Charge-transfer theory of surface enhanced Raman spectroscopy: Herzberg–Teller contributions

John R. Lombardi, Ronald L. Birke, Tianhong Lu, and Jia Xu
Department of Chemistry, City College of New York, New York, New York 10031

(Received 13 August 1985; accepted 31 December 1985)

A comprehensive development of the charge-transfer theory of surface enhanced Raman scattering (SERS) is presented. We incorporate the Herzberg–Teller mixing of zero-order Born–Oppenheimer electronic states by means of vibronic interaction terms in the Hamiltonian. This is similar to the theory of Tang and Albrecht\textsuperscript{12} except that we include metal states as part of a molecule–metal system. When this is done we may no longer discard a term involving mixing of ground-state vibrations. The theory is comprehensive in that both molecule-to-metal and metal-to-molecule transfer is considered. Furthermore, both Franck–Condon and Herzberg–Teller contributions to the intensity are obtained. The former, however, contribute only to the intensity of totally symmetric vibrations, while the latter contribute to nontotally symmetric vibrations as well. Since overtones are observed in SERS only weakly if at all, the Herzberg–Teller terms are most consistent with experimental findings. The resulting formulas may be interpreted as a type of resonance Raman effect in which the intensity for the charge transfer transitions is borrowed from an allowed molecular transition. We may also carry out the sum over metal states. This procedure predicts a logarithmic resonance at the Fermi level of the metal. We thus predict intensity vs voltage profiles such as $I \propto | \ln(\omega_{\omega} - \omega + i\Gamma) |^2$ which fits the experimental curves quite well.

I. INTRODUCTION

It is now widely accepted that two separate mechanisms must be involved to explain the phenomenon of surface enhanced Raman spectroscopy (SERS).\textsuperscript{1–3} The electrodynamic model involves small surface irregularities which allow optical frequency surface plasmon resonances resulting in strong local enhancement of the electric field both of incoming and scattered radiation.\textsuperscript{4} This model does not require specific chemical bonds between adsorbate and metal, and explains among other things the observation of enhancement at some distance from the metal surface, as well as the angular dependence of the enhancement with respect to the direction of incoming radiation. Realistic electromagnetic enhancement ratios of up to $10^4$ can be explained by this mechanism.\textsuperscript{5}

However, early in the research into this phenomenon, it was realized that certain types of molecules displayed enhancement ratios still greater by factors of 10 to 1000. These were molecules such as pyridine or piperidine, which contained a lone pair of electrons available for bonding with the surface. Further, when observed on an electrode surface these molecules show a resonance shaped intensity profile as a function of applied potential. Since the observed Raman scattering cross sections were on the order of resonance Raman spectra, while no known molecular transition existed in that spectral region, it was speculated that when considering the molecule and metal system as a whole, charge transfer transitions were possible both in the ground and excited states which could explain the effect. It was suggested that the Fermi level of the metal lay between the molecular ground state and one or more of the excited states of the molecule. It was assumed that transitions from the Fermi level to the excited state or from the ground state to the Fermi level were involved. This model, usually called the charge-transfer model was first suggested by researchers in this laboratory approximately at the same time as several others.\textsuperscript{6,7} These ideas were bolstered by the observations of Demuth and Sanda\textsuperscript{8} of low energy-transfer bands in pyridine and pyrazine on silver by high resolution electron energy loss experiments. For pyridine, an affinity level has definitively been identified by inverse photoemission at 2.6 eV above the Fermi level by Otto, Frank, and Reihl.\textsuperscript{9}

