Theory of Raman scattering by molecules adsorbed on electrode surfaces

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(Received 15 May 1978)

In this work, we provide a simple classical model to explain the enormous intensity enhancement observed for Raman scattering from molecules adsorbed on electrode surfaces. It is proposed that the origin of the intensity enhancement arises from very large changes in the polarizability derivative with respect to a normal coordinate, by virtue of the image field at the admolecule. A qualitative discussion of the role of adsorbed counter ions is presented. We tentatively propose that the dependence of the intensity enhancement on counter ion concentration may be understood in terms of nearest neighbor dipole–dipole stabilization of surface clusters of counter ions with the adsorbate molecule. We also discuss some limitations of the classical model, and propose some further experiments that may lead to clarification of the ideas presented in this work.

I. INTRODUCTION

Until recently, there was a dearth of information for Raman scattering from molecules adsorbed on metallic and nonmetallic surfaces. The major contributing factor to this state of affairs was the relatively weak spectra that had been observed in the very few investigations that had been initially carried out. This undoubtedly contributed to the belief that surface Raman spectroscopy was not likely to prove to be a highly promising technique for investigations of surface adsorbed molecules.

Early investigations were concerned principally with Raman scattering from molecules adsorbed on nonmetallic surfaces.[1-7] Hendra and co-workers[2-6] examined the Raman spectra obtained from pyridine adsorbed on a variety of oxide surfaces, and were then able to extract important information on the nature of bonding between pyridine and the oxide substrates, and they were also able to differentiate between physical versus chemically bound pyridine. The Raman spectra obtained in this work were for the most part reasonably well resolved, though no attempt was made to compare the intensity from adsorbed molecules with the intensity obtained from solutions of the same molecule.

A novel approach has been employed by Levy *et al.*[8] for the acquisition of Raman spectra of thin films using a waveguide configuration. A fairly satisfactory spectrum was reported for methyl methacrylate film on a glass support. With metallic substrates, the situation had, until recently, been less successful. Greenler and co-workers employed Raman spectroscopy to examine thin films on metal substrates. These authors obtained rather poor spectra of benzoic acid and polystyrene films on a silver metal substrate.[9,10] A recent report of Raman scattering from adsorbed molecules at tungsten and nickel interfaces apparently arises from instrumental artifacts.[11]

The first successful realization of highly resolved Raman spectra at a metal surface was obtained by Fleischmann *et al.*[12] for pyridine adsorbed on a silver electrode. Hendra and co-workers[13-20] and others[21-24] have expanded this area to a wide variety of surface

adsorbed molecules including diatomics (e.g., CO^{18}), a number of aromatic and aliphatic amines,[22-24] and some dye molecules.[23] The metal electrodes employed have been silver, copper, platinum, and mercury/platinum. A most important and perhaps unexpected aspect of some of these investigations is the rather high quality of the recorded spectra.

Though no consideration was given to the effective intensity of the adsorbed species in the early investigations by Hendra *et al.*, later work showed[22,23] that the apparent surface enhancement of the Raman intensity from an adsorbed molecule relative to the same molecule in the nonadsorbed state was very large in the spectra recorded by Hendra *et al.*[22] Jeanmaire and Van Duyne[23] were the first to recognize the magnitude of this effect, with enhancements of 10^5–10^6 obtained from adsorbed species on carefully prepared electrodes. The latter authors then proceeded to elucidate a number of the underlying effects which appear to be essential for observing extraordinarily intense spectra of surface adsorbed molecules. The relevant experimental details from the illuminating study of Jeanmaire and Van Duyne will be discussed in subsequent sections of this paper. Apparently, Albrecht and Creighton[22] have also independently observed large intensity enhancements (~10^5) for pyridine adsorbed on a silver electrode. The extensive investigations of Van Duyne, Jeanmaire, and Allen on a variety of molecules points to the generality of this effect.[23,24]

The purpose of the present paper is to provide a theoretical basis for understanding the nature of the anomalously intense Raman spectra that have been observed for adsorbed molecules at electrode surfaces. Two other groups have considered the problem of Raman scattering from surfaces, and it is appropriate to point out these contributions. In a recent paper, Philpott[25] theorized that a molecule in contact with a metal surface might display a resonance Raman effect, brought about by the interaction between excited states of the molecule and the surface plasmons of the metal. The net result of this interaction is to cause a broadening of the virtual levels of the admolecule, thus allowing the possibility of a vanishing denominator in the polarizability expres-

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sion and hence a resonance effect. While this mechanism may be applicable in some experiments, it does not appear to be crucially important in the present problem, although it certainly may be involved in a secondary role. Our reasons for this suggestion are as follows: The Philpott mechanism predicts a widely varying change in intensity with variation of the wavelength of the incident light. A semiquantitative wavelength dependent study by Jeanmaire and Van Duyne between 4579 and 6300 Å showed an approximate fourth power wavelength dependence. This finding is not consistent with the above proposal of a resonance enhancement mechanism. It should be noted, however, that more recent results by Creighton et al.[26] show that the intensity of surface Raman scattering in the Ag/pyridine system *decreases with increasing laser excitation frequency*. Further experiments are now in progress to determine which of these conflicting results is in fact correct.[24] A second difficulty with the above mechanism is that the surface plasmon frequency of silver ($\hbar\omega_s \approx 3.5$ eV for the electrode) may be too large to be strongly coupled to the relevant levels of adpyridine at wavelengths such as 5145 Å. Furthermore, experiments on dye molecules (which already exhibit the resonance Raman effect) give rise to further intensity enhancements when adsorbed on the electrode surface, which strongly suggests a second mechanism independent of the resonance enhancement is important for the adsorbed dye. It therefore appears that Philpott's resonant enhancement mechanism is insufficient to explain the observations.

