

THEORY OF RAMAN SCATTERING BY MOLECULES ADSORBED AT ELECTRODE SURFACES. MODEL CALCULATIONS FOR RESONANCE RAMAN SCATTERING BY AN ADSORBED DIATOMIC

Frederick W. KING and George C. SCHATZ

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA

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Model calculations of the resonant Raman cross section of a homonuclear diatomic adsorbate on a metallic electrode surface are performed. If the excited intermediate electronic state is weakly dipole coupled to the electronic ground state (relative to some other excited electronic states), electric field induced intensity borrowing is found to be very large for the adsorbate. The important excited state involved is that describing charge transfer from the adsorbate to the metallic substrate. We have also carried out a simplified calculation of the vibrational Franck–Condon factors for the adsorbate. Combining electronic with vibrational enhancement factors, we find that there may be an overall intensity enhancement for the adsorbate of 10^4 – 10^8 depending on the electric field strength.

1. Introduction

A number of groups have now reported the acquisition of intense Raman spectra from adsorbed molecules at an electrode surface [1–4]. Jeanmaire and van Duyne [3] recognized that there is an enormous enhancement in the intensity of the Raman scattering from the adsorbed molecules relative to scattering from the same molecules in solution. Indeed, for pyridine on a silver electrode, the intensity enhancement has been estimated to be $\approx 10^5$ – 10^6 [2,3]. The purpose of the present work is to discuss some possible mechanisms for this enormous intensity enhancement using a simplified quantum mechanical approach.

There has been some recent theoretical interest in the enhancement of Raman scattering by adsorbates on metal surfaces. Philpott [5] theorized that surface plasmon contributions may lead to level broadening in the adsorbate and hence to the possibility that a resonance condition may be obtained. Wavelength dependent studies showing ν^4 dependence [6] do not support this suggestion for molecules adsorbed on electrode surfaces. Burstein [7,8] and co-workers have proposed that by using surface electromagnetic waves, it should be possible to obtain an intensity enhancement of two orders of magnitude for Raman scattering by a thin overlayer on a silver surface. Although

this mechanism may be a contributing factor for the experiments carried out on electrode surfaces, it is not sufficient to account for the enormous intensity enhancements observed.

In a previous paper on this topic [9], the present authors attempted to provide a qualitative understanding of the observed intensity enhancements using classical arguments. It was proposed that the intensity enhancement could be rationalized on the basis of large changes in the derivative of the polarizability of the admolecule with respect to a normal coordinate, caused by a surface induced image dipole field at the admolecule.

The object of this work is to investigate whether a large perturbation of the admolecule polarizability may result from local electric fields arising from the substrate. The classical model concentrated on the case of adsorbed pyridine at a silver electrode. In this work, however, we consider the much simpler situation of an adsorbed model diatomic molecule. At the present time, only two diatomic molecules have been investigated experimentally, I_2 adsorbed on a Pt electrode [10], and CN^- adsorbed on a Ag electrode [4]. Unfortunately, both of these molecules are too large for the Raman scattering cross section to be evaluated, so we have resorted to a model diatomic in order to carry out calculations. To greatly simplify the calcula-

tions, our attention is focused on resonance Raman scattering. Although most ad molecules have been investigated using normal Raman scattering, two dyes, methyl orange and crystal violet, adsorbed on a silver electrode, have been found to give resonance Raman scattering [3]. Precise estimates have not yet been made, but van Duyne [11] reports an additional enhancement of the resonant Raman cross section when the dyes are adsorbed on the electrode surface.

The local electric field considered in this work is composed of a number of contributions and obviously depends on the environment around the ad molecule. Such contributions could include the intrinsic field arising from the charge distribution of surface elec-

trons, electrode fields due to applied external potentials, and static image fields due to permanent or induced adsorbate dipoles. The latter would include image field contributions arising from neighboring adsorbate species. In the usual experimental setup [1-3], contributions to the local field from all three of the aforementioned fields would occur. However, for the experimental work on CN^- [4], which was carried out at a silver-air interface, the local electric field would include only the first and third contributions indicated above. Since these first and third contributions are always present, the mechanism we propose below should apply to resonant Raman scattering in many different interfacial environments.

2. Theory of intensity enhancement

The Raman scattering tensor may be written as [12]

$$(\alpha_{\rho\sigma})_{gi,gj} = A + B, \quad (1)$$

where

$$A = \sum_{e \neq g} \sum_v \left[\frac{\langle g_0 | R_\sigma | e_0 \rangle \langle e_0 | R_\rho | g_0 \rangle}{E_{ev} - E_{gi} - \hbar\omega} + \frac{\langle g_0 | R_\rho | e_0 \rangle \langle e_0 | R_\sigma | g_0 \rangle}{E_{ev} - E_{gj} + \hbar\omega} \right] \langle i | v \rangle \langle v | j \rangle, \quad (2)$$

and

$$B = \sum_{e \neq g} \sum_v \sum_s \sum_a \left\{ \left[\frac{\langle g_0 | R_\sigma | e_0 \rangle \langle e_0 | h_a | s_0 \rangle \langle s_0 | R_\rho | g_0 \rangle}{E_{ev} - E_{gi} - \hbar\omega} + \frac{\langle g_0 | R_\rho | e_0 \rangle \langle e_0 | h_a | s_0 \rangle \langle s_0 | R_\sigma | g_0 \rangle}{E_{ev} - E_{gj} + \hbar\omega} \right] \frac{\langle i | v \rangle \langle v | Q_a | j \rangle}{E_{e_0} - E_{s_0}} \right. \\ \left. + \left[\frac{\langle g_0 | R_\sigma | s_0 \rangle \langle s_0 | h_a | e_0 \rangle \langle e_0 | R_\rho | g_0 \rangle}{E_{ev} - E_{gi} - \hbar\omega} + \frac{\langle g_0 | R_\rho | s_0 \rangle \langle s_0 | h_a | e_0 \rangle \langle e_0 | R_\sigma | g_0 \rangle}{E_{ev} - E_{gj} + \hbar\omega} \right] \frac{\langle i | Q_a | v \rangle \langle v | j \rangle}{E_{e_0} - E_{s_0}} \right\}. \quad (3)$$

In eqs. (1), (2) and (3), g designates the ground electronic state, e and s are excited electronic states, i and j are the vibrational states of g , v is a vibrational state of e . R_σ and R_ρ are the σ and ρ components of the electric dipole operator, h_a is the vibronic coupling operator ($\partial H / \partial Q_a$), where H and Q_a are the electronic hamiltonian and the a th coordinate of the ground electronic state. Subscript 0 denotes an electronic wavefunction for the equilibrium position $Q_a = 0$. E_{gi} and E_{e_0} are the energies of the states $|gi\rangle$ and $|e_0\rangle$, and ω is the frequency of the exciting light. To avoid confusion with a superscript 0 which will appear in the next section, the subscript will be implicitly assumed from this point.

