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## Silver-Molecule Separation Dependence of Surface-Enhanced Raman Scattering

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Surface-enhanced Raman scattering from a layer of organic molecules adsorbed on aluminum oxide and covered by a controlled-roughness silver film has been studied. The molecule-silver distance dependence of the Raman-scattering enhancement by the surface was measured in four separate experiments. Large enhancements ( $\sim 10^3$ ) persist in our samples for molecule-silver separation as large as 100 Å, and thus the use of surface-enhanced Raman scattering is shown to be a viable technique for vibrational spectroscopy of a large variety of interface systems.

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The discovery<sup>1</sup> of surface-enhanced Raman scattering (SERS), giant enhancements of the order of  $10^4$ – $10^6$  of the Raman scattering from monolayers of certain molecules on roughened surfaces of silver, has aroused considerable excitement. Numerous models have been proposed to explain SERS,<sup>2-17</sup> but to date, its microscopic origins are still controversial.<sup>2</sup> We report in this Letter the results of SERS experiments which use samples that are thin-film multilayered structures of Al/Al<sub>2</sub>O<sub>3</sub>/Raman-active molecule/spacer/rough Ag film. We find a large ( $\sim 10^3$ ) SERS for molecules

separated by distances  $\sim 100$  Å from the silver surface. This enhancement is adequate for observing a monolayer of molecules of ordinary Raman cross section with present experimental techniques.

We have performed two types of experiments: (a) A smooth layer of a weak Raman scatterer, poly-methylmethacrylate (PMMA), was placed between a strongly Raman-active monolayer of chemisorbed *p*-nitrobenzoic acid (PNBA) and a rough Ag film; and (b) variable-thickness films of a strongly Raman-active polymer, poly(*p*-nitro-

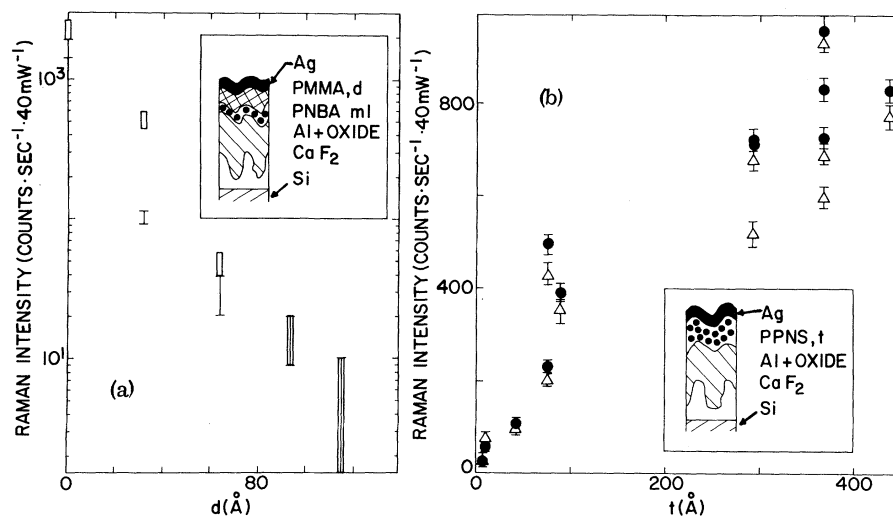


FIG. 1. (a) Spacer experiment 1(a) (inset shows the geometry). The intensity of the 1595-cm<sup>-1</sup> (open symbols) and 1425-cm<sup>-1</sup> (closed symbols) Raman peaks of PNBA above the background (logarithmic scale) vs *d*. Error bars are the size of the symbols and represent statistical accuracy only. (b) Thickness experiment 1(b) (inset shows the sample structure). The intensity of the 1596-cm<sup>-1</sup> (circles) and 1346-cm<sup>-1</sup> (triangles) Raman peaks of PPNS above the background (linear scale) vs *t*. Error bars represent statistical accuracy only.

styrene) (PPNS), were placed adjacent to a silver surface. In experiments of type (a) (spacer experiments), the Raman spectrum of the PNBA monolayer is monitored as it is spaced a distance  $d$  away from the surface of the Ag film; in experiments of type (b) (variable-thickness experiments), the Raman scattering is monitored from the PPNS as a function of its thickness  $t$ . Each type of experiment has been performed in two geometries. Structure 1 (insets of Fig. 1) is similar to the inelastic tunneling structures first shown to exhibit SERS by Tsang, Kirtley, and Bradley.<sup>18</sup> Structure 2 (insets of Fig. 2) is a new configuration. The four separate experiments will be referred to as experiments 1(a), 1(b), 2(a), and 2(b) [corresponding to Figs. 1(a), 1(b), 2(a), and 2(b), respectively].