Not long ago, Furtak et al.\textsuperscript{10,11} found that in an electrochemical cell, the voltage at which the intensity reached a maximum ($V_{\text{MAX}}$) varied linearly with the excitation frequency ($\omega$); similar experiments were done by Otto and co-workers on pyridine\textsuperscript{12,13} and CN\textsuperscript{–}.\textsuperscript{14} At about the same time, we showed this effect to exist for a variety of molecules.\textsuperscript{15} We showed further that the molecules could be divided into two classes; those for which $V_{\text{MAX}}$ had a positive slope with $\omega$ and those for which the slope was negative. We also showed that this effect could be correlated with the electron withdrawing ability of the ground or excited electronic states of the molecules involved. These experiments together with others were taken as evidence for the existence of a charge-transfer mechanism to explain SERS. In fact two types of charge transfer could be envisioned. Molecule to metal transfer, in which an electron is transferred from the highest occupied molecular orbital to the Fermi level of the metal was associated with the negative slope in $V_{\text{MAX}}$ vs $\omega$. Conversely positive slopes were associated with transitions in which an electron is transferred from the Fermi level of the metal to the lowest unoccupied orbital in the molecule.

There are, however, several other pertinent experimental observations which must be explained by any comprehensive theory.\textsuperscript{16} First, it is noted that even though the above interpretation of SERS as a type of resonance Raman transition through a charge-transfer transition can explain the observed intensity enhancement, it still must explain why overtones are observed only weakly, if at all in SERS even though they are predicted to be commonplace by the usual resonance Raman theory.\textsuperscript{17} Second, experimental depolariz-
tion ratios in SERS are all in the range 0.6 to 0.75 even for totally symmetric vibrations, at least some of which would be expected to the considerably lower. Third, a comprehensive theory would also explain the observed profile of intensity vs applied potential. This profile does not fit either Lorentzian or Gaussian shapes, and until now no theory has been able to predict correctly its shape.

We present here a theory of Raman intensities based on the Herzberg–Teller coupling mechanism following Albrecht. The theory includes both molecule-to-metal and metal-to-molecule charge transfer. A similar approach has been taken by Adrian, who introduced vibronic coupling into the quantum mechanical expression for the polarizability limiting his consideration only to metal-to-molecule charge transfer. When this is done, two types of terms arise, one dependent only on Franck–Condon overlap integrals, and a second dependent on intensity borrowing from nearby allowed transitions. This latter term is called the Herzberg–Teller term. Adrian then claims the latter term should be overwhelmed by the former and thereby ignores it. In considering the Franck–Condon term, Adrian obtains the correct dependence of \( V_{\text{MAX}} \) with excitation frequency, however we have found that his intensity vs voltage profile does not fit experimental profiles for reasonable values of the damping constants. His theory fails to explain adequately why overtones are observed only weakly, if at all in SERS. Furthermore the Franck–Condon term indicates that totally symmetric modes should be enhanced considerably more than nontotally symmetric modes. This is also contrary to observation. For example in piperidine we have observed that both \( a' \) and \( a'' \) modes are equally enhanced.

Metal-to-molecule transfer has also been considered by Lippitsch. He included vibronic coupling of the ground electronic state with states of the metal in an attempt to complement Adrian's theory. Unfortunately this theory also falls short in that it fails to predict any dependence of \( V_{\text{MAX}} \) on excitation frequency. In the theory presented here the difficulties of both Adrian's and Lippitsch's theories are resolved. In the next section we apply the Herzberg–Teller conditions to a molecule–metal system without the approximation that the lowest energy gap is large, thereby maintaining the \( C^* \) term. In Sec. III we apply the theory to predict the intensity vs voltage profile for SERS and fit the results to experimental plots.

II. CHARGE-TRANSFER THEORY OF SERS

The intensity of a Raman transition is related to the polarizability tensor by the expression

\[
I = \left[ 8\pi (\omega \pm \omega_{\text{FT}})^4 I_L / 9 e^4 \right] \sum |a_{\text{FT}}|^2 ,
\]

where \( I_L \) is the incident laser intensity at frequency \( \omega \), while \( \omega_{\text{FT}} \) is a molecular transition frequency between states \( I \) and \( F \). \( \rho \) and \( \sigma \) each represent the three spatial directions \( x,y,z \) involved in the tensor. Using second-order perturbation theory it may be shown that

\[
\begin{align*}
\alpha_{op} &= \sum_{k \neq \pm F} \left[ \frac{\langle I | \mu_\sigma | K \rangle \langle K | \mu_\rho | F \rangle}{E_K - E_I - \hbar \omega} \right. \\
&\quad \left. + \frac{\langle I | \mu_\rho | K \rangle \langle K | \mu_\sigma | F \rangle}{E_K - E_F + \hbar \omega} \right].
\end{align*}
\]