To greatly simplify matters, we restrict our calculation to the Condon contribution (term A) and ignore the Herzberg-Teller contribution (term B). For the model basis set to be discussed in the next section only the zz component of the scattering tensor is nonzero, and we define

$$(\alpha_{zz})_{gi,gj} = A_{zz}, \quad (4)$$

where

$$A_{zz} = \langle g | R_z | e \rangle \langle e | R_z | g \rangle f \quad (5)$$

and

$$f = \sum_v \frac{\langle i|v\rangle\langle v|j\rangle}{E_{ev} - E_{gi} - \hbar\omega + i\gamma} \quad (6)$$

In eq. (6) we have introduced a linewidth factor, since we are going to discuss resonance scattering. For a particular frequency ω , vibrational level v , and electronic state e , for which the resonance condition

$$E_{ev} - E_{gi} - \hbar\omega = 0 \quad (7)$$

is satisfied, eq. (6) simplifies to

$$f = \langle i|v\rangle\langle v|j\rangle/i\gamma. \quad (8)$$

The observed resonance Raman intensity I is therefore determined from eqs. (1), (5) and (6) to be

$$I \propto |\langle g|R_z|e\rangle\langle e|R_z|g\rangle\langle i|v\rangle\langle v|j\rangle|^2/\gamma^2. \quad (9)$$

Our primary objective is the calculation of the relative intensity enhancement I_E , defined as

$$I_E = I_A/I_S, \quad (10)$$

where subscripts A and S denote the adsorbed state and solution phase respectively. If we introduce the assumption that the factor γ is approximately the same for both the admolecule and its solution phase counterpart, then the intensity enhancement is given by

$$I_E = f_E f_V, \quad (11)$$

where the electronic factor f_E is

$$f_E = |\langle g_A|R_z|e_A\rangle\langle e_A|R_z|g_A\rangle|^2/|\langle g_S|R_z|e_S\rangle\langle e_S|R_z|g_S\rangle|^2 \quad (12)$$

and the vibrational enhancement factor f_V is given by

$$f_V = |\langle i_A|v_A\rangle\langle v_A|j_A\rangle|^2/|\langle i_S|v_S\rangle\langle v_S|j_S\rangle|^2. \quad (13)$$

The subscripts A and S have the same meaning as discussed above. The next section details a simple model for the calculation of the enhancement factors f_E and f_V .

3. Model for resonance scattering

3.1. Electronic factor f_E

To incorporate the electrode surface, we adopt a very simplified description of the interactions between the admolecule and the metal surface. It will be assumed that the surface provides a single level, which can participate in bonding with the electrons of the diatomic adsorbate. The electronic ground state will be denoted by the Slater determinant

$$e_1^0 (= e^0) = |\Phi_M \sigma_b \bar{\sigma}_b|, \quad (14)$$

where Φ_M is the one electron Schmidt orthogonalized metallic orbital which is a function of the atomic orbital available to bond with the diatomic; in the case of interest in this work, this is the 5s orbital of silver, denoted ϕ_{5s} . Φ_M is given by

$$\Phi_M = \{\phi_{5s} - \langle \phi_{5s} | \sigma_b \rangle \sigma_b - \langle \phi_{5s} | \sigma_a \rangle \sigma_a\} \{1 - \langle \phi_{5s} | \sigma_b \rangle^2 - \langle \phi_{5s} | \sigma_a \rangle^2\}^{-1/2}. \quad (15)$$

The bonding molecular orbital of the diatomic is denoted by σ_b and the bar designates spin β . States at zero elec-

trode field strength are denoted by a superscript 0. Here for simplicity we model the diatomic as a two electron molecule, with a bonding molecular orbital given in terms of 1s orbitals by

$$\sigma_b = (1s_a + 1s_b)/[2(1 + S_{ab})]^{1/2}, \quad (16)$$

where the overlap S_{ab} is

$$S_{ab} = \langle 1s_a | 1s_b \rangle \quad (17)$$

and subscripts a and b denote molecular centers of the diatomic (the metallic site is denoted by subscript c). The other molecular orbitals appearing in eq. (15) will be defined below.

Although resonance Raman scattering involves only one excited configuration for the solution phase molecule, the situation is considerably more complex for the admolecule, as will become apparent shortly. The other electronic configurations that are included fall into two categories. The first consists of

$$e_2^0 = 2^{-1/2} \{ |\Phi_M \sigma_b \bar{\sigma}_a| - |\Phi_M \bar{\sigma}_b \sigma_a| \}, \quad (18)$$

$$e_3^0 = 6^{-1/2} \{ 2|\bar{\Phi}_M \sigma_b \sigma_a| - |\Phi_M \bar{\sigma}_b \sigma_a| - |\Phi_M \sigma_b \bar{\sigma}_a| \}, \quad (19)$$

$$e_4^0 = 2^{-1/2} \{ |\Phi_M \sigma_b \bar{\sigma}^*| - |\Phi_M \bar{\sigma}_b \sigma^*| \}, \quad (20)$$

$$e_5^0 = 6^{-1/2} \{ 2|\bar{\Phi}_M \sigma_b \sigma^*| - |\Phi_M \bar{\sigma}_b \sigma^*| - |\Phi_M \sigma_b \bar{\sigma}^*| \}. \quad (21)$$