A  $\text{CaF}_2$  layer, typically 400 Å mass thickness (thickness if smooth with bulk density), is used in experiments 1(a), 2(a), and 1(b) to produce reproducible and uniform-size roughness<sup>18</sup> features over areas of 5–10 cm<sup>2</sup>. In structure experiments 1(a) and 1(b) (Fig. 1 insets, structure 1), the  $\text{CaF}_2$  is evaporated onto a smooth Si substrate and then the remaining layers—Al (~2500 Å + 20–25 Å of aluminum oxide), scatterer (monolayer or  $t$  Å), spacer ( $d$  Å), and Ag (~200 Å)—are deposited on the rough  $\text{CaF}_2$ . In experiment 2(a) [Fig. 2(a) inset], the Al, scatterer, and spacer layers are deposited onto the smooth Si substrate, the  $\text{CaF}_2$  is

evaporated on top, and the Ag is deposited directly on the rough  $\text{CaF}_2$ . In experiment 2(b), a rough Ag film is evaporated directly on top of the polymer ( $t$  Å) with no  $\text{CaF}_2$  layer.

The PNBA in experiments 1(a) and 2(a) is deposited from solution onto the native Al oxide, spun dry,<sup>19</sup> then washed to remove all but the strongly chemisorbed first layer as discerned by infrared spectroscopy (IR).<sup>20</sup>

The polymers PMMA and PPNS were deposited by spin-coating techniques.<sup>19</sup> Thicknesses were measured by a combination of ellipsometry and reflection IR spectroscopy.<sup>21</sup> The PMMA in experiment 2(a) is uniform to  $\pm 2$  Å over the ~20 cm<sup>2</sup> sample area, and smooth on at least a several-hundred-angstrom scale by scanning electron microscopy (SEM) and x-ray photoemission spectroscopy (XPS) measurements.<sup>22</sup> The PPNS films are not as smooth, as indicated by slight opacity.

The Raman measurements were performed with ~40 mW of  $p$ -polarized 4880-Å argon-laser excitation in a line focus at 45° incidence with  $f/2.4$  optics, a SPEX double-grating monochromator (width ~9 cm<sup>-1</sup>) and standard photon-counting techniques. We obtain typical counting rates from the PNBA monolayer (no spacer,  $d=0$ ) of 10<sup>4</sup> counts/sec in structure 2. This corresponds to roughly 10<sup>6</sup> enhancement based on direct calibration with sodium  $p$ -nitrobenzoate in solution. Enhancements by a factor of ~3 × 10<sup>4</sup> are obtained

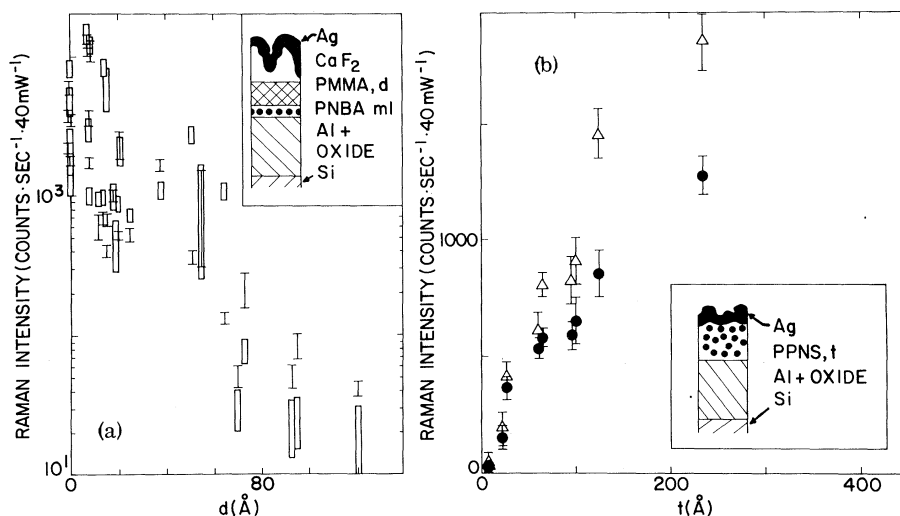


FIG. 2. (a) Spacer experiment 2(a) (inset shows sample configuration). Intensities of the 1595-cm<sup>-1</sup> (open symbols) and 1130-cm<sup>-1</sup> (closed symbols) peaks in the Raman spectrum of PNBA (logarithmic scale) vs  $d$ . The size of the symbols represents both measurement accuracy and variations of intensity for each mode over a 5-cm<sup>2</sup> sample area. (b) Thickness experiment 2(b) (inset shows the sample structure). Intensities of the 1596-cm<sup>-1</sup> (circles) and 1346-cm<sup>-1</sup> (triangles) Raman peaks of PPNS above background (linear scale) vs  $t$ . Error bars represent both measurement accuracy and sample uniformity.

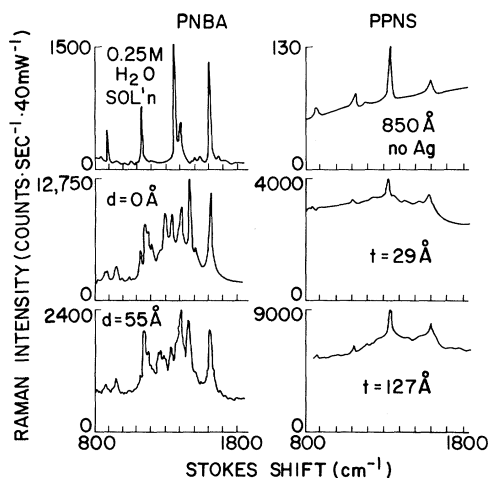


FIG. 3. Representative Raman spