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Communications to the Editor

On the Mechanism of Chemical Enhancement in Surface-Enhanced Raman Scattering

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Surface-enhanced Raman scattering (SERS) has been both studied extensively as a phenomenon and used widely as an analytical technique for the nearly two decades since its discovery.[1,2] Despite this intensive scrutiny, however, the microscopic origins of the enhancement are not quantitatively understood. It is generally agreed that there are two enhancement mechanisms which act in parallel, i.e., multiplicatively. These have come to be called electromagnetic and chemical, respectively. The former arises from the excitation of electromagnetic resonances in certain metals with roughness features (or particle sizes) on the order of 100 nm. The simplest view of the latter is resonance Raman scattering via new electronic excitations (possibly charge transfer) of adsorbed molecules which serve as resonant intermediate states. Enhancement factors for the electromagnetic mechanism can be of the order 10^4-10^6, whereas the chemical contribution is thought to be of the order 10^2.

It has been difficult to study the chemical enhancement mechanism selectively because most SERS studies are conducted using roughened surfaces (or particles) for which both mechanisms contribute simultaneously. We report here the preliminary results of a study of the chemical enhancement mechanism using an atomically flat, smooth single-crystal surface for which the electromagnetic contribution is small and well-understood. For pyromellitic dianhydride (PMDA) adsorbed on Cu(111), we observe SERS with an enhancement factor of ca. 30 and show that the enhancement is correlated with the appearance of a low-energy absorption in the electronic spectrum of adsorbed PMDA which is not present in the isolated molecule. Our results provide strong support for the resonance Raman mechanism.

The experiments were conducted using an ultrahigh-vacuum (UHV) surface Raman spectroscopy system which has been previously described.[3] Briefly, PMDA was dosed from a heated effusive source onto a cooled Cu(111) surface which had been prepared and characterized using standard ultrahigh-vacuum (UHV) surface science techniques. Raman spectra were obtained with a multichannel surface Raman spectrometer, and the electronic absorption spectra were obtained using high-resolution electron energy loss spectroscopy (HREELS).

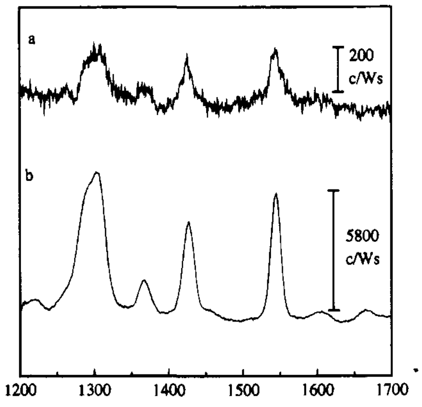

Figure 1. Raman spectra of PMDA, chemisorbed at monolayer coverage on Cu(111) at 110 K: (a) 725.0 nm excitation; (b) 647.2 nm excitation.

Figure 1 shows a portion of the surface Raman spectra of a monolayer of PMDA chemisorbed on Cu(111) at 110 K, excited at 647.2 nm (b) and 725.0 nm (a). Previous work has shown that PMDA chemisorbs as a bidentate surface carboxylate on this surface, by splitting out carbon monoxide from one anhydride ring. The other anhydride ring remains intact. We proposed a bonding geometry in which the phenyl/anhydride plane and the carboxylate plane tilted away from the surface normal and rotated with respect to each other. We assigned the vibrational bands for this limited region of the spectrum as follows: 1305 cm^{-1} to a C—O—C stretch and 1329 cm^{-1} to a C—C stretch, 1442 and 1563 cm^{-1} to the symmetric and antisymmetric carboxylate stretches, respectively, and 1624 cm^{-1} to the phenyl C=C stretch. It is immediately obvious, from the high count rate observed with 647.2 nm excitation, that the scattering is enhanced. We rule out electromagnetic enhancement due to adsorbate-induced surface roughening by the following experiment. After the surface Raman spectrum of PMDA was taken, the adlayer was thermally desorbed. The surface was recooled to 110 K, benzene deposited to roughly monolayer coverage, and its spectrum recorded. The resulting spectrum was unenhanced.

There have been a number of theories of chemical enhancement which invoke resonance Raman scattering via a charge transfer intermediate state.[1] Although the language of these theories varies somewhat, the central idea is the same. Adsorbate molecular orbitals are broadened into resonances by interaction with the conduction electrons. Resonances whose energies lie near the Fermi energy are partially filled while those lying well below are completely filled. The inclusion of metal states in chemisorption introduces new possibilities for resonance excitation at frequencies much lower than those of the intrinsic intramolecular excitations of the free molecule. There are two possibilities for new excitations: electrons can be excited from the filled adsorbate orbitals to unfilled metal orbitals above the Fermi level (molecule−metal charge transfer), or metal electrons can be excited to the partially filled adsorbate affinity level (metal−molecule charge transfer). The most convincing experimental evidence for this picture comes from spectroelectrochemical experiments where metal−molecule charge transfer excitations red shift upon making the electrode potential more negative (increasing the Fermi energy) and molecule−metal charge transfer excitations blue-shift.[4−6] A comprehensive theory has been developed which makes specific predictions about enhancement profiles, mode selectivity, and overtones and combinations.[7]

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(1) Moskovitz, M. *Rev. Mod. Phys.* **1985**, *57*, 783−826.

(2) Brandt, E. S.; Cotton, T. M. *Physical Methods of Chemistry, Vol. IX*; B. W. Rossiter and R. C. Baetzold: New York, 1993; p 633.

(3) Ivanecky, J. E., III; Child, C. M.; Campion, A. *Surf. Sci.* **1995**, *325*, L428−L434.

(4) Billman, J.; Otto, A. *Solid State Commun.* **1982**, *44*, 105−107.

(5) Furtack, T. E.; Macomber, S. H. *Chem. Phys. Lett.* **1983**, *95*, 328−332.

(6) McMahon, J. J.; Dougherty, J. J.; Riley, T. P.; Babcock, G. T.; Carter, R. L. *Surf. Sci.* **1985**, *158*, 381−392.

(7) Lombardi, J. R.; Birke, R. L.; Sanchez, L. A.; Bernard, I.; Sun, S. C. *Chem. Phys. Lett.* **1984**, *104*, 240−247.

0002-7863/95/1517-11807$09.00/0

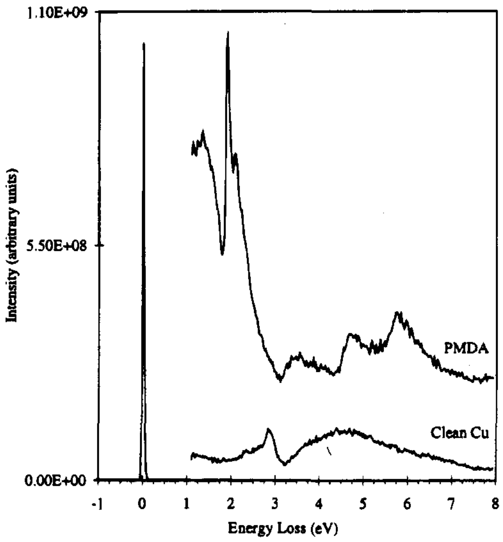

Figure 2. HREELS spectrum of a 10 Å PMDA thin film adsorbed on Cu(111) at 110 K. The primary beam energy was 11 eV, and the spectral resolution was 50 meV.

Direct spectroscopic detection of new charge transfer resonances would provide convincing confirmation of this general picture and allow quantitative testing of proposed mechanisms. We have used HREELS to obtain the electronic absorption spectra of adsorbed PMDA by increasing the primary beam energy and by scanning loss energies which correspond to electronic excitations. Figure 2 shows the electronic HREELS spectrum of a 10 Å film of PMDA adsorbed on Cu(111) at 110 K, along with that of the clean copper surface. The features at 2.8 and 4.5 eV are both assigned to interband transitions in agreement with previous work.[8] The thin PMDA film comprises approximately two monolayers, a chemisorbed first layer and a physisorbed second layer. Although the electronic spectrum of PMDA has not been assigned in the literature, the losses we observe at energies greater than 3 eV correspond approximately to the well-known intramolecular excitations of benzene: 3.3 eV to the $^3B_{1u}$ state, 4.7 eV to the $^1B_{2u}$ state, and 5.8 eV to the $^1B_{1u}$ state. As Avouris has shown,[9] the transition energies of neutral adsorbate excitations are not much shifted upon chemisorption, so the correspondence we observe is reasonable. The striking feature of the spectrum is, of course, the very sharp, intense loss at 1.90 eV which is certainly not intrinsic to PMDA, a colorless compound. There is even a well-resolved vibronic band, at 1411 cm^{-1} higher energy than the (0,0) band, which can be assigned to the symmetric carboxylate stretch in the excited state. Coverage dependent studies show that the intensity of this feature increases until the chemisorbed monolayer saturates; the intensity then decreases as multilayers of physisorbed PMDA condense, screening the excitation. The intensities of the bands with energies greater than 3 eV increase monotonically with exposure, eventually saturating at an exposure two to three times as great as that which produced the chemisorbed layer.

The coverage dependence of both the surface Raman spectra and the HREELS spectra demonstrates that both the enhanced Raman scattering and the low-energy feature in the electronic absorption spectrum arise from the chemisorbed monolayer. Although we have not yet mapped out the frequency dependence of the Raman scattered intensity, several observations provide strong evidence that we are indeed observing resonance Raman scattering via this new intermediate state. First, this is clearly a resonance phenomenon; the scattered intensity observed when exciting near the peak of the absorption is much greater than when exciting to the red of the maximum. Second, the enhancement factor observed is in rough agreement with what is expected if the scattering process is dominated by one intermediate level. It is easy to show that, for a single intermediate level, at laser frequencies much larger than vibrational frequencies, the enhancement factor is given approximately by the ratio $(\hbar\omega/\Gamma)^2$ where $\hbar\omega$ is the laser frequency and Γ is the width of the intermediate state. For the present case where $\hbar\omega \approx 1.9$ eV and $\Gamma \approx 0.1$ eV, the enhancement factor is estimated to be as large as several hundred. Although larger than our measured value of ca. 30, we have not yet obtained a spectrum excited at the absorption maximum nor have we gone sufficiently to the red to assure that we are indeed "off" resonance. The present measurement, therefore, should be regarded as a lower limit of the true enhancement factor.

In summary, then, we have provided the first direct experimental evidence linking new features in the electronic spectrum of an adsorbate to SERS, under conditions where electromagnetic enhancement is unimportant. These results strongly support the resonance Raman chemical enhancement mechanism. Experiments to determine the frequency dependence of the enhancement, the nature of the excitation, and the generality of the effect are underway.

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JA952578S

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(8) Jenkins, L. H.; Chung, M. F. *Surf. Sci.* **1971**, *26*, 151–164.

(9) Avouris, Ph.; DiNardo, N. J.; Demuth, J. E. *J. Chem. Phys.* **1984**, *80*, 491–502.