The antibonding molecular orbital σ_a is given by

$$\sigma_a = (1s_a - 1s_b)/[2(1 - S_{ab})]^{1/2} \quad (22)$$

and σ^* is

$$\sigma^* = \frac{\{\sigma_a^* - \langle \sigma_a^* | \Phi_M \rangle \Phi_M - \langle \sigma_a^* | \sigma_b \rangle \sigma_b - \langle \sigma_a^* | \sigma_a \rangle \sigma_a\}}{\{1 - \langle \sigma_a^* | \Phi_M \rangle^2 - \langle \sigma_a^* | \sigma_b \rangle^2 - \langle \sigma_a^* | \sigma_a \rangle^2\}^{1/2}}, \quad (23)$$

where

$$\sigma_a^* = (2p_{\sigma_a} - 2p_{\sigma_b})/[2(1 - S_{\sigma})]^{1/2} \quad (24)$$

and

$$S_{\sigma} = \langle 2p_{\sigma_a} | 2p_{\sigma_b} \rangle. \quad (25)$$

The excited electronic configurations e_i^0 , $i = 2-5$, describe excitations localized to the diatomic substrate. The second category includes

$$e_6^0 = |\sigma_a \sigma_b \bar{\sigma}_b|, \quad (26)$$

$$e_7^0 = |\Phi_M \sigma_b \bar{\Phi}_M|. \quad (27)$$

The excited electronic states e_6^0 and e_7^0 describe charge transfer interactions between the surface level and the diatomic. The configuration e_6^0 denotes the formation of "hole" on the surface, where an electron is transferred to an antibonding molecular orbital of the adsorbate. The configuration e_7^0 denotes charge transfer from the diatomic adsorbate to the metallic substrate.

The size of the atomic orbital basis set and the number of excited electronic configurations have both been restricted in order to keep the model calculations as simple as possible. We have included only those electronic configurations that seem to us to be most important within the constraints of the basis set. A more sophisticated treatment of the problem would allow for the possibility of excitations localized on the substrate. This may be an important omission in the present treatment.

The electronic wavefunctions in the denominator of f_E are all simple Slater determinants, that is, the electronic wavefunctions for the molecule in solution are identified with the unperturbed eigenfunctions e_i^0 , $i = 1-5$ (the

charge transfer states e_6^0 and e_7^0 are of course excluded in solution). This is not true, however, in the electronic states in the numerator of f_E . The electronic states of the adsorbed diatomic molecule are coupled due to the presence of the large electric field at the electrode surface. The adsorbate electronic wavefunctions in the presence of an electric field become

$$e_i = \sum_{j=1}^7 c_{ij} e_j^0, \quad (28)$$

where the coefficients c_{ij} are a function of the electric field strength at the adsorbate. In the following development we will consider situations where the strength of the electric field is too large to allow us to use perturbation theory to determine the coefficients c_{ij} . In such cases, these coefficients must be determined by solving the equation

$$\begin{vmatrix} E_{e_1^0} + \langle e_1^0 | ezE | e_1^0 \rangle - \epsilon & \langle e_2^0 | ezE | e_1^0 \rangle & \dots \\ \langle e_1^0 | ezE | e_2^0 \rangle & E_{e_2^0} + \langle e_2^0 | ezE | e_2^0 \rangle - \epsilon & \dots \\ \vdots & \vdots & \ddots \\ \langle e_1^0 | ezE | e_7^0 \rangle & \dots & \dots \end{vmatrix} = 0, \quad (29)$$

where

$$E_{e_i^0} = \langle e_i^0 | \mathcal{H}^0 | e_i^0 \rangle \quad (30)$$

and \mathcal{H}^0 is the unperturbed electronic hamiltonian. E is the electric field strength and e is the electronic charge. Solution of eq. (29) then allows the electronic enhancement factor f_E to be calculated.

3.2. Vibrational enhancement factor f_V

As a very simple model, we use vibrational wavefunctions $|i\rangle$ and $|j\rangle$ for the ground electronic state given by

$$|i\rangle = N_i H_i(\xi) \exp(-\xi^2/2), \quad (31)$$

where H_i is the i th Hermite polynomial, N_i is the normalization constant, $N_i = (1/2^i i! \pi^{1/2})^{1/2}$ and the dimensionless coordinate ξ is related to the normal coordinate by

$$\xi = (2\pi\nu/\hbar)^{1/2} Q, \quad (32)$$

where ν is the vibrational frequency in the ground electronic state. For excited electronic states, we take

$$|v\rangle = N_v H_v(\xi - \Delta) \exp[-(\xi - \Delta)^2/2]. \quad (33)$$

Δ is the separation between the equilibrium position of the ground and excited electronic states. It is furthermore assumed that the vibrational frequency is the same for the ground and excited electronic states. In this case, the vibrational overlap $\langle v|j\rangle$ may be readily evaluated to be

$$\begin{aligned} \langle v|j\rangle &= \frac{1}{2} \pi^{1/2} e^{-\Delta^2/4} N_v N_j \sum_{l=0}^v \sum_{n=0}^j \sum_{r=0}^l \sum_{s=0}^n a_{vl} a_{jn} \binom{l}{r} \binom{n}{s} \Delta^{l+n-r-s} (-1)^{l+r} [1 + (-1)^{r+s}] \\ &\times [1 \cdot 3 \cdot 5 \cdots (r+s-1)] 2^{-l-n+r/2+s/2}, \end{aligned} \quad (34)$$

where $\binom{l}{r}$ is the binomial coefficient and the coefficients $a_{r,l}$ are obtained from the expansion of the Hermite

polynomial [13]

$$H_v(x) = \sum_{l=0}^v a_{vl} x^l \quad (35)$$

The factor $[1 \cdot 3 \cdot 5 \cdots (r+s-1)]$ equals 1 when $r+s=0$. Alternative expressions for $\langle v|j\rangle$ have been known for a long time [14], however, eq. (34) is very convenient for computer evaluation. The above expressions for the vibrational wavefunctions and overlaps apply to the molecule in solution. For the admolecule in the presence of the electrode field, the vibrational wavefunctions are modified. For the electronic ground state of the adsorbate, the vibrational wavefunction will be approximated by

