TUNABLE LASER EXCITATION PROFILE OF SURFACE ENHANCED RAMAN SCATTERING FROM PYRIDINE ADSORBED ON A COPPER ELECTRODE SURFACE

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The wavelength dependence of surface enhanced Raman (SER) scattering from pyridine on a copper electrode surface has been measured and found to correlate closely with the optical properties of copper metal. The results are interpreted in the light of the image field model of the SER mechanism.

1. Introduction

In recent years, the study of Raman scattering from molecules on metal surfaces has been stimulated by the recognition of a millionfold enhancement in scattering cross section for pyridine adsorbed on a silver electrode in aqueous solution [+]. Recent calculations based on an image field model [2–5] of the surface enhancement process indicate that the Raman enhancing ability of a metal is a strong function of the frequency dependent dielectric constants of the metal and of the distance between the molecule and the image plane of the metal. According to the calculations for molecules adsorbed on copper, the interband transitions in the visible region cause suppression of the enhancement phenomenon by damping the optically driven oscillations of the conduction electrons [3] [‡]. Copper is expected to show strong enhancement in the IR and red regions of the visible spectrum, but its enhancing ability is expected to drop sharply near 2.0 eV (16132 cm^{-1}). In contrast, silver is expected to show Raman enhancement from the infrared up to the bulk plasma absorption edge (3.5 eV).

Enhanced Raman scattering from pyridine on copper electrodes was first reported by Pettinger and co-

workers [7] using the 647.1 nm line of the Kr^+ laser. An earlier study of the pyridine/Cu system by Hendra and co-workers using 514.5 nm, Ar^+ excitation found Raman signals only at potentials where surface multilayers were present [8]. In the more recent study, strong Raman scattering was observed after a mild anodization of the electrode surface and was found to be dependent upon both the applied potential and the angle of laser incidence. While strong signals were reported with 647.1 nm excitation, no scattering could be observed for 568 nm light.

We have studied the surface Raman enhancement for pyridine on Cu as a function of the excitation energy using a tunable dye laser. Our results indicate that the short wavelength limit for SER observation in the Py/Cu system is near 2.0 eV (16132 cm^{-1}) and the wavelength dependence of the surface Raman enhancement factor [#], ϵ, can be understood within the context of the image field model of SERS.

2. Experimental

The spectrometer system and data acquisition system have been previously described [1]. The excitation source was CR-490 (Coherent Radiation) jet

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[‡] The experimental development of SERS has been recently reviewed, see ref. [1]

[+] For a review of theoretical models of SERS see ref. [6].

[#] We define the enhancement factor as the ratio of the Raman intensity for an adsorbed molecule to that for the same molecule in solution.

stream dye laser pumped by the 514.5 nm line of a Coherent Radiation model CR-8 Ar$^+$ laser Using rhodamine B dye, a useful tuning range of 600 to 660 nm was achieved. All intensity measurements were made versus an internal standard of neat pyridine-d_5 ($\nu = 965$ cm^{-1}). The electrochemical cell and internal standard configuration have been described elsewhere [1,9]. The electrode surface was prepared by mechanical polishing with alumina (0.3 μm) followed by rinsing in distilled, deionized water. The anodization conditions were similar to those of Pettinger. a single triangle wave cycle from −0.6 to −0 05 V and back at 20 mV/s. The Cu electrode was potentiostatted at −0.6 V versus SCE for all Raman scans.

3. Results

Fig. 1 shows SER spectra from pyridine (bulk concentration 0.05 M) with 0.1 M KCl added as supporting electrolyte. Figs. 1a and 1b show spectra from anodized silver and copper electrodes. The vertical scale in fig. 1b has been expanded 6X for clarity, laser power in both spectra was 120 mW at 630 nm. In
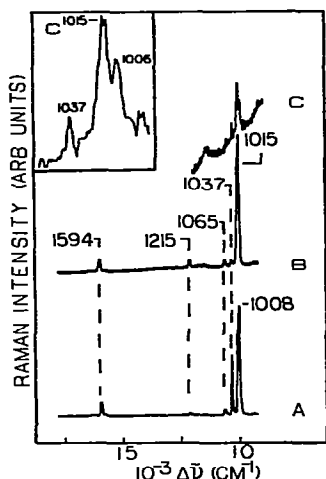

Fig. 1. Surface enhanced Raman (SER) spectra from pyridine adsorbed on electrode surfaces. Curve A is pyridine on an anodized Ag surface $E_{appl} = -0.6$ V Laser power. 120 mW at 635 nm. Curve B: as in A but on a Cu surface. Curve C SER spectrum of pyridine on an unanodized Cu electrode. Laser power 120 mW at 645 nm. Vertical scale expansion factors are A = 1X (no expansion), B = 6X, C = 70X and inset C = 180X.

fig. 1c and inset (vertical expansion 780X and 180X respectively) we show the SER spectrum obtained from a copper electrode that has been mechanically polished only and potentiostatted at −0.6. The laser power in this case was 120 mW at 645 nm.

