) may be found in Ref. 73.

Several polaronlike states near the Fermi level have been identified in silver-molecule interfaces by ultraviolet photoelectron spectroscopy. Two states at \( \approx 1.6 \) and \( \approx 0.6 \) eV are seen below the Fermi level and are presumed to result from a metal-to-molecule charge transfer.

As discussed in the Introduction and the review of previous work, since the resulting enhancement factor at resonance is proportional to the square of the polarizability, it is proportional to \( \Gamma^{-4} \). This extreme sensitivity to the value of \( \Gamma \) is important in assessing the magnitude of charge-transfer contributions to SERS. In (I) we merely used the observed linewidth of the potential-dependent excitation profile (0.3 eV). This led to enhancement factors estimated to be approximately \( 10^{-10} \). However, as was not emphasized at the time, there are strong inhomogeneous contributions to the observed profile width, and \( \Gamma \) is the homogeneous width of the charge-transfer transition. Thus, our previously estimated enhancement factor should be considered a lower limit. In fact, the correct value for \( \Gamma \) is quite difficult to determine in these experiments, and assumptions are often made in order to fit experimental data without detailed determination of the inhomogeneous contributions. Thus, \( \Gamma \) is almost always overestimated. Note that just a factor of 2 narrowing of the measure of \( \Gamma \) will result in an order of magnitude increase in the estimated enhancement factor. In their DFT calculations on \( \text{Ag}_{20} \) nanoparticles, Zhao \textit{et al.}\(^43\) used a value of about 0.1 eV (once again just to obtain a good fit to the observed data) and estimated the charge-transfer contribution to the enhancement to be about \( 10^3 \). This is consistent with the above discussion.

Some sources of inhomogeneous broadening in SERS are most likely polydispersity in particle size, the possibility
of varying surface sites for molecular attachment, and possibly other factors such as solvent effects, counterion effects, and, on the electrode, the influence of surface charge on the electrical double layer. Some of these sources can be controlled. For example, it is becoming increasingly common to produce nanoparticles with a uniform particle size. Of course, the ultimate in monodispersity is the single-particle experiment. A careful excitation profile in these experiments would be of considerable value in obtaining accurate estimates of $\Gamma$, leading to better estimates of the degree to which charge-transfer effects contribute to surface enhancement of the Raman signal.

APPLICABLE TO SEMICONDUCTOR NANOPARTICLE

Originally, it was not thought possible to extend SERS to semiconductor surfaces since the plasmon resonances in such systems are far in the infrared and therefore cannot contribute to any observed enhancement. However, recently, there have been several reports of SERS in semiconductor nanoparticles (see the Introduction), and it is likely that some sort of charge-transfer effect is important in these systems. Indeed, the enhancements observed are small ($10^2 - 10^4$), often on the order of those expected for charge-transfer contributions. Note that one of the reasons that we might expect measurable CT enhancements in semiconductors is the value of the polaron-coupling constant, which tends to be larger in semiconductors than in metals. The examination of the coupling of electrons to longitudinal optical phonons was pioneered by Huang and Rhys and later expanded by Duke and Mahan. For semiconductors, polaron interaction is usually expressed as phonon-electron scattering, and this coupling takes the form of an increase in the effective mass ($m^*$) of the electron due to the slowing down of the electrons from the drag of the phonons,

$$m_{\text{pol}} = m^* \left(1 + \frac{1}{\alpha} \right),$$

(24)

where $\alpha$ is the polaron-coupling constant defined as

$$\frac{1}{2} \alpha = \frac{\delta \epsilon_{\text{def}}}{\hbar \omega_{\text{ph}}}.\quad (25)$$

Here, $\omega_{\text{ph}}$ is the longitudinal phonon frequency. For semiconductors we can write

$$\delta \epsilon_{\text{def}}/\Delta = - \alpha \hbar \omega_{\text{ph}}/(2 \Delta).\quad (26)$$

This indicates that the enhancement factor [which is proportional to $(\delta \epsilon_{\text{def}}/\Delta)^2$] for a semiconductor quantum dot should be proportional to the square of the polaron-coupling constant $\alpha$. Since there are no optical phonon modes in covalent semiconductors such as Si or Ge, $\alpha$ is usually small (0.04 for Ge). No surface enhancement has been observed for these species despite several attempts. For ionic crystals, with optical phonon modes, the coupling constant can be much larger. For example, $\alpha$ is 0.85 for ZnO, which has shown an enhancement factor of $10^3$. In CdS (Ref. 41) $\alpha$ is 0.527 and an enhancement of $10^2$ has been observed. It should be pointed out that other factors, such as $\omega_{\text{ph}}$ or the ratio of the exciton Bohr radius to the quantum dot radius, will be important and possibly counter the trends in polaron coupling.

Moreover, relatively monodisperse samples of semiconductor quantum dots are becoming increasingly routine to synthesize. This should reduce at least some of the inhomogeneous contributions to the enhancement. In addition, when the particle radius is less than the exciton Bohr radius (11.6 nm in GaAs and 46.0 nm in PbS), quantum confinement effects further narrow the linewidths in the conduction band. In metals, the charge-transfer effect can be observed clearly by obtaining the resonance Raman excitation profile scanning either the excitation wavelength or the Fermi level through the applied potential. In semiconductor quantum dots, however, the Fermi level is somewhat below the conduction band, and the levels are unfilled, except by photoinduced charge transfer. However, for quantum dots, where quantum size effects are important, the Raman excitation profile can be scanned either optically or by varying the particle size. To the extent that the bands are narrow enough (and the sample is sufficiently monodisperse) to be homogeneous and distinct from adjacent bands, we can use the simpler equation [Eq. (17)] for time dependence. This raises the possibility that in a carefully controlled experiment, rather large enhancements may be achieved. Indeed, using isolated self-assembled quantum dots of AlInAs, Petroff and Medeiros-Ribeiro found photoluminescence linewidths on the order of 0.2 meV, as compared with 40–60 meV for a broad array of similar quantum dots. This illustrates the degree to which a truly monodisperse sample can result in considerable narrowing of the observed linewidth, especially in the strong confinement case. Note that in the case of charge transfer, there should be a similar narrowing of the linewidth since the level to which transfer from the molecule takes place is the same as that responsible for photoluminescence. If there were a concomitant narrowing of the linewidth, then we would expect the enhancement factor due to charge transfer to be increased to about $10^{12}$ per molecule.

CONCLUSIONS

We have revised the Herzberg-Teller theory of charge-transfer contributions to SERS. The static KHD framework has been recast in terms of the time-dependent picture of Raman spectroscopy. The Herzberg-Teller contributions to the charge-transfer effect in SERS show a resonance at the molecule-to-metal (B term) or metal-to-molecule transition (C term) while retaining the selection rules associated with normal Raman spectroscopy (i.e., harmonic oscillator, as opposed to Franck-Condon overlaps). The enhancement factor scales as $\Gamma^{-4}$, where $\Gamma$ is the homogeneous linewidth of the charge-transfer transition. The magnitude of the enhancement is therefore extremely sensitive to the linewidth measurement. We have identified the Herzberg-Teller coupling constant with the electron-phonon (polaron) interaction and have derived an expression for the time evolution operator in both the strong and weak confinement limits. The implications of our result are discussed for metal as well as semiconductor nanoparticles.
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