$$|i_A\rangle = N_i H_i(\xi - \Delta') \exp[-(\xi - \Delta')^2/2], \quad (36)$$

where Δ' is the separation between the equilibrium position with the electric field on and with the field off. For the excited electronic states, we use

$$|v_A\rangle = N_v H_v(\xi - \Delta'') \exp[-(\xi - \Delta'')^2/2], \quad (37)$$

where Δ'' denotes the difference between the equilibrium position of the excited electronic state in the presence of the field and the ground electronic state in the absence of the field. The vibrational overlap $\langle v_A|j_A\rangle$ is given by eq. (34), except Δ is now replaced by the quantity δ which is given as

$$\delta = \Delta' - \Delta'' \quad (38)$$

4. Computational details

4.1. Electronic enhancement factor

The excited electronic configuration e_4^0 was employed to calculate the resonance Raman scattering cross section for the solution phase. The qualitative results for other excited states are considered in the discussion section.

The basis functions employed were Slater type atomic orbitals. The orbital exponents that were employed for the calculations presented in this paper were $\zeta_{1s_a} = 1.0$, $\zeta_{1s_b} = 1.0$, $\zeta_{2p_{\sigma_a}} = 2.4$, $\zeta_{2p_{\sigma_b}} = 2.4$ and $\zeta_{5s_c} = 1.6$ (with the 5s principal quantum number $n = 4$). Small variations of these exponents do not change the conclusions obtained using the exponents just reported. The scattering cross section is most sensitive to the orbital exponents $\zeta_{2p_{\sigma_a}}$ and $\zeta_{2p_{\sigma_b}}$ and relatively insensitive to variations of ζ_{1s_a} , ζ_{1s_b} and ζ_{5s_c} . The matrix elements of R_z were evaluated from standard formulae developed for Slater type orbitals [15]. The geometric parameters employed were $R_{ab} = 2.5$ au and $R_{bc} = 2.0$ au. These values would typify a diatomic like CN^- tightly bound to the surface. The most difficult step in the determination of the scat-

tering cross section in the above model is the evaluation of the energies $E_{e_i^0} = \langle e_i^0 | \mathcal{H}^0 | e_i^0 \rangle$. To avoid this expensive complication, we have assigned the relative energy levels of the states e_i^0 empirically. The ground electronic state energy is 0 eV, and the excited state energies have been assigned as $E_{e_2^0} = 2.5$ eV, $E_{e_3^0} = 2.6$ eV, $E_{e_4^0} = 3.0$ eV, $E_{e_5^0} = 3.1$ eV, $E_{e_6^0} = 4.0$ eV, and $E_{e_7^0} = 5.0$ eV. The lowest excited states have been assigned energies corresponding to the visible region to model the situation which is likely to be obtainable in an experiment on electrode surfaces. A constant shift of all the excited states to higher energies will not alter the results to any significant degree. When e_4^0 is the excited electronic state of interest, it turns out that the calculated intensity enhancement I_E is not very sensitive to small changes in the assigned energies. Since our main interest is in order of magnitudes, changes in the energies do not alter the principal conclusions.

There is some rationale behind the assumed ordering of the energy values of the states e_i^0 . In the type of experiment that is being modeled in this work, the adsorbate is physisorbed, or at most, weakly chemisorbed. Given this situation, the charge transfer states of the adsorbate-substrate system must lie above the

lowest excited states of the adsorbate. It is for this reason, that the charge transfer configurations e_6^0 and e_7^0 have been assigned energies higher than e_4^0 . Also, the σ_a molecular orbital of a diatomic lies lower in energy than the σ^* molecular orbital, and hence the states e_2^0 , e_3^0 must be of lower energy than e_4^0 , e_5^0 . Large variations in the scattering cross section are only expected when the energy of the charge transfer configurations are assigned energies approximately equal to or below e_4^0 .

The calculations reported in this work are based on values of the electric field at the midpoint of the diatomic adsorbate. Variations of E over the diatomic molecule have been ignored. For very large electric field strengths, and for admolecules (particularly heteronuclear diatomics) tightly bound to the surface, the assumption of a uniform field over the admolecule is likely to be less valid than in the present model, where the field strengths are not exceptionally high, and in the present calculations which are concerned with a homonuclear diatomic.

In table 1, the electronic contribution to the intensity enhancement f_E is tabulated as a function of the electric field strength for the parameters discussed in this section. Table 2 shows the effect of small changes in the relative energies. Comparison of tables 1 and 2

Table 1

Electronic contribution to the intensity enhancement as a function of electric field. These results are calculated with the parameters discussed in section 4

Electric field at adsorbate (V/cm)	Energy separation $\Delta E = E_{e_4} - E_{e_1}$ (eV)	Electronic intensity enhancement factor f_E
1.97×10^5	3.000	1.44
3.94×10^5	3.000	2.02
5.91×10^5	3.000	2.76
7.88×10^5	3.000	3.68
9.85×10^5	3.000	4.82
1.18×10^6	3.000	6.21
1.77×10^6	3.000	12.2
1.97×10^6	3.000	14.9
5.91×10^6	3.002	237
9.85×10^6	3.005	1.24×10^3
1.38×10^7	3.010	4.07×10^3
1.77×10^7	3.016	1.05×10^4
1.97×10^7	3.020	1.58×10^4
3.94×10^7	3.076	3.03×10^5
5.91×10^7	3.160	1.86×10^6

Table 2

Effect of small changes in the assigned electronic energy levels on the calculated enhancement factor f_E . The assigned energies are $E_{e_1^0} = 0$, $E_{e_2^0} = 2.2$, $E_{e_3^0} = 2.7$, $E_{e_4^0} = 3.0$, $E_{e_5^0} = 3.1$, $E_{e_6^0} = 4.0$, and $E_{e_7^0} = 5.2$