We see in fig. 1c that strong SER scattering can be observed for pyridine on Cu without anodization. This is in accord with our previous results on silver [1,9] but is in contrast with the authors of ref. [7] who state that an oxidation−reduction cycle is an absolute prerequisite for observation of SERS. In fact, we find that it is possible to obtain SERS enhancements of $\approx 10^4$ for a variety of molecules on "smooth" (i e., no roughness on a scale $\geqslant 250$ Å) unanodized surfaces [10]. Subsequent anodization does increase intensities by as much as two orders of magnitude but it is *not* an absolute requirement for obtaining SER scattering. Thus it appears that one should only attempt to account for a maximum SERS enhancement of $\approx 10^4$ by a roughness independent mechanism such as that addressed by the image field model [2−5].

The low frequency shoulder in fig. 1c at 1006 cm^{-1} is due entirely to pyridine in the bulk solution; the feature at 1015 cm^{-1} arises from adsorbed pyridine. A simple calculation based on illuminated areas and volumes indicates that without anodization, the py/Cu system shows an enhancement of approximately 1700. Anodization increases this by a factor of 35 to about 6.0×10^4 at 645 nm. This is about a factor 20 weaker than Ag ($\epsilon = 1.1 \times 10^6$) at comparable wavelengths [1,9].

It should be noted that we have found a time dependent degradation of SERS signals on Cu. The decay is rather fast; the intensity is down by a factor of two over the time required to complete one 800 cm^{-1} scan (1 cm^{-1}/s), hence one must be careful to employ an internal standard with a scattering feature near the SERS band of interest. A better approach would be to employ a spectrograph as the dispersive device and an optical multichannel analyzer for detection. Chang and co-workers have demonstrated acquisition times of 25 ms for such a system [11].

Due to this decay, the relative intensities within a spectrum are perturbed. The use of a low power ($\leqslant 10$ mW) HeNe laser as excitation source, gives a spectrum which shows negligible degradation over the course of a scan and shows an intensity ratio of $I_{1015}/I_{1594} = 5.0$ compared with 10.1 for excitation with 100 mW

of power from a dye laser at the same wavelength.

In fig. 1b we find, as observed by Pettinger and co-workers, only a weak feature at 1037 cm^{-1} ($\epsilon \approx 6$ × 10^3 at 645 nm) in contrast with the strong band in the py/Ag system. In earlier investigations of the pyridine/silver wavelength dependence [1,9] we noted a time dependent decay of the 1037 cm^{-1} band which led to Ag SER spectra that strongly resemble fig. 1b. In fig. 2 we show a comparison of SER spectra for pyridine on Ag (600 nm, 100 mW) and Cu (645 nm, 120 mW). Fig. 2a is Ag; irradiation time. 5 min, fig 2b is the same system after ≈2 h of irradiation. Fig 2c shows representative data from the Cu/py wavelength dependence measurements, irradiation time· 5 min. The sharp band at 965 cm^{-1} is normal Raman scattering from the neat pyridine-d_5 internal standard which is illuminated with part of the incident laser beam and provides intensity and wavenumber calibration. (The standard intensity in fig. 2c involved a different pathlength and hence is not directly comparable with figs. 2a and 2b.)

The degradation of the py/Ag SERS scattering was observed only upon irradiation of wavelengths longer than 580 nm and was manifested by slow loss of scattering intensity at 1037 cm^{-1} and by the movement of the peak at 1008 cm^{-1} to 1012 cm^{-1}. In contrast to the authors of ref. [7] we find this peak shift only after prolonged irradiation and loss of the 1037 cm^{-1} intensity, not just upon changing excitation wave-

lengths. This indicates that there are at least two different surface species observable by SERS in the Ag case and that one of these can be selectively removed by prolonged irradiation. The similarity of the irradiated Ag to the Cu case suggests that this surface species is either absent on Cu or is degraded on a time scale faster than the measurement. The overall spectral degradation of the Cu system mentioned above indicates that the latter hypothesis merits investigation.

Using the enhancement factor calculated at 645 nm and the relative enhancement determined using the py-d_5 standard, one can plot the log of the measured enhancement versus the incident excitation energy (fig. 3, open diamonds). The points represent averages of successive runs at each wavelength and the error bars represent the estimated error in enhancement factor determination. No spectrum could be obtained at 16500 cm^{-1} (606 nm) excitation indicating an enhancement factor of less than 3 × 10^3 at that wavelength which was our detection limit in the current experiment. The chained line in fig. 3 indicates that limit.

The solid line in fig. 3 is the theoretical SERS excitation profile based on an image field model and is calculated according to [3]

$$\epsilon = \tfrac{15}{8} \, |1 + R_p^i|^2 |1 + R_p^o|^2 \, \sin^2\theta_i \, \sin^2\theta_o$$

$$\times \, |1 - \gamma\alpha_{zz}/4R^3|^{-4} . \qquad (1)$$

Here R_p^i and R_p^o are the Fresnel reflection coefficients for the incoming and outgoing p-polarized light, θ_i and θ_o are the intensity optimizing angles of the incident and outgoing beams with respect to the surface normal. γ is defined as $(\epsilon_M - \epsilon_A)/(\epsilon_M + \epsilon_A)\epsilon_A$, α_{zz} is the zz component of the polarizability tensor and R is the average distance between the point dipole representing the molecule and the image plane of the metal [2,3].

With the exception of R, all parameters used in evaluating eq. (1) are the same as in ref. [3]. The average R value used here is taken as 1.5 Å value in contrast with the 1.6 Å value used for Ag [3]. The smaller covalent radius for Cu (1.34 versus 1.4 Å for Ag) as well as the smaller radius parameter ($r_s = 3.02$ au versus 2.67 au for Cu [12]) argue that the smaller value is appropriate for Cu. In addition, the 0.1 Å shift in going from Ag to Cu is similar to estimates of the image plane shift based on free electron gas calcula-
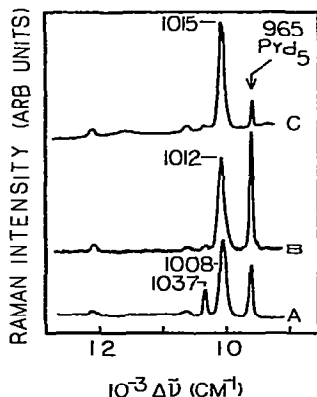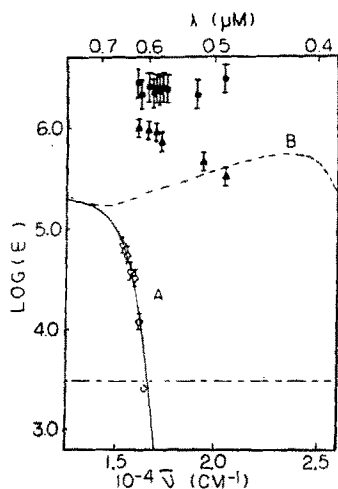

Fig. 2. Comparison of SER spectra obtained on fresh Ag (A), irradiated Ag (B) and fresh Cu (C) electrode surfaces. Labeled band is scattering from neat pyridine-d_5 employed as an internal standard. Laser powers: A, B 100 mW at 600 nm C. 120 mW at 635 nm

Fig. 3. Plot of the log of the measured enhancement factor versus excitation energy for the 1015 cm^{-1} feature of pyridine adsorbed on copper at -0.6 V (SCE) (open diamonds). The error bars indicate uncertainty in enhancement factor determination. Solid line (A) is the calculated [eq. (1)] excitation profile for pyridine adsorbed on a copper surface according to the image field model of SERS. Dashed line (B) is the analogous curve calculated for pyridine on Ag. The solid triangles and circles are the experimentally obtained enhancement factors for the 1008 cm^{-1} and the 1215 cm^{-1} modes of pyridine respectively. The chained line is the observation threshold for this experiment; systems with enhancement factors below 3×10^3 were not observable with the internal standard configuration.

tions [13]. The shape of the calculated curve is not, in general, a strong function of R, however, the use of $R = 1.55$ Å does cause a uniform decrease in ϵ by a factor of 2 to 3 over the wavelength range investigated. The calculated curve for Ag and the experimentally determined [9] enhancement factors for the 1008 cm^{-1} and the 1215 cm^{-1} (solid triangles and circles respectively) are shown in fig. 3b for comparison. (Note the flatness in $\epsilon(\omega)$ for the 1215 band.) The curves predict equal enhancements for Cu and Ag near 750 nm.

These experimental data confirm that there is a wavelength threshold for observation of SERS from pyridine on copper. Similar results have been obtained for MoO_4^{2-} and $Ru(CN)_6^{4-}$ on Cu [14] indicating that the observed wavelength dependence is indicative of the enhancement mechanism not just a characteristic of the py/Cu system. The calculated enhancement factors show excellent agreement both in

excitation energy dependence and magnitude with the experimental results. Although the image field model is not unique in predicting a threshold in the red for copper (the surface plasmon models [6] do as well), the experimental results [15] seem to indicate that the image field model is useful in predicting the behavior of metal systems other than Ag.

The observed forty-fold increase in scattering upon electrochemical anodization indicates that surface roughness is important in the enhancement process. However, further experiments are needed with controlled (scale and extent) of surface roughness to determine the magnitude of its role. At the present time, our results indicate that the roughness generated by electrochemical treatment of the surface is *not an absolutely necessary requirement* for the observation of SERS. The total SERS enhancement for the py/Cu system ($\epsilon = 6 \times 10^4$ at 645 nm) appears to have at least two contributions: (1) a factor of $\approx 2 \times 10^3$ from an anodization independent mechanism and (2) a factor of $\approx (3-4) \times 10^1$ from an anodization (i.e., roughness) dependent mechanism. The observed time dependence of the py/Cu SERS and of the 1037 cm^{-1} vibration merit further investigation to determine their origin.

Acknowledgement

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