Burstein and co-workers[27,28] have proposed a mechanism by which Raman scattering by thin overlayers on a silver surface can lead to intensity enhancements of the order of 10^2 using surface electromagnetic radiation (SEM) (generated in an ATR configuration). Experiments have been carried out with electrode surfaces[12] that have been less carefully prepared than those of Jeanmaire and Van Duyne,[23] and it is not unreasonable to assume that such surfaces exhibit greater roughness. If the SEM waves played a major role, an additional intensity enhancement might be expected on the more roughened surfaces. This expectation is, however, contrary to the experimental observation that intensity decreases as the electrode is further roughened by electrochemical anodization.[23]

The format of the remainder of this paper is as follows: In Sec. II, a simple electrostatic model is developed to account for the observed intensity enhancements. In Sec. III, the possible role of the adsorbed counter ions is discussed qualitatively. We conclude with a discussion of some of the limitations of the present model and indicate some interesting experiments which may clarify the ideas presented in this paper.

II. THEORETICAL MODEL

In order to delineate the role of various contributing factors, we adopt a fairly simplistic model of the adsorbate–substrate system. A *realistic* quantum mechanical treatment of the complex situation at the electrochemical interface seems a remote possibility at the present time. Instead, we propose to describe the prob-

lem in simple electrostatic terms. In this respect, we are able to call upon a rather rich and diverse literature on both electrostatic models of gas phase adsorption and adsorption at the electrochemical interface. The major fact that we wish to explain is the enormous enhancement in the Raman scattering ($\sim 10^5$–10^6)[22,23] from molecules such as pyridine adsorbed at the surfaces of electrodes such as silver.

Since pyridine adsorbed on silver represents the most thoroughly investigated system reported thus far, we will consider its Raman spectrum in this section. Pyridine has two favorable features for Raman studies; it is a strong Raman scatterer, and it is strongly adsorbed on the silver electrode. We will discuss the situation for other molecules in the discussion section.

Before embarking on a discussion of the electrostatic model, it is first necessary to address the question of pyridine orientation on the silver electrode. Although adsorption of neutral molecules at the electrochemical interface has received considerable attention,[29–31] insufficient investigation has been devoted to the present system prior to the series of Raman studies that we are trying to explain. Conway and co-workers[32–35] have investigated the orientation of pyridine at the mercury electrode. There are two extreme configurations: a flat adsorbed orientation of pyridine on the surface, or a perpendicular configuration. For the latter situation, there are two extreme modes of adsorption: coordination to the metal surface via the N atom, or the opposite situation in which the pyridine is adsorbed with the N atom away from the electrode. Intermediate conformations, such as edge adsorption, may also be possible in some circumstances. In an early study, Conway and Barradas[34] suggested that both the flat and perpendicular configurations were possible on mercury. These authors interpreted abrupt changes in $\Delta G°$ versus coverage plots to be due to reordering of flat pyridine to the perpendicular configuration at higher surface coverage, the results being rationalized on the basis that pyridine will have a low (or no) pi affinity for the mercury surface in the flat orientation and small fields or higher surface coverage will more easily orient the pyridine admolecules into a perpendicular configuration. Conway and Barradas have also made two further observations that are relevant to the present work. They suggest that pyridine is essentially physisorbed on Hg rather than chemisorbed, a fact we shall make use of below (and substantiate further for the Ag–pyridine system). It has also been proposed that, for surfaces charged negatively with respect to the points of zero charge (pzc), pyridine is oriented with the N lone pair away from the surface, and it is suggested that preferential solvation of the N lone pair takes place.[34]

It is of course necessary to exercise caution in regarding the conclusions reached for the mercury electrode as being directly applicable to the silver electrode. In the treatment below, however, we shall assume the Raman bands observed originate from adpyridine molecules that adopt a perpendicular configuration, and are coordinated via the N atom. Although the enhancement mechanism to be discussed does apply to other configu-
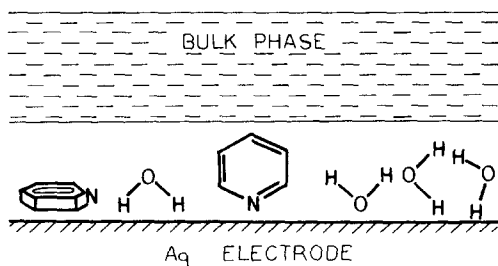
FIG. 1. Model of the electrode interface when the counterion is not adsorbed. Pyridine is adsorbed in the flat and perpendicular configurations, and water molecules at the interface are randomly oriented.

rations (with, however, smaller enhancements and different selection rules), the assumed configuration is based on several pieces of experimental evidence. From the Raman spectra of the surface adsorbed pyridine, a band in the region ~216 cm^{-1} characteristic of a metal–nitrogen band is found. Although the band is rather weak, it may support the assumption that the N atom is coordinated to the surface.[23] An amine of particular interest that has been examined by Jeanmaire and Van Duyne is pyrazine. Adsorbed pyrazine gives a very weak surface spectrum. This result is consistent with the fact that pyrazine is thought to have a preference for the flat configuration (on Hg).[32,34] This suggests that an admolecule must take on a perpendicular conformation to give rise to a measurable surface Raman spectrum. The observed depolarization values also support the perpendicular conformation. A pyridine molecule oriented in the flat configuration would give rise to depolarization ratios of zero. This is contrary to what is found experimentally, where depolarization ratios for the admolecule of around 0.6–0.7 have been determined. Jeanmaire and Van Duyne have given a simple rationale of the observed depolarization ratios assuming an axial bound pyridine which is able to rotate freely about the perpendicular axis.[23]

Our basic view of the electrode interface when no adsorbed counter ions are present is shown in Fig. 1. Although both orientations of pyridine may be present, we consider here scattering involving only the perpendicular orientation. Two points should be immediately noted from our visualization of the interfacial region: (i) the effective separation between adsorbed pyridine molecules, and (ii) the random solvent orientation at the interface. It has been suggested that low surface coverages ($0 < \theta < 1$) of pyridine on a Hg electrode are a result of islands of pyridine adlayers where locally $\theta = 1$.[36] We assume that, in the apparent equilibrium situation envisioned in the Raman experiment, island formation is not important. Indeed, from energetic arguments (see Sec. III), such a system would not be as favored as the one shown in Fig. 1. The question of solvent orientation at the electrode interface merits consideration. Bockris et al.[37] have presented a detailed discussion of the possible solvent orientations at the charged interface. These authors propose a model in which the first water layer at the interface is largely oriented in one direction at negative surface charge. In the presence of

adsorbed organic molecules and counter ions, this viewpoint may require modification, a fact appreciated by Bockris et al. For a simple two state picture, with $N_t(N_i)$ denoting the number density of solvent molecules with up(down) position, then Bockris et al.[37] propose

$$\frac{N_t - N_i}{N_t + N_i} = \tanh\left[\frac{\mu E}{kT} - \frac{U\sigma}{kT}\frac{(N_t - N_i)}{(N_t + N_i)}\right], \quad (1)$$

where E is the electrode field experienced by the solvent molecules of dipole moment μ. U is the interaction energy per pair of dipoles and σ denotes the coordination number of surrounding dipoles. If we adopt the values $\mu = 1.87$ D, $\sigma = 8$, $E = 10^6$ V/cm, then we find $(N_t - N_i)/(N_t + N_i)$ to be ~0.006 and ~0.013 when the dipole–dipole separation is taken as 3 and 4 Å, respectively. For this choice of parameters, $N_t \approx N_i$, i.e., there is a rough equivalence of the numbers of solvent dipoles pointing away and to the electrode surface. The actual solvent situation will be somewhat more disordered than the above two-state model indicates. A more rigorous treatment must account for the dipoles being able to adopt random configurations. The introduction of adsorbed organic molecules will clearly complicate this simplistic estimate. In view of the approximate estimated $N_t \approx N_i$, it would seem that the situation depicted in Fig. 1 is probably a reasonable approximation.

The essence of the electrostatic approach is to assume that the pyridine molecule can be crudely approximated as a point dipole located at the center of the molecule. The induced dipole μ_{py}^{ind} of pyridine adsorbed on a metal surface in the presence of an electric field E is then

$$\mu_{py}^{ind} = \alpha_{py}(E + E_{image}), \quad (2)$$

where E_{image} is the image field of the pyridine dipole, α_{py} is the differential polarizability tensor of pyridine, and the field E of interest for determining Raman scattering intensities is the electric field of the light beam. In what follows, we will consider only the component of Eq. (2) perpendicular to the surface (which we take to be the z direction). Assuming that α_{py} is diagonal in this direction, the z component of Eq. (2) is simply

$$\mu_{py}^{ind} = \alpha_{py}(E + E_{image}), \quad (3)$$

where we have omitted the subscript z everywhere. The influence of the x and y components of μ_{py}^{ind} will be considered below.

In general, α_{py} can be expanded in powers of the field as in

$$\alpha_{py} = \alpha_{py}^0 + \beta_{py}(E + E_{image}) + \cdots,$$

where α_{py}^0 and β_{py} are the polarizability and hyperpolarizability of pyridine for the perpendicular orientation, respectively. A precise estimate of the hyperpolarizability of pyridine appears to be unknown, but if we employ the reasonable value $\beta_{py} = 0.3 \times 10^{-30}$ esu,[38] we find that the nonlinear correction to α_{py} can be ignored for typical values of the fields to be considered.

The z component of the image dipole field evaluated at the position of the pyridine dipole is given by
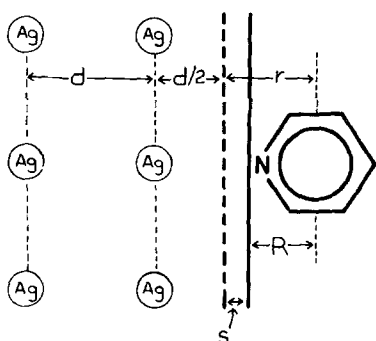
FIG. 2. Relevant separation of the image dipole from the conventionally defined surface r and the effective surface R.

$$E_{image} = \gamma(\mu_{py}^{ind}/4r^3) , \tag{4}$$

where r is the separation of the induced dipole from the metal surface, and $\gamma = (\epsilon_M - \epsilon_A)/(\epsilon_M + \epsilon_A)$, with ϵ_M and ϵ_A being the frequency dependent dielectric constants of the metal and adsorbate, respectively. The basic electrostatic model for the induced dipole has been discussed by a number of authors in connection with work function changes and the determination of apparent polarizabilities of adsorbed ions and molecules on metal surfaces.[39–43] In the present context, the adsorbed pyridine is too close for either the point dipole approximation for E_{image} or the continuum dielectric model used to get γ to be quantitative. However, experience with similar models in other applications[39–43] indicates that the qualitative consequences of the point dipole model should be retained in the real system.

Note that, in using Eq. (2), only the image field arising from the metal surface has been included, since it is assumed that the image or polarization fields arising from the surrounding solvent are negligible in comparison. Pyridine–pyridine interactions have also been ignored, since it is assumed that, at the surface coverages involved, each pyridine is surrounded by a solvent shell.