Electric field at adsorbate (V/cm)	Energy separation $\Delta E = E_{e_4} - E_{e_1}$ (eV)	Electronic intensity enhancement factor f_E
1.97×10^5	3.000	1.40
3.94×10^5	3.000	1.90
5.91×10^5	3.000	2.53
7.88×10^5	3.000	3.30
9.85×10^5	3.000	4.25
1.18×10^6	3.000	5.38
1.77×10^6	3.000	10.2
1.97×10^6	3.000	12.4
5.91×10^6	3.002	182
9.85×10^6	3.006	935
1.38×10^7	3.011	3.07×10^3
1.77×10^7	3.018	7.88×10^3
1.97×10^7	3.022	1.18×10^4
3.94×10^7	3.085	2.09×10^5
5.91×10^7	3.182	1.31×10^6

shows that the electronic contribution to the intensity enhancement is not especially sensitive to small changes in the values of the energies $E_{e_i^0}$. However, if the important charge transfer state e_7^0 is assigned an energy

Table 3

Effect of a large change in the assignment of the energy of the charge transfer configuration e_7^0 on the calculated enhancement factor f_E . The energy of e_7^0 is taken as $E_{e_7^0} = 2.7$ eV; the other energies are given in section 4

Electric field at adsorbate (V/cm)	Energy separation $\Delta E = E_{e_4} - E_{e_1}$ (eV)	Electronic intensity enhancement factor f_E
1.97×10^5	3.000	1.51×10^{-1}
3.94×10^5	3.000	4.26×10^{-3}
5.91×10^5	3.000	1.17×10^{-4}
7.88×10^5	3.000	4.30×10^{-2}
9.85×10^5	3.000	4.08×10^{-1}
1.18×10^6	3.000	1.66
1.77×10^6	3.000	19.3
1.97×10^6	3.000	33.4
5.91×10^6	3.003	2.78×10^3
9.85×10^6	3.007	1.12×10^4
1.38×10^7	3.013	2.14×10^4
1.77×10^7	3.021	2.89×10^4
1.97×10^7	3.026	3.09×10^4

Table 4
Effect of the applied electrode field on the electronic energies

Electrode field strength at adsorbate (V/cm)	Energies of electronic states (eV)						
	e_1	e_2	e_3	e_4	e_5	e_6	e_7
0	0	2.5	2.6	3.0	3.1	4.0	5.0
1.97×10^5	-0.003	2.497	2.597	2.997	3.097	4.000	4.994
5.91×10^5	-0.008	2.492	2.592	2.992	3.092	4.000	4.983
1.18×10^6	-0.017	2.484	2.583	2.984	3.084	4.000	4.967
1.77×10^6	-0.025	2.475	2.575	2.975	3.075	4.000	4.950
1.97×10^6	-0.028	2.473	2.572	2.973	3.073	4.000	4.945
5.91×10^6	-0.084	2.419	2.516	2.918	3.017	4.001	4.836
9.85×10^6	-0.143	2.365	2.459	2.862	2.962	4.003	4.727
1.38×10^7	-0.203	2.314	2.401	2.807	2.906	4.006	4.620
1.77×10^7	-0.264	2.263	2.342	2.752	2.850	4.010	4.513
1.97×10^7	-0.296	2.237	2.313	2.724	2.822	4.013	4.460

lower than e_4^0 , there is a noticeable effect on the intensity enhancement as shown in table 3. The results in table 3 were calculated with the values of $E_{e_i^0}$ discussed above, except $E_{e_7^0} = 2.7$ eV. The charge transfer state e_6^0 is not directly dipole coupled to e_4^0 , but the inclusion of e_6^0 in the calculation does alter the weight coefficients c_{ij} in eq. (28), and hence indirectly has a small bearing on the intensity enhancement of a resonant Raman scattering involving the state e_4^0 .

The effect of the electric field on the energy levels is shown in table 4. These results are obtained from eq. (29). The results presented in table 4 do not reflect subtle effects, such as changes in geometry with high field strength. The diatomic bond length was assumed fixed for the calculation of the electronic enhancement contribution. From table 4, it is apparent that the state most sensitive to changes in the electric field strength is the charge transfer configuration e_7^0 . This is entirely expected of course, since the charge transfer state e_7^0 is one of the two most ionic states included in the calculation, and the energy of such an ionic state is most easily shifted in an electric field.

4.2. Vibrational factor f_V

The calculation of the vibrational intensity enhancement f_V has been carried out with initial and final vibrational levels $j = 0$ and $i = 1$, respectively. Three different intermediate levels, $v = 0$, $v = 1$ and $v = 2$ have been considered, and the variation of f_V as a func-

tion of the two geometry distortion parameters Δ and δ of section 3.1 has been determined. Our aim is to determine if there is any range for these two parameters which leads to a large f_V . In principle, Δ may be determined by optimizing the energy (as a function of orbital exponents) for the states e_1^0 and e_4^0 . δ could be determined, with greater difficulty, by carrying out a similar optimization procedure, except e_1^0 and e_4^0 are now replaced by e_1 and e_4 (eq. (28)).

In fig. 1 the intensity factor $|\langle 1|v\rangle\langle v|0\rangle|^2$ is shown as a function of Δ for the three intermediate vibrational states $v = 0$, $v = 1$, and $v = 2$. This figure shows the expected variation in intensity of the Raman band for the diatomic molecule in solution. Figs. 2, 3 and 4 show $\log f_V$ as a function of the two geometric

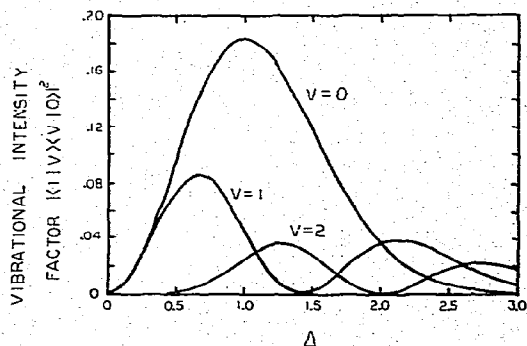


Fig. 1. Vibrational intensity factor as a function of the geometric distortion parameter Δ for the zero field case.

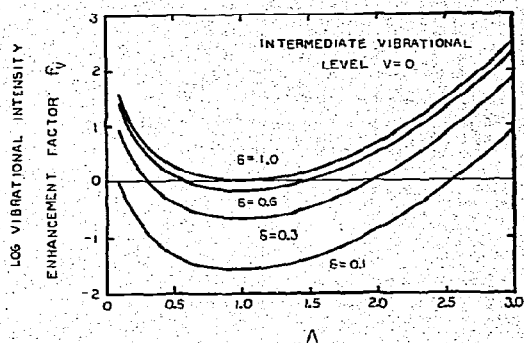


Fig. 2. Logarithm of the vibrational intensity enhancement factor f_V , as a function of the geometric distortion parameters Δ and δ for the intermediate vibrational level $\nu = 0$.

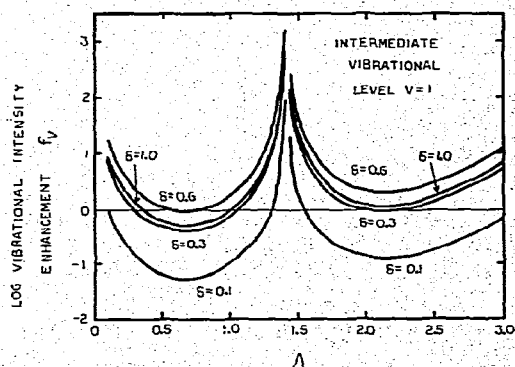


Fig. 3. Logarithm of the vibrational intensity enhancement factor f_V , as a function of the geometric distortion parameters Δ and δ for the intermediate vibrational level $\nu = 1$.

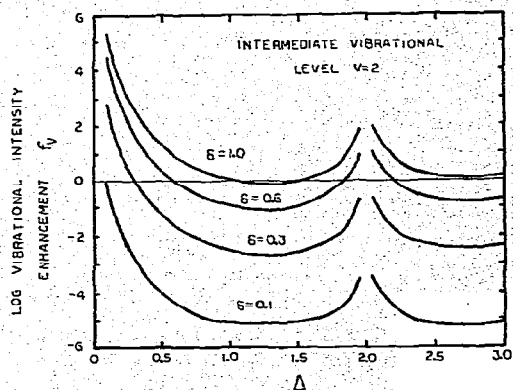


Fig. 4. Logarithm of the vibrational intensity enhancement factor f_V , as a function of the geometric distortion parameters Δ and δ for the intermediate vibrational level $\nu = 2$.

parameters Δ and δ for the cases $\nu = 0$, $\nu = 1$ and $\nu = 2$, respectively.

5. Discussion

It is apparent from table 1 that a very large intensity enhancement can arise from the electronic factor f_E . The mechanism of this intensity enhancement will now be explained. The zz component of the scattering tensor for the diatomic molecule in solution is determined by the size of the matrix element $\langle e_1^0 | R_z | e_4^0 \rangle$. For the adsorbate, the scattering tensor is determined from the quantity $\langle e_1 | R_z | e_4 \rangle \langle e_4 | R_z | e_1 \rangle$, where e_1 and e_4 are defined in eq. (28). Now included in the excited electronic states in that equation is one which is of particular importance. This is the charge transfer state e_7^0 . There are two quantities involving the state e_7^0 which are important for a discussion of the mechanism of the intensity enhancement. The first is the ratio of transition matrix elements between the ground state and the excited electronic states e_4^0 and e_7^0 . In the present model, using the parameters of section 4.1,

$$|\langle e_1^0 | R_z | e_4^0 \rangle / \langle e_1^0 | R_z | e_7^0 \rangle| \approx 10^{-3}. \quad (39)$$

The second quantity is the matrix element $\langle e_4^0 | R_z | e_7^0 \rangle$. The scattering tensor to first approximation is of the form

$$\alpha_{zz} \approx \langle e_1^0 + \dots | R_z | e_4^0 + \lambda_7 e_7^0 + \dots \rangle \times \langle e_4^0 + \lambda_7 e_7^0 + | R_z | e_1^0 + \dots \rangle, \quad (40)$$

where λ_7 denotes the mixing coefficient for the states e_4^0 and e_7^0 due to the presence of the electric field. In first order perturbation theory

$$\lambda_7 = \langle e_4^0 | e R_z E | e_7^0 \rangle / (E e_4^0 - E e_7^0). \quad (41)$$

Of course when the field is too large for perturbation theory to be applied, λ_7 must be identified with the appropriate coefficient resulting from the configuration interaction treatment. For the diatomic in solution, the electric field strength arising from the electrode surface that perturbs the molecule is zero, that is $\lambda_7 = 0$, and hence there is no mixing of the state e_4^0 with e_7^0 (nor with any other electronic state). In the adsorbed state, however, E is very large, and the mixing parameter λ_7 is sizeable, a fact directly dependent

on the size of the matrix element $\langle e_2^0 | R_z | e_7^0 \rangle$. In this case, eq. (40) can be simplified to

$$\begin{aligned} \alpha_{zz} \approx & \langle e_1^0 | R_z | e_4^0 \rangle \langle e_4^0 | R_z | e_1^0 \rangle \\ & + \lambda_7 \{ \langle e_1^0 | R_z | e_4^0 \rangle \langle e_1^0 | R_z | e_7^0 \rangle \\ & + \langle e_1^0 | R_z | e_7^0 \rangle \langle e_4^0 | R_z | e_1^0 \rangle \} \\ & + \lambda_7^2 \langle e_1^0 | R_z | e_7^0 \rangle \langle e_7^0 | R_z | e_1^0 \rangle. \end{aligned} \quad (42)$$

The first term represents the solution contribution to the scattering tensor, the second and third describe intensity borrowing from the charge transfer state e_7^0 . Despite the fact that λ_7 is somewhat less than 1, the second and particularly the third term of eq. (42) far outweigh the leading term. This is a direct consequence of the size of the dipole matrix element between the ground and charge transfer states, which results in the ratio in eq. (39) being very small. The charge transfer state e_6^0 is not an important source for intensity borrowing since $\langle e_4^0 | R_z | e_6^0 \rangle = 0$. The charge transfer state e_6^0 will only play an important role when resonant Raman scattering involves an excited electronic state which is strongly dipole coupled with e_6^0 .

Table 5 lists the important contributions to the enhancement factor f_E for a field strength $E = 1.38 \times 10^7$ V/cm. The remaining 2378 terms contribute a factor of only 3.375 to the sum in table 5. The value of f_E at $E = 1.38 \times 10^7$ V/cm is 4.07×10^3 . Three terms of importance that contribute to the intensity enhancement have been indicated in eq. (42) and arise from the mixing of e_7^0 with e_4^0 . A large contribution (second and third entries in table 5) is also made when the ground state e_1^0 mixes with e_7^0 , which leads to the following term

$$\lambda_7 \{ \langle e_7^0 | R_z | e_4^0 \rangle \langle e_7^0 | R_z | e_1^0 \rangle + \langle e_1^0 | R_z | e_7^0 \rangle \langle e_4^0 | R_z | e_7^0 \rangle \}.$$

The only other electronic state which appears in table 5 is e_2^0 . The state e_2^0 has a strong transition dipole with e_1^0 , and eq. (39) is also true for e_2^0 replacing e_7^0 . However, the states e_4^0 and e_2^0 are weakly coupled, that is $\langle e_4^0 | R_z | e_2^0 \rangle$ is much smaller than $\langle e_4^0 | R_z | e_7^0 \rangle$. As a result, the mixing coefficient λ_2 is much smaller than λ_7 . In table 5, the "solution term" $\langle e_1^0 | R_z | e_4^0 \rangle \langle e_4^0 | R_z | e_1^0 \rangle$ makes a contribution of just slightly less than 1 to the sum, which is due to the fact that both c_{11} and c_{44} (eq. (28)) are very close to 1 at the field strength $E = 1.38 \times 10^7$ V/cm.

In the present calculation, intensity borrowing

Table 5

Component analysis of the electronic contributions to the electronic intensity enhancement factor f_E . Electrode field strength at adsorbate is 1.38×10^7 V/cm. The parameters used are the same as those employed to calculate table 1

Important electronic states contributing to f_E				Contribution to intensity sum ^{a)}
<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	
1	7	7	1	25.7836
1	7	4	7	9.8904
7	4	7	1	9.8904
1	4	7	1	5.0674
1	7	4	1	5.0674
7	4	4	7	3.7916
1	4	4	7	1.9438
7	4	4	1	1.9438
1	7	1	1	-1.8815
1	1	7	1	-1.8815
1	2	7	1	-1.3731
1	7	2	1	-1.3731
1	4	4	1	0.9960
1	7	4	4	0.9271
4	4	7	1	0.9271
7	4	7	7	0.8168
7	7	4	7	0.8168
2	7	7	1	0.7853
1	7	7	2	0.7853
7	4	1	1	-0.7218
1	1	4	7	-0.7218
7	4	2	1	-0.5267
1	2	4	7	-0.5267
				$\Sigma = 60.4266$
				$f_E = (\Sigma)^2 = 3.651 \times 10^3$

^{a)} The contributions to f_E have the form

$$\frac{c_{1i} c_{4j} c_{4k} c_{1l} \langle e_i^0 | z | e_j^0 \rangle \langle e_k^0 | z | e_l^0 \rangle}{\langle e_1^0 | z | e_4^0 \rangle \langle e_4^0 | z | e_1^0 \rangle}.$$

takes place almost totally from a state which is intimately connected with the presence of the metal surface. This mechanism for intensity enhancement would not therefore apply to Raman scattering from the diatomic in solution in the presence of a very large externally applied electric field. In order that an applied external field lead to an intensity enhancement for resonant scattering from a molecule in solution, two conditions must be satisfied. The resonance Raman scattering must involve an excited electronic state whose dipole matrix element with the electronic ground state is small relative to some other electronic

state which is strongly dipole coupled to the electronic ground state. The other electronic state must also be strongly dipole coupled to the excited electronic state involved in the Raman scattering. If the diatomic is however complexed to a metal in solution, then the intensity borrowing mechanism involving charge transfer configurations would again be possible, although the degree of state mixing may be quite different than occurs for the same molecule adsorbed on a metal surface. Small intensity enhancements in non-resonant Raman scattering due to the formation of charge transfer complexes in solution have been observed experimentally [16].

An important consideration that emerges from the electronic enhancement factor calculations is that all Raman transitions are not enhanced in the present model. If resonant Raman scattering had involved the excited state e_2^0 in place of e_1^0 , then a decrease in the intensity would result. This is easy to understand by applying the perturbative arguments presented earlier. The scattering tensor is now of the form

$$\alpha_{zz} \approx \langle e_1^0 + \dots | R_z | e_2^0 + \lambda_1 e_1^0 + \dots \rangle \\ \times (e_2^0 + \lambda_1 e_1^0 + \dots | R_z | e_1^0 + \dots) \quad (43)$$

In the present model, the matrix element $\langle e_1^0 | R_z | e_2^0 \rangle$ is much larger than all other dipole-matrix elements except $\langle e_1^0 | R_z | e_1^0 \rangle$, which it approximately equals. Now as the applied electric field is increased, the other excited electronic states mix with e_2^0 , and because of the relative size of the dipole matrix elements just mentioned, the intensity decreases. It therefore follows that if all Raman bands for any given molecule undergo an intensity enhancement when the molecule is adsorbed, then the charge transfer dipole matrix elements must be larger than the dipole matrix elements for the excited electronic states involved in the resonance Raman scattering.

The considerations of the last paragraph also apply to the case of non-resonant Raman scattering, for in this situation, there is a sum over all excited electronic states. The scattering cross section for the molecule in solution is to a first approximation, determined by those electronic states which have large dipole matrix elements with the ground state. If the charge transfer dipole matrix elements are approximately the same size as the molecular dipole matrix elements, there will be no intensity enhancement by the me-

chanism of intensity borrowing from the charge transfer states. The possibility exists, however, that charge transfer dipole matrix elements involving the substrate, will be much larger than all adsorbate dipole matrix elements. In this situation, there will be a non-resonant Raman intensity enhancement by an intensity borrowing mechanism.