2

We consider states, \( I,K,F \) to be vibronic in that they are assumed to be products of purely electronic functions with purely nuclear functions.

\[
\Psi_I(q,Q) = \Theta_I(q;Q) \Phi_I(Q) ,
\]

where \( \Phi_I(Q) \) is the vibration of state \( I \) with \( i \) quanta of the normal mode \( Q \) excited. \( \Theta_I(q;Q) \) is the electronic part of the wave function for the state \( I \) which depends on the electronic coordinates \( q \) and parametrically on the nuclear coordinates \( Q \). In the following it will be more convenient to use for Eq. (3) the shorthand notation

\[
| I \rangle = | I_e \rangle | I_n \rangle ,
\]

where the subscript \( e \) indicates a purely electronic function. In this notation \( | K \rangle = | K_e \rangle | K_n \rangle \) represents the vibronic excited states and the final Raman transition is written \( | F \rangle = | I_n \rangle | f \rangle \). Following Tang and Albrecht we consider the electronic transition moment to be written

\[
\begin{align*}
\langle I | \mu | K \rangle &= \langle i | M_{IK}(Q) | k \rangle , \\
M_{IK}(Q) &= \langle I_e | \mu | K_e \rangle ,
\end{align*}
\]

which is assumed through Eq. (3) to be weakly dependent on the nuclear coordinates. It is the heart of Herzberg–Teller theory that even small vibrations may cause mixing of zero order Born–Oppenheimer states, allowing us to write

\[
| K_e \rangle = | K_e , 0 \rangle + \sum \lambda_{KM}(Q) | M_e , 0 \rangle ,
\]

\[
\lambda_{KM}(Q) = h_{KM}(Q) / (E_{K_e}^0 - E_{M_e}^0) ,
\]

\[
h_{KM}(Q) = \langle K_e , 0 | \partial H' / \partial Q | M_e , 0 \rangle ,
\]

where zeros refer to zero order Born–Oppenheimer states. The sum over \( M \) runs over all the excited states. \( h_{KM}(Q) \) are coupling matrix elements for terms in the Hamiltonian \( H' \) normally neglected in the Born–Oppenheimer approximation. They represent the degree to which a particular vibration \( Q \) can mix state \( M \) with state \( K \). Similarly for the ground state

\[
| I_e \rangle = | I_e , 0 \rangle + \sum \lambda_{IM}(Q) | M_e , 0 \rangle ,
\]

\[
\lambda_{IM}(Q) = h_{IM}(Q) / (E_{I_e}^0 - E_{M_e}^0) .
\]

Substituting into Eq. (2) we obtain

\[
\alpha_{op} = A + B + C ,
\]

\[
A = \sum_{k \neq \pm F} \sum_{k'} \left( M_{K_k}^* (Q_0) M_{F_{k'}}^* (Q_0) / h(\omega_{kF} - \omega) + M_{K_k}^* (Q_0) M_{F_{k'}}^* (Q_0) / h(\omega_{kF} + \omega) \right) \langle i | k \rangle \langle k | f \rangle ,
\]

\[
B = \sum_{k \neq \pm F} \langle I | \mu_\rho | K \rangle \langle K | \mu_\sigma | F \rangle / (E_K - E_F + \hbar \omega),
\]

\[
C = \sum_{k \neq \pm F} \langle I | \mu_\sigma | K \rangle \langle K | \mu_\rho | F \rangle / (E_K - E_I - \hbar \omega).
\]
This is the expression derived by Tang and Albrecht.\textsuperscript{17} At this point they observed that in most molecular systems the energy gap between the ground state and all the other states is much larger than the gaps between excited states, or that \(|\omega_{KM}| >> |\omega_{KM}|\). On this basis they ignore the term \(C\). However, we are considering a molecule-metal system in which this cannot be done. We shall assume that states \(|I, 0\rangle\) and \(|K, 0\rangle\) are ground and excited zero order Born-Oppenheimer states of the molecule, while the states \(|M\rangle\) are chosen to be the metal states, assumed to represent the conduction band. We assume that states \(|M\rangle\) may lie between \(|I\rangle\) and \(|K\rangle\) and therefore \(C\) cannot be discarded [see Fig. 1(a)]. We assume further that there is at least one state \(K\) to which there is an allowed transition from the ground state (i.e., \(M_{IK} \neq 0\)). Note that in the limit of large distance between molecule and metal we should expect that the matrix elements \(M_{IM\langle K\rangle}\) and \(M_{KM\langle K\rangle}\) representing molecule-to-metal and metal-to-molecule charge transfer transitions to be zero. However, when the molecule forms a weak chemical bond with the surface, we can no longer treat the molecule and metal as separate systems, and there is no reason to expect them to be zero. Furthermore the matrix elements \(h_{IM}\) and \(h_{KM}\) representing the vibronic mixing of metal states with ground and excited states are assumed to be nonzero in the combined system.

We now consider the situation in which the frequency of the exciting light is far from any molecular resonance \((\omega \ll \omega_{IM})\). Then in each of the Eqs. (10)–(12) we may remove the frequency dependent terms from the summation over all vibrational states \(k\). Utilizing the closure relation \(\Sigma \langle i | k \rangle \langle k | = 1 \) we see that in Eq. (10) \(\Sigma \langle i | k \rangle \langle k | f \rangle = \langle i | f \rangle\) which vanishes in the harmonic oscillator approximation unless \(i = f\). Thus far from a molecular resonance the term \(A\) contributes only to the Rayleigh line. If alternately we consider in term \(A\) those states in which either \(K\) or \(I\) is actually a metal state, we might expect resonant contributions to the intensity, and we cannot carry out the sum over vibrational states if the laser width is less than molecular vibrational spacings. In the latter case a single vibration will dominate the sum. We have for \(|K\rangle = |M\rangle\):

\[
A_I = \frac{2}{\hbar} \sum_{MI} M'_{MI} \langle i | k \rangle \langle k | f \rangle \frac{\omega_{MI} + \omega_f}{(\omega_{MI} + \omega_f)^2 - \omega^2}
\]

while for \(|I\rangle = |M\rangle\) we obtain

\[
A_K = \frac{2}{\hbar} \sum_{KM} M'_{KM} \langle i | k \rangle \langle k | f \rangle \frac{\omega_{KM} + \omega_f}{(\omega_{KM} + \omega_f)^2 - \omega^2}
\]
\[ C = -\left(2R^2\right) \sum_{K \neq I} \sum_{M \neq I} \left(M_{MK}^0 M_{Kl}^0 + M_{MK}^0 M_{lI}^0 \right) \left(\omega_{Kl}^2 - \omega^2\right) \frac{\omega_{Kl}^2}{\rho_{lM}} \left(\omega_{Kl}^2 - \omega^2\right) \left(\omega_{lI}^2 - \omega^2\right) \] \tag{16}

We may now interpret these results in terms of SERS. Term \( B \) represents molecule-to-metal charge transfer from the molecular ground state to one of the unoccupied metal levels \( M \). This transition obtains its intensity via \( M_{MK} \) through intensity borrowing from the (assumed) allowed transition \( I \rightarrow K \). This is illustrated in Fig. 1(b). The borrowing mechanism is vibronic coupling through \( h_{KM} \) which represents coupling of the metal to excited molecular states through some vibrational mode. The requirement that this term be nonvanishing imposes some symmetry restrictions on the vibrations which may be responsible for the mixing. Note that the enhancement comes through the resonance denominator \( \omega_{KM}^2 - \omega^2 \).

Term \( C \) represents metal-to-molecule charge transfer from one of the filled metal levels \( M \) to the excited state \( K \). This transition obtains its intensity via \( M_{MK} \) through intensity borrowing from the allowed \( I \rightarrow K \) transition. \( h_{MK} \) represents vibronic coupling of the metal to the ground molecular level through some vibrational mode. This is illustrated in Fig. 1(c). Note that the enhancement comes through the resonance denominator \( \omega_{MK}^2 - \omega^2 \).

Equations (15) and (16) indicate that in order for \( B \) or \( C \) to be nonvanishing \((\langle i | Q | f \rangle)\) must be nonzero. This leads to the usual selection rule that \( f = i \pm 1 \) in the harmonic oscillator approximation. It is further required for \( B \) that neither \( h_{KM} \) nor appropriate components of \( M_{KK} \) and \( M_{MI} \) vanish. For \( C \) we require neither \( h_{MK} \) nor components of \( M_{MK} \) and \( M_{MI} \) vanish. For \( B \) assuming a totally symmetric ground state, these observations imply that the symmetry species \( \Gamma_M \) and \( \Gamma_K \) of these electronic states must each correspond to \( \Gamma_\rho \), the species of at least one transition. At the same time the direct product \( \Gamma_K \times \Gamma_Q \times \Gamma_M \) must contain the totally symmetric representation to prevent \( h_{KM} \) from vanishing. By \( \Gamma_Q \) we mean the irreducible representation for which \((\partial H'/\partial Q)\) is a basis which is the same as that for \( Q \). Thus if \( \Gamma_K = \Gamma_\rho \) and \( \Gamma_M = \Gamma_\rho \), it must correspond to at least one of the species contained in \( \Gamma_K \times \Gamma_M \), which are the normal selection rules for the Raman effect. A similar analysis for the term \( C \) leads to the identical conclusion. Note however, we must recognize that the symmetry species considered above belongs to the point group corresponding to the molecule-metall system, which will most likely be of lower symmetry than that of the molecule alone. In fact unless the surface is considered perfectly smooth and some symmetry axis of the molecule is exactly perpendicular to the surface plane, or that the active site in which the molecule sits is relatively symmetric, it is more than likely that no symmetry elements will exist. Thus all irreducible representations above will (trivially) be totally symmetric, implying all vibrations allowed, and furthermore no particular variation in the depolarization ratios among the various normal modes. This is in fact in accord with observations.

III. SERS INTENSITY PROFILE

We may now carry out the sum over metal states by recognizing that the metal states are so closely spaced that the sum may be replaced by an integral over energy (or frequency). Furthermore we see that since adjacent metal states will have essentially the same wave function, we may write such terms as \( M_{IM} h_{MK} = M_{IO} h_{ME} \rho(\omega_{MI}) \) where the terms with superscript 0 are independent of energy, and \( \rho(\omega_{MI}) \) is just the metal density of states. We then have

\[ A_f = (2R^2) M_{fK}^0 M_{fI}^0 (i | k \rangle \langle k | f) \int_{\omega_{fi}}^{-\omega_{fi}} \frac{\rho_f(\omega_{MI}) d\omega_{MI}}{(\omega_{MI} + \omega_f)^2 - \omega^2} \] \tag{17}

\[ A_k = (2R^2) M_{fK}^0 M_{fK}^0 (i | k \rangle \langle k | f) \int_{\omega_{ka}}^{-\omega_{ka}} \frac{\rho_f(\omega_{KM}) d\omega_{KM}}{(\omega_{KM} + \omega_k)^2 - \omega^2} \] \tag{18}

\[ B = -\left(2R^2\right) \sum_{K \neq I} \left[ M_{fK}^0 M_{fK}^0 + M_{fI}^0 M_{fI}^0 \right] \int_{\omega_{KI}}^{-\omega_{KI}} \frac{\rho_f(\omega_{MI}) d\omega_{MI}}{(\omega_{KI} - \omega_f)^2 - \omega^2} \int_{\omega_{KI}}^{-\omega_{KI}} \frac{\rho_f(\omega_{MI}) d\omega_{MI}}{(\omega_{MI} + \omega_f)^2 - \omega^2} \] \tag{19}

\[ C = -\left(2R^2\right) \sum_{K \neq I} \left[ M_{fK}^0 M_{fK}^0 + M_{fI}^0 M_{fI}^0 \right] \int_{\omega_{KI}}^{-\omega_{KI}} \frac{\rho_f(\omega_{MI}) d\omega_{MI}}{(\omega_{KI} - \omega_f)^2 - \omega^2} \int_{\omega_{KI}}^{-\omega_{KI}} \frac{\rho_f(\omega_{MI}) d\omega_{MI}}{(\omega_{MI} + \omega_f)^2 - \omega^2} \] \tag{20}

Transitions in \( A_f \) and \( B \) are molecule-to-metal transitions, and therefore \( \rho_f \) represents the density of unfilled metal states above the Fermi level, while \( A_k \) and \( C \) represents metal-to-molecule transitions and \( \rho_f \) refers to the density of filled states (including the levels of occupation). It is illustrative to take the simplest possible function for the density of states. We choose it to be a constant within the conduction band and zero outside.

\[ \rho_{\omega_{MI}} = \begin{cases} \rho_0 & \text{for } \omega_{KI} < \omega_{MI} < \omega_{BI} \\ 0 & \text{elsewhere} \end{cases} \] \tag{21}

\[ \rho_{\omega_{KM}} = \begin{cases} \rho_0 & \text{for } \omega_{KI} < \omega_{KM} < \omega_{KF} \\ 0 & \text{elsewhere} \end{cases} \]

where \( \omega_A \) and \( \omega_B \) are the lower and upper limits of the conduction band, \( \omega_F \) is the Fermi level, and \( \omega_{FI} = \omega_F - \omega_I, \omega_{BI} = \omega_B - \omega_I, \) etc. Notice this assumption represents the 0 K limit. For finite temperatures we may obtain a better fit by inserting the Fermi function. Additional improvements could come from a more realistic density of states function for a particular metal (see below). It is not obvious for example that a sharp cutoff at the band edges is correct. However in order to simplify the mathematics,
and since we are mainly interested in the behavior near $\omega_{FI}$, we feel this is a good starting point. We may further simplify the mathematics by considering only borrowing from a single state $K$, eliminating the sum over $K$. It is a simple matter to rectify this if needed. Defining $\kappa_A$ as the coefficient of the integrals in $A_f$ and $A_k$ and $\kappa_B \omega_C / (\omega_{FI}^2 - \omega^2)$ as the coefficient of the integrals in $B$ and $C$, respectively, and carrying out the integrations we obtain

$$A_f = \kappa_A \rho_0 \left[ \ln \frac{\omega_{FI} + \omega_f - \omega}{\omega_{BI} + \omega_f - \omega} + \ln \frac{\omega_{FI} + \omega_f + \omega}{\omega_{BI} + \omega_f + \omega} \right],$$

$$A_k = \kappa_A \rho_0 \left[ \ln \frac{\omega_{KF} + \omega_k - \omega}{\omega_{KI} + \omega_k - \omega} + \ln \frac{\omega_{KF} + \omega_k + \omega}{\omega_{KI} + \omega_k + \omega} \right],$$

$$B = \frac{\kappa_B \rho_0}{2} \left[ \frac{1}{\omega_{KI} - \omega} \ln \frac{\omega_{FI} - \omega}{\omega_{BI} - \omega} \right] + \frac{1}{\omega_{KI} + \omega} \ln \frac{\omega_{KI} + \omega}{\omega_{BI} + \omega},$$

$$C = \frac{\kappa_C \rho_0}{2} \left[ \frac{1}{\omega_{KI} - \omega} \ln \frac{\omega_{KI} - \omega}{\omega_{KF} - \omega} \right] + \frac{1}{\omega_{KI} + \omega} \ln \frac{\omega_{KI} + \omega}{\omega_{KF} + \omega}. $$

Notice that all these terms have logarithmic singularities. When the excitation frequency is near a singularity we should include a phenomenological damping factor $i \Gamma$ where $\Gamma$ is the inverse of some characteristic damping time in the conduction band. Considering only the dominant term, we then expect the surface enhanced Raman spectroscopy line shape in each case to be

$$I \propto \left\{ \ln [\omega_{FI} - \omega + i \Gamma] \right\}^2,$$

$$I \propto \left\{ \ln [\omega_{KF} - \omega - i \Gamma] \right\}^2,$$

$$I \propto \left\{ \ln [\omega_{FI} - \omega + i \Gamma] \right\}^2,$$

$$I \propto \left\{ \ln [\omega_{KF} - \omega + i \Gamma] \right\}^2.$$ 

These terms give the correct dependence of excitation frequency and $V_{\text{MAX}}$. Since $h \omega_F = E_F(0) + eV$ where $E_F(0)$ is the Fermi level at an arbitrary zero applied potential with respect to a reference electrode, we can see that for metal-to-molecule transfer [Eqs. (26b) and (26d)] we predict a positive slope for $V_{\text{MAX}}$ against $\omega$, while for molecule-to-metal transfer [Eqs. (26a) and (26c)] we predict a negative slope. This is exactly what is observed. Note that resonances are also predicted [in Eqs. (22)–(25)] for $\omega = \omega_{KI}$ or $\omega_{BI}$. These “band edge” resonances should be relatively independent of voltage. To our knowledge such resonances have never been observed, and in fact may be weak or very broad if the band edge is not sharp (see below).

As a test of the line shapes we have fit Eqs. (22)–(25) to a variety of experimental data, using $\Gamma$ as an adjustable parameter and choosing $\omega_{KI}$ to be the lowest lying allowed molecular transition frequency. The resonance frequency is selected so that the peak of the observed profile matches the calculated curve. In Fig. 2 we show a fit of the predicted intensity–voltage profile for the case of molecule-to-metal transfer. The example chosen is the 1020 cm$^{-1}$ line in pipercine on a silver electrode. For the optimum fit we use a linewidth $\Gamma$ of 0.3 eV and $\omega_{KI} = 9$ eV. Similarly in Fig. 3 we

![FIG. 2. Intensity–voltage profile for the 1020 cm$^{-1}$ line of pipercine on a silver electrode. Dots show the best fit of Eq. (26) using a linewidth parameter $\Gamma = 0.3$ eV.](image-url)
show a fit for the case of metal-to-molecule transfer in the 1008 cm$^{-1}$ line in pyridine. We choose $\Gamma$ of 0.3 eV and $\omega_{Rf} = 4$ eV. In both cases the fit may be termed excellent. The value for $\Gamma$ is consistent with typical metal damping times and is not too sensitive to the choice of $\omega_{Rf}$.

Note that there are several factors which can affect the shape of the intensity profile, such as desorption or electrode reactions. For example, adsorbed methylviologen dications are reduced to monocation radicals on a roughened silver electrode at $-0.55$ V. In Fig. 4 we show the profile of the 840 cm$^{-1}$ line of the methylviologen dication. The fit is good until the voltage reaches $-0.55$ V at which point the experimental curve drops rapidly indicating an electrode reaction is taking place.

A word should be added concerning the effect of variations in the density of states function. If we consider for example by comparison with Eqs. (17)–(20) the following integration by parts

![Graph of intensity vs. potential](image1)

**FIG. 3.** Intensity–voltage profile for the 1008 cm$^{-1}$ line of pyridine on a silver electrode. Dots show the best fit of Eq. (25) using a linewidth parameter $\Gamma = 0.3$ eV.

![Graph of intensity vs. potential](image2)

**FIG. 4.** Intensity–voltage profile for the 840 cm$^{-1}$ line of methylviologen on a silver electrode. Note that at $-0.55$ V a reduction takes place so that a fit to Eq. (25) is only good for the region before the onset of the reaction. This illustrates the effect of electrode reaction on the derived profiles.
we see that [assuming \( \rho(\omega) \) vanishes at \( \pm \infty \)] there is an increase in intensity predicted whenever \( \partial \rho / \partial \omega \) is large. For the step function in the above examples we then obtained logarithmic resonances. However even when the density function changes less rapidly we expect some contribution to the enhancement. For example, in silver the density of states function\(^{11}\) has a peak near the Fermi level (at 0 V). We might expect this peak to have only weak voltage dependence, but considerable intensity nevertheless since there are regions where \( \partial \rho / \partial \omega \) is large. Thus we would expect the corrected profile to consist of several possibly overlapping peaks some of which may not have a very rapid voltage dependence. This may explain the fact that the observed slopes of plots of \( V_{\text{MAX}} \) against \( \omega \) are not unity, as predicted by the above theory. It should be added that localized metal states have also been implicated in this process.\(^{10}\) If the metal state in the vicinity of an atomic scale defect is directly perturbed by the electrolyte, the metal state could be shifted more than the molecule state, reducing the slope of \( V_{\text{MAX}} \) against \( \omega \).

Let us now examine the circumstances under which various terms [Eqs. (22)–(25)] contribute to the SERS intensity. Most generally we expect either molecule-to-metal transfer in which \( A_r \) and \( B \) must be considered or metal-to-molecule transfer in which \( A_k \) and \( C \) must be considered. It is unlikely that charge transfer in both directions would occur simultaneously. In either case notice that due to the term \( \langle i | k \rangle \langle k | f \rangle \) in \( A_r \), these terms should only contribute to Raman transitions \( (i \rightarrow f) \) which are totally symmetric (assuming \( \langle i \rangle \) is totally symmetric). However intense overtones are possible. The terms \( B \) or \( C \) have a factor \( \langle i | Q | f \rangle \) which enables both totally symmetric or nontotally symmetric vibrations. In the harmonic oscillator approximation we expect no overtones to be allowed, although they would be weakly allowed if slight anharmonicities are allowed.

Very few observations of overtones in SERS have been reported, and even those that have are quite weak.\(^{22}\) Though this calls into question the magnitude of the contribution of the \( A \) terms, it does not rule them out. Since nontotally symmetric vibrations are often as intense as totally symmetric ones in SERS, it is likely that the \( B \) and \( C \) terms are at least as important if not more so than the \( A \) terms. It is probably safe to regard totally symmetric vibrations as having possible contributions from both \( A_r \) (or \( A_k \)) and \( B \) (or \( C \)) terms while nontotally symmetric vibrations can have contributions only from either \( B \) or \( C \). This viewpoint has an added feature of explaining why the voltage maximum of intensity \( V_{\text{MAX}} \) is often slightly different for totally symmetric vibrations than for nontotally symmetric vibrations.\(^{23}\)

Note that in Eqs. (26a) and (26b) the resonances occur at \( \omega = \omega_k + \omega_f \) or \( \omega = \omega_k + \omega_b \) while in Eqs. (26c) and (26d) the resonances occur at \( \omega = \omega_k + \omega_f \) or \( \omega_k + \omega_b \), respectively. Since \( \omega_f \) and \( \omega_b \) are vibrational frequencies (~0.2 eV) we would expect shifts of this order of magnitude for different vibrations which is about the size of the observed shifts. Furthermore we predict that for molecule-to-metal charge transfer totally symmetric modes should display \( V_{\text{MAX}} \) at a voltage more negative than nontotally symmetric modes. The reverse should be true for metal-to-molecule transfer. This is just as we have observed.\(^{23}\) In piperidine (molecule-to-metal transfer) the \( a' \) modes peak at \(-0.8 \) V while the \( a^* \) modes peak near \(-0.5 \) V, while in pyridine (metal-to-molecule transfer) the \( a \) modes peak near \(-0.6 \) V while the \( b_i \) modes peak at \(-0.9 \) V.

ACKNOWLEDGMENTS

The authors are indebted to Professor D. L. Akins for helpful discussions concerning this work. We are also indebted to the National Science Foundation RIMI program (RTT-8305241), the PSC-BHE Research Award Program (1309) of the City University of New York, and the National Institutes of Health MBRS program (RR08168) for financial assistance.