One point which requires some discussion concerning Eq. (4) is what is the meaning of the distance r. If we locate the dipole at the center of the pyridine molecule, then r has often been interpreted to be the distance from the center of the adsorbed species to the silver nuclei of the metal lattice minus one-half the separation between the silver lattice planes, as illustrated in Fig. 2. In this work, the metal surface is assumed to be separated from the last lattice place by the covalent radii of Ag. If we assume a model in which the pyridine is coordinated directly to a surface silver atom (and not located in the cavity between surface silver atoms), then using a value of 0.7 Å for the radius of the coordinated nitrogen leads to a separation distance r of 2.1 Å.

A number of investigations have been concerned with the response of a metal surface to an external static charge distribution. Two of these studies are of particular interest. Appelbaum and Hamann[44] and Lang and Kohn[45] have both carried out calculations to determine the effective image law when a charge is brought near a surface. Both groups locate the effective position of the metal surface further away from the silver lattice as shown in Fig. 2. Similar calculations have been carried out by Zaremba and Kohn[46] for the case of an atom near a solid surface. The separation distance s was found to be ~0.75 Å (Lang and Kohn) and ~0.45 Å (Appelbaum and Hamann). These estimates are for silver for which the radius parameter (r_s) is 3.0. In the present situation, we expect that an analogous separation distance exists since the static polarization of the metal electrons by the adsorbate is still present. We therefore adopt this refinement by replacing r by the distance $R = r - s$ in Eq. (4). Instead of regarding R as exactly determinable, which would necessitate knowledge of the precise value of s, and further refinements as to the exact location of the induced image dipole of the admolecule, we instead examine the variation of the Raman intensity as a function of R. Presumably, the most reasonable values of R lie between the geometrical value of 2.1 Å and values which are shifted by the above mentioned estimates of s.

We should also note that, for the separations we envisage to be important $(r \sim 2 \text{ Å})$, screening effects are likely to become significant. In addition, the idealization of the electrode surface as a smooth surface is rather tenuous, but this assumption is certainly necessary to avoid a number of highly intractable problems. Although it is felt that pyridine should be regarded as essentially physisorbed, the evidence to exclude weakly chemisorbed pyridine is far from compelling. The dividing line between these two situations is of course not clear cut. If the chemisorbed situation prevails to any extent, then charge transfer between the pyridine and the metal is a likely possibility, and this has a direct and subtle consequence on the appropriate choice of R. Unfortunately, no direct experimental information is yet available for the detailed geometry of the Ag–pyridine interface. It would be of interest to understand whether pyridine admolecules take up a configuration above a Ag atom as assumed above, or whether in fact pyridine is able to pack in between the surface Ag atoms.

From Eqs. (3) and (4), the induced dipole moment is

$$\mu_{py}^{ind} = \alpha_{py}^0 [1 - \gamma(\alpha_{py}^0/4R^3)]^{-1} E . \tag{5}$$

The apparent polarizability (α_{APP}) of an admolecule is defined as[41]

$$\alpha_{APP} = \mu^{ind}/E , \tag{6}$$

which from Eq. (5) leads to the apparent polarizability of adpyridine as

$$\alpha_{APP} = \alpha_{py}^0 [1 - \gamma(\alpha_{py}^0/4R^3)]^{-1} . \tag{7}$$

The actual quantity of interest for the purpose of intensity calculations is the rate of change of α_{APP} with respect to the appropriate vibrational coordinates. If the apparent polarizability is expanded as a Taylor series in the nuclear coordinate Q:

$$\alpha_{APP}(Q) \sim \alpha_{APP}(Q_0) + (Q - Q_0)\left[\frac{\partial \alpha_{APP}(Q)}{\partial Q}\right]_{Q_0} + \cdots , \tag{8}$$

then the Raman intensity will depend on $\{[\partial\alpha_{APP}(Q)/\partial Q]_{Q_0}\}^2$. By simply differentiating Eq. (7), we obtain

$$\frac{\partial\alpha_{APP}(Q)}{\partial Q} = \left[\frac{\alpha_{APP}(Q)}{\alpha_{py}^0(Q)}\right]^2 \frac{\partial\alpha_{py}^0(Q)}{\partial Q} . \tag{9}$$

Two additional topics require discussion before the Raman intensities can be determined. The first concerns the effective field of the light beam E that is experienced by the admolecule at the electrochemical interface. The continuity equation for the electric displacement of the light beam across the outer Helmholtz layer is

$$\epsilon_{ad}E_{ad} = \epsilon_{soln}E_{soln} , \tag{10}$$

where subscripts denote adsorbed and solution environments, respectively. To proceed further requires a knowledge of the dielectric constant of the solvent–admolecule system. Although this problem has received some consideration,[47-53] we find it difficult to make an accurate choice for ϵ_{ad} for the very heterogeneous environment pictured in Fig. 1 (which is even further complicated when counter ion adsorption is included). Consequently, we adopt the simplifying assumption that

$$E_{ad} \approx E_{soln} . \tag{11}$$

The second topic concerns the treatment of the components of the induced dipole moment in Eq. (2) parallel to the metal surface (in the x and y directions). Assuming that the solution polarizability tensor α_{py} is diagonal, it is not difficult to show that the x and y components of α_{APP} are given by expressions similar to Eq. (7) but with α_{py}^0 replaced by the appropriate x and y components and $4R^3$ replaced by $8R^3$ (because the image field is only half as large for this orientation). These enhanced x and y components of α_{APP} do not however contribute to surface Raman scattering. This is because the scattered radiation arises from emission from both induced and image dipoles. Since the x and y components of these dipoles are oriented out of phase with each other, the net radiation of these components cancels at large distances. The perpendicular components, on the other hand, are oriented in phase and thus add constructively to the outgoing radiation field. This argument also underlies the previously developed selection rules for infrared adsorption involving molecules adsorbed on surfaces[54] and our model is consistent with these selection rules.

The Raman intensity of a particular mode can be expressed in terms of the polarizability tensor α using the general expression

$$I_{mn} = \frac{2^7\pi^5}{3^2 c^4} I_0(\nu_0 - \nu_{mn})^4 \sum_{\rho\sigma}|(\alpha_{\rho\sigma})_{mn}|^2$$

$$= \frac{2^7\pi^5}{3^2 c^4} I_0(\nu_0 - \nu_{mn})^4 |Q_{mn}|^2 \sum_{\rho\sigma}\left|\left(\frac{\partial\alpha_{\rho\sigma}}{\partial Q}\right)\right|^2 , \tag{12}$$

where I_0 (proportional to E^2) is the incident light intensity. Equation (12) can be used directly for determining the solution intensity, but must be modified for determining the surface intensity for several reasons. First, as mentioned above, both the induced and image dipole contributions to the scattering amplitude need to be

summed in determining the total intensity, and this introduces an approximate factor $(1 + \gamma)^2$ into the expression. Second, only the zz component of the adsorbate polarizability tensor needs to be considered in the sum over ρ and σ. We will use the analogous element in determining the solution intensity as well, so that the ratio of surface to solution intensities will involve the ratio $(\partial\alpha_{APP}/\partial Q)/(\partial\alpha_{py}^0/\partial Q)$. Third, in summing the surface intensity expression over all outgoing photon directions, only one hemisphere of solid angles should be included. (This leads to a factor of $1/2$ in the intensity expression.) Fourth, if we assume that the pyridine adopts a fixed conformation on the surface, then the intensity expression should not be averaged over molecular orientations [as is implicit in Eq. (12)]. This means that a factor of $1/3$ in Eq. (12) should be replaced by $\sin^2\theta_0$, where θ_0 is the angle between the incident beam direction and the normal to the surface. Since other refinements to the treatment of orientation effects are possible,[9] but are not very important to the size of the enhancement effect, we will arbitrarily take $\theta_0 = \pi/4$ in the following treatment.

After including for all of the above contributions to the adsorbate intensity, and then dividing by the corresponding solution intensity, we arrive at the following expression for the intensity enhancement:

$$I_E = \frac{I_{ad}}{I_{soln}} = \frac{I_{0ad}}{I_{0soln}}\frac{3}{4}(1+\gamma)^2\left(\frac{\partial\alpha_{APP}}{\partial Q}\bigg/\frac{\partial\alpha_{py}^0}{\partial Q}\right)^2$$

$$= \frac{3}{4}(1+\gamma)^2\left(1 - \frac{\gamma\alpha_{py}^0}{4R^3}\right)^{-4} , \tag{13}$$

where we have used Eq. (11) to eliminate I_{0ad}/I_{0soln}.

To obtain a crude estimate of the intensity enhancement from Eq. (13), we assume α_{py}^0 can be approximated by its zero frequency value

$$\alpha_{py}^0 \sim 12 \text{ Å}^3 \text{ (Ref. 55)}.$$

The ratio $\gamma = (\epsilon_M - \epsilon_A)/(\epsilon_M + \epsilon_A)$ can be estimated using the known frequency dependent dielectric constant of silver[56] and assuming a value of 2 for the adsorbate dielectric constant ϵ_A. This latter number is similar in value to the bulk dielectric constant of either pyridine or water at visible frequencies (2.27 for pyridine and 1.78 for water), although we should certainly state that the use of bulk dielectric constants to characterize adsorbed molecules is very likely not accurate. It is, however, consistent with our earlier assumption leading to Eq. (11). Since ϵ_M is frequency dependent, the ratio γ is also frequency dependent, approaching 1 at low frequencies and becoming large near the surface plasmon frequency. At the experimentally accessible wavelengths between 5000–6000 Å, γ has values in the range 1.3–1.6; we will use 1.4 in the following evaluation. Note that the frequency dependence of γ causes I_E to increase with increasing frequency. At low frequencies ($\lambda > 6000$ Å), however, this frequency dependence is quite weak.

In Fig. 3, the logarithm of the intensity enhancement is shown as a function of the pyridine dipole–electrode surface separation R. The range of experimentally ob-
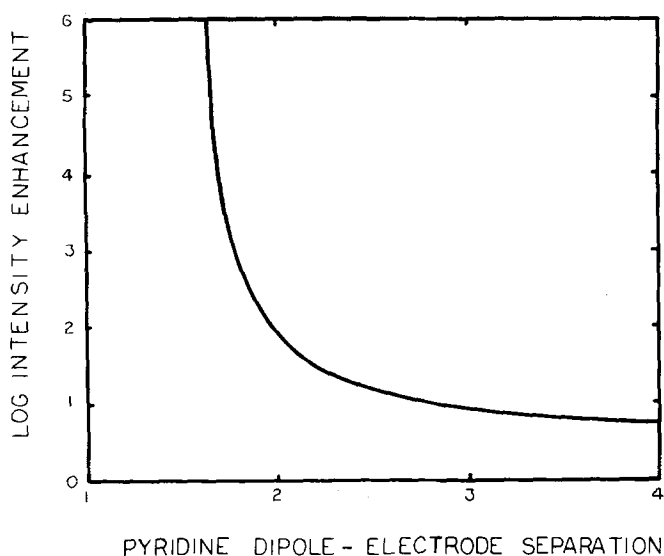
FIG. 3. Logarithm of the Raman intensity enhancement as a function of the pyridine image–electrode separation R (in Å).

served intensity enhancements $\sim 10^5 - 10^6$ is seen to correspond to a value $R \simeq 1.65$ Å. For $r = 2.1$ Å, this implies a separation s of 0.45 Å which agrees with the estimate of s made in Ref. 44. More important, it is seen that, for reasonable values of the parameters appearing in Eq. (13), an intensity *enhancement of several orders of magnitude is possible at physically attainable separations between surface and adsorbate due to the image dipole mechanism.*

III. ROLE OF COUNTER ION

Experimental results indicate that, for very dilute counter ion solutions (e.g., $10^{-5}M$ Cl⁻), the relative Raman scattering intensity is decreased by a factor of $\sim 10^2$ compared to that for $0.1M$ Cl⁻. This result has been observed for both dilute and moderate bulk concentrations of pyridine.[24] It has also been observed that, for the sequence of counterions ClO_4^-, SO_4^{2-}, Cl^-, Br^-, the relative intensity increases going from ClO_4^- to Br^-. The important point to recognize with this sequence of counter ions is that adsorption also increases from ClO_4^- to Br^- at the silver electrode.[57]

In the presence of moderate bulk concentrations of Cl⁻ ($0.1M$), the situation we envisage is shown in Fig. 4. Note that we do not view the pyridine coordinated to the surface via an intermediate adsorbed counter ion. Jeanmaire and Van Duyne have carried out experiments (see Fig. 5, Ref. 23) in which the normalized intensity was determined as a function of bulk chloride ion concentration. Two separate bulk pyridine concentrations were considered (5 and 50 mM), and for each pyridine solution, the intensity maximum was reached at a *bulk* chloride ion concentration twice the *bulk* pyridine concentration. From this result, Jeanmaire and Van Duyne[23] inferred a chloride ion : pyridine ratio on the electrode as 2 : 1. This hypothesis assumes that, at these low bulk concentrations, surface adsorption of chloride ions and pyridine is proportional to the bulk concentration of each

species. It might be imagined that a higher coordination number of four (or perhaps more) chloride ions around each pyridine is not favored, since at least two of the surrounding chloride ions in the *surface cluster* will have their electron clouds overlapping with the π cloud of pyridine, a less than favorable situation for charged ions. This however is an over simplified view. The adpyridine molecule should be more realistically considered as being able to rotate about its perpendicular axis, so in effect à chloride ion of the cluster experiences an *averaged* interaction with the pyridine π cloud. Therefore, it might be more realistic to adopt a higher coordination number of four or six chloride ions around each pyridine. Further experimental work is necessary to probe the nature of the surface cluster.

In order to provide a qualitative understanding of the possible role played by the counter ions in altering the relative intensity, we must consider the adsorbed counterion–adsorbed pyridine interactions. It is well known that, for a homogeneously ordered adlayer, the admolecules surrounding a particular central molecule interact via dipole–dipole forces (among others) which are always destabilizing when the dipoles are aligned (or induced) by the electrode field. For the surface clusters we are considering here, the above situation does not apply. For this heterogeous situation, the counterion–pyridine, dipole–dipole interactions result in net stabilization of the complex as we will now show.

The induced chloride ion dipole may be expressed as a sum of two contributions, an image dipole and a polarization dipole:

$$\mu_{cl}^{ind} = \mu_{image} - \mu_{pol}$$
$$= 2r_{cl}ze - \alpha_{cl}^0 E_0 \qquad (14)$$

where E_0 is the static electrode field. The surface charge density is assumed to be positive in Eq. (14), and hence the image and polarization contributions have opposite signs. α_{cl}^0 is the polarizability of the free counterion, e is the electronic charge, and z is the charge on the counterion and should incorporate the effects of screening. The image dipole is taken to be that formed between the counterion charge and its image charge, where r_{cl} is the distance of the counterion charge (assumed to be located at the center of the counterion) from the effective electrode surface. For typical electrode fields, the image contribution dominates the polarization term in Eq. (14). Thus, the overall induced dipole of the counterion will be pointing in the opposite direction to the induced dipole of the adpyridine, result-
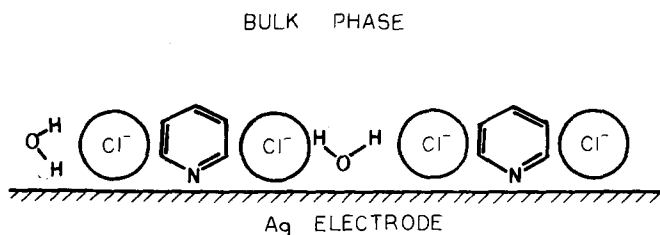
BULK PHASE

FIG. 4. Model of the electrochemical interface when the counterion is adsorbed.
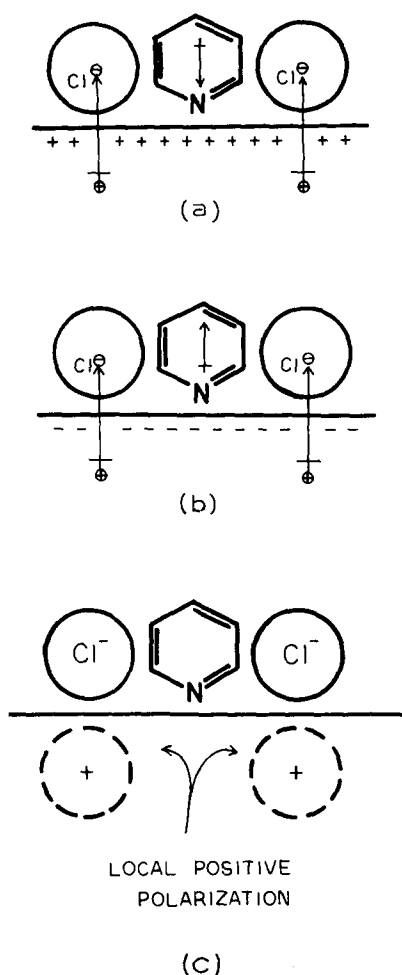
FIG. 5. Orientation of the image dipole for a positive charged surface (a) and a negative charged surface (b); and the local surface image charge polarization arising from the counterions (c).

ing in a net stabilization of the cluster. The strength of this stabilization is approximately 5–20 kcal/mole per counterion.

Jeanmaire and Van Duyne have carried out the bulk of their experimental investigations at ~ -0.6 V (vs SCE). The pzc for silver with a supporting $0.1M$ chloride ion electrolyte is ~ -0.7 V; therefore, the experimental situation is as shown in Fig. 5(a). For this case, the image and polarization contributions in Eq. (14) have opposite signs. Jeanmaire and Van Duyne have also investigated intensity vs applied electrode potential and found intensity enhancements on surfaces charged negatively (with respect to pzc). Thus, we have the situation illustrated in Fig. 5(b). In both Figs. 5(a) and 5(b), the chloride ion dipole points away from the surface. For the negatively charged surface, the polarization and image contribution to the counterion dipole are of the same sign. Figure 5(a) clearly illustrates the situation which is most favorable from the point of view of surface cluster stabilization. As soon as the local surface charge adjacent to the adpyridine becomes sufficiently negative to counter the induced positive polarization arising from the counter ions, the surface cluster be-

comes unstable, and desorption of both pyridine and chloride ion will occur. A point we do want to emphasize is that an intensity enhancement should be expected at small *overall* negatively charged surfaces, but it should be borne in mind that the *local* surface charge near the admolecule is still likely to be positive. If the latter situation did not prevail, this would appear to indicate a less important role for the counterion on negatively charged surfaces, a fact contrary to experimental evidence. As the surface is more negatively charged, the above mentioned cluster destruction seems to be supported by experiment, for there is observed a decreasing intensity enhancement for slightly negatively charged surfaces and then an abrupt change at ~ -1.2 V (vs SCE), at which point the pyridine no longer gives the spectrum characteristic of the adsorbed state. Since the overall stability of the surface cluster depends on the abilities of the two species involved to coordinate to the electrode surface, changing the surface charge in either direction will of course affect the stability of the cluster. Since the maximum adsorption of neutral organic molecules is around the pzc (or at surfaces slightly negatively charged), this would appear to be an optimum region for observing the maximum intensity enhancement. In Fig. 5(c), we summarize some of the above comments, showing that the effect of the counter ion image charges is to polarize the electrode surface in a positive manner in the region *local to the adsorbed pyridine*. The net effect of this positive polarization is to create a stabilization of the adsorbed pyridine.

The drop in the intensity as the counterion concentration is lowered can be attributed to either a direct or indirect effect. The indirect mechanism can be understood on the basis of the above discussion. If it is assumed that Raman scattering is most favorable from adpyridine in the perpendicular configuration, it is to be expected that the population density of molecules in this configuration will be reduced as the counterion concentration is decreased. This is due to the fact that a decrease in the number density of adsorbed counterions leads to a reduction in the stabilizing dipole–dipole interactions between the adcounterion and adpyridine. As a direct consequence of this destabilization, the number density of adpyridine molecules will decrease, and hence the intensity will also decrease.

The other possibility is that the adjacent counterions give rise to a direct perturbation of the polarizability of the adpyridine, which contributes to the overall intensity enhancement. A possible source of this perturbation may be the electric field arising from the chloride ion image dipole. When the counter ion concentration is reduced, the intensity enhancement would also decrease. Unfortunately, a more quantitative statement cannot be made, since presently available experimental results cannot differentiate between the case where the counterion population surrounding the adsorbed pyridine is decreased, or the case where the number of surface clusters is simply reduced at lower counterion concentrations.

It is interesting to point out that, for concentrated ($\sim 0.1M$) ClO_4^- solutions, the estimated intensity enhance-

ment is at least an order of magnitude smaller than the intensity enhancement obtained with Cl⁻. It might be speculated that an even greater reduction in the intensity enhancement should be observed with ClO_4^- as the supporting counterion, since this anion is poorly adsorbed at the silver electrode (relative to Cl⁻ ion). It must be stressed, however, that the relative adsorption of the two ions is for electrode surfaces in the absence of any organic molecule. It may well be the case that the relative degrees of adsorption for ClO_4^- and Cl⁻ are not so widely separated in the presence of adpyridine (or other admolecules). It is also to be stressed that any halide ion impurities in the perchlorate salt are likely to have significant consequences, even when present in very small amounts.

IV. DISCUSSION

The electrostatic model that has been proposed is quite general; indeed, it should be applicable to any molecule that is adsorbed on an electrode surface (although the magnitude of the effect is strongly dependent on the nature of adsorbate and electrode surface). For pyridine adsorbed on silver in particular, the electrostatic model predicts intensity enhancements of several orders of magnitude using reasonable values for parameters appearing in it. The important conditions that must be met in order to obtain a large intensity enhancement like this are as follows: (i) The molecule to be examined must be strongly adsorbed, with the most favorable conformation being that having the smallest R and largest diagonal element of the polarizability tensor. (ii) A stable cluster with adsorbed counterions appears to be important though perhaps not essential. Electrode fields for which counterion stabilization is most favorable appear to give the maximum observed intensity enhancement. (iii) A metallic surface is necessary to provide the image field.

The enhancement mechanism predicts predominantly fourth power wavelength dependence of the scattering intensity at low frequencies, with a stronger dependence on frequency as the surface plasmon frequency is approached. We should caution here that very likely the quantitative dependence on frequency predicted by Eq. (13) is incorrect, since the classical model clearly must break down when the denominator in that equation gets too large. Qualitatively, however, the trends contained in this model seem reasonable.

To apply the electrostatic model to *resonance* Raman scattering, the quantity α_{py}^0 in Eq. (13) must now be replaced by the axial component of the resonant polarizability. With this assignment, we predict an *additional intensity enhancement over and above the resonance effect*. In order to provide a qualitative estimate of the expected intensity enhancement, it is necessary to provide an estimate of R, the distance of the induced image dipole of the admolecule from the electrode surface. The molecules which have been observed to give resonance Raman scattering in the region ~ 5145 Å[23] are for the most part somewhat more bulky admolecules than pyridine, and therefore the effective location of the image dipole should be located in the range $\sim 4-10$ Å depending on the particular admolecule. Typical estimates for α^0 for the resonance situation will be $\sim 10^2-10^3$ Å³. Depending on values of α^0 and R, it is still possible that a substantial intensity enhancement (several orders of magnitude) arises from the mechanism discussed in Sec. II.

The possibilities for future experimentation in this area seem rather enormous. The key difficulties at the moment that need to be overcome in order to make this a widely applied approach to the study of surfaces are as follows: (i) problems associated with molecules that are not strongly adsorbed, (ii) difficulties arising from low solubility of many interesting compounds in aqueous solution, and (iii) problems with fluorescence. Preliminary attempts with nonaqueous solvents have not proved successful.[23] Further efforts in this direction might open up some highly promising avenues of research.

There are some highly interesting possible experiments for probing the soundness of the electrostatic model. It should be possible to delineate the role of counterion participation in stabilizing the admolecule. This might be successfully examined by study of adsorbed molecules with bulky side chains, with the hope that these bulky groups may prevent the counterions from forming a surface cluster. Substituted derivatives of pyridine might also be employed to settle unambiguously the question of how the adpyridine is oriented on the surface. Studies of the latter are presently in progress by Allen and Van Duyne.[24] The importance of nonlinear corrections (βE) might be tested with appropriate molecules. The charge transfer complex pyridine–I_2, for which a value of β (static) has been determined to be 30 times larger than pyridine,[38] might be an interesting candidate, though other effects due to charge transfer may turn out to be important.

An important experiment that is needed is one which is able to probe the rate of falloff of the electrode field with distance from the electrode. Van Duyne and Allen are currently carrying out experiments to probe the intensity enhancements of functional groups that are more remote from the electrode surface. Such experiments will be of extreme interest, as they provide a means to ascertain the upper bound on the R dependence of the electrostatic model. Almost all the experiments that have been carried out have been with admolecules on positively charged surfaces. In view of the expected decreased role played by the counterion, desorption of both counterion and admolecule, and the possibility for reorientation, experiments on negatively charged surfaces merit consideration. Of particular interest is the possibility that this surface Raman effect can provide a direct and quantitative measure of the desorption rates of admolecules.

There are a few difficulties associated with the electrostatic model in its present form that require comment. A "bottleneck" in the electrostatic model is the need to estimate the precise separation of pyridine from the electrode surface. It is important to realize that, even for a quantum model, difficulties associated with

defining meaningful separations of admolecule from metal surfaces would also be a key problem to overcome. Throughout Sec. II we assumed that pyridine assumed a perpendicular conformation and was "coordinated" to the surface by the nitrogen atom. The other extreme possibility for the perpendicular configuration is with the nitrogen away from the electrode surface. Although the latter situation would be expected to be less favorable energetically, particularly on positively charged surfaces, the important question is whether or not such a conformation would give rise to an intensity enhancement. Since the same mechanism would apply, the electrostatic model would predict an intensity enhancement, though perhaps somewhat smaller in magnitude, since the admolecule R value would be slightly larger for this configuration.

A related statement can be made concerning pyridine which is adsorbed flat on the electrode surface. In this case, although R may be somewhat smaller, the component of α_{py}^0 perpendicular to the plane of the molecule is much smaller (factor of 2) than that parallel, so a net decrease in enhancement is probable. Equally important is the fact that the selection rules for scattering in the flat geometry would be very different from those for perpendicular (with out of plane bending modes enhanced instead of ring stretching). The experimentally observed selection rules[23] are clearly in better agreement with those predicted using the perpendicular orientation.

A brief comment seems appropriate on what is to be expected from admolecules with additional functional groups. When such groups of the admolecule are located very close to the surface, two extreme situations are possible. If the functional group is oriented parallel to the surface, then the expected intensity enhancement will be weak or absent; if the functional group takes on a perpendicular orientation with respect to the surface, then a sizable intensity enhancement is to be expected. For functional groups located at "moderate" displacements from the electrode, the question of intensity enhancements is more difficult to answer. For the latter question, the principal factors in the electrostatic model which are altered are as follows: (i) change in the differential polarizability; (ii) readjustment in the location of the image dipole, i.e., R is larger; and (iii) reduction in the electric field perturbation by the surrounding counter ions.

The electrostatic model clearly indicates that the maximum intensity is likely when R is a minimum. Such a situation is likely for small "compact" molecules. Since the polarizability is expected to decrease for such molecules, it is necessary to choose admolecules which maximize the quantity $\alpha/4R^3$. Perhaps some highly adsorbed and strong Raman scattering diatomic molecules might prove to be interesting candidates for investigation.

In summary, we have proposed that the observed intensity enhancements are a result of two major factors: the change in the molecular polarizability derivative due to the image field of the electrode surface, and the stabilization of a surface complex due to favorable dipolar interactions involving adsorbed counterions. Raman scattering provides a highly convenient and direct probe of adsorbed molecules, and this technique certainly appears to be very promising for future investigations. It is hoped that the present model can serve as a basis for a qualitative understanding of the observed intensity enhancements.

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