We now turn our attention to the vibrational intensity factor. Since we have not determined a priori the geometric distortion parameters Δ and δ , we limit this discussion to the range of values of those parameters that *will* lead to an intensity enhancement.

Large intensity enhancements for the $\nu = 0$ case result under two conditions. (i) The geometric distortion for the solution molecule is large; that is, $\Delta \approx 2-3$, and application of the field reduces the overall distortion to intermediate values, i.e., $\delta \approx 1.0$. (ii) The other situation occurs when the geometric distortion for the solution molecule is very small, $\Delta \approx 0.1$, and the presence of the electric field increases the distortion to higher values, such that $\delta \approx 0.5-1.0$. For these two situations, an intensity enhancement contribution in the range 10^1-10^2 might be realized. There is one other extreme, and this leads to an intensity *decrease*. This occurs when the geometric distortions for the solution molecule are moderate, i.e., $\Delta \approx 1$, and the applied field either greatly decreases or increases the distortion, that is, $\delta \approx 0.1$ or $\delta \approx 2-3$.

Essentially the same conclusions apply when the intermediate vibrational level is $\nu = 1$, though the likely intensity enhancement may at best be an increase of approximately a factor of ten. There is, however, an additional feature present for the $\nu = 1$ case. There is an intermediate range of Δ for which large vibrational intensity enhancements are obtained. From eq. (34) it is easy to show that for $\nu = 1$, the quantity $|\langle 1 | 1 \rangle \langle 1 | 0 \rangle|^2$ is zero for $\Delta = 2^{1/2}$ (i.e., the transition is Franck-Condon forbidden for the molecule in solution). From fig. 2, it is apparent that large vibrational intensity enhancements for a very wide range of δ values will be obtained when the geometric distortion of the solution molecule is approximately $2^{1/2}$.

The other intermediate vibrational level considered is $\nu = 2$. It is apparent from fig. 4 that the most likely situation for an intensity enhancement is that of case (ii) discussed for $\nu = 0$. For the $\nu = 2$ case, $|\langle 1 | 2 \rangle \langle 2 | 0 \rangle|^2$ is zero for $\Delta = 2$, and as a result, there

is a narrow region around $\Delta = 2$ for which large intensity enhancements are obtained. For most values of Δ , fig. 4 indicates that there will be a very large intensity decrease, and therefore, the intermediate vibrational level $\nu = 2$ can clearly be regarded as the least favorable of the three considered in terms of producing an intensity enhancement.

6. Concluding remarks

In the present work, we have discussed how intensity enhancements for resonant Raman scattering may arise from an electric field induced intensity borrowing mechanism when a molecule is adsorbed on a metal electrode surface. Although our simple model of the scattering process did not require us to explicitly identify all the microscopic contributions to this field, a number of possible contributions to it exist, and these were discussed in the introduction.

There are a couple of features of the present model that have been treated very simply. The most important defect is the simplistic treatment of the metallic substrate. A local site approximation has been employed in this work, however a more realistic treatment should accommodate the delocalized nature of the metallic electrons. The electronic basis set should be expanded, though the size of the calculation escalates very quickly as the number of electrons (and number of configurations) is increased. We hope to elaborate on these topics in the future.

Note how the present model differs from our earlier classical model [9] of surface Raman scattering. There, no change in the static adsorbate properties was needed to cause the enhancement induced by the oscillating image dipole. Here, the changes in molecular states induced by adsorption are responsible for the enhancement. Evidently both processes will occur in real systems, with the degree of importance of each dependent on the nature of the system.

In summary, we have carried out model calculations to determine the intensity enhancement for resonant Raman scattering from a diatomic adsorbate. For reasonable values of the electric field strength at the adsorbate (5×10^6 – 5×10^7 V/cm), we find an enhance-

ment factor resulting from electronic terms to be $\approx 10^2$ – 10^6 . The origin of the electronic intensity enhancement is intensity borrowing from the charge transfer state resulting from interaction of the adsorbate with the metallic surface. Under favorable conditions, the vibrational factor may give an additional enhancement of $\approx 10^1$ – 10^2 for realistic values of the distortion parameters Δ and δ . A combination of the electronic and vibrational intensity factors could lead to an overall intensity enhancement of $\approx 10^4$ – 10^8 .

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References

- [1] M. Fleischmann, P.J. Hendra and A.J. McQuillan, *Chem. Phys. Letters* 26 (1974) 163.
- [2] M.G. Albrecht and A. Creighton, *J. Am. Chem. Soc.* 99 (1977) 5215.
- [3] D.L. Jeanmaire and R.P. van Duyne, *J. Electroanal. Chem.* 84 (1977) 1.
- [4] A. Otto, *Surface Sci.* 75 (1978) L392.
- [5] M.R. Philpott, *J. Chem. Phys.* 62 (1975) 1812.
- [6] C.S. Allen and R.P. van Duyne, unpublished results.
- [7] Y.J. Chen, W.P. Chen and E. Burstein, *Phys. Rev. Letters* 36 (1976) 1207.
- [8] D.L. Mills, Y.J. Chen and E. Burstein, *Phys. Rev. B* 13 (1976) 4419.
- [9] F.W. King, R.P. van Duyne and G.C. Schatz, *J. Chem. Phys.* 69 (1978) 4472.
- [10] R.P. Cooney, E.S. Reid, P.J. Hendra and M. Fleischmann, *J. Am. Chem. Soc.* 99 (1977) 2002.
- [11] R.P. van Duyne, private communication.
- [12] J. Tang and A.C. Albrecht, in: *Raman spectroscopy*, Vol. 2, ed. H.A. Szymanski (Plenum Press, New York, 1970).
- [13] M. Abramowitz and I.A. Stegun eds., *Handbook of mathematical functions* (Dover, New York, 1970) p. 801.
- [14] E. Hutchinson, *Phys. Rev.* 36 (1930) 410.
- [15] H. Ichimura and A. Rauk, *J. Chem. Phys.* 59 (1973) 5720.
- [16] G. Maes and Th. Zeegers-Huyskens, *Chem. Phys. Letters* 44 (1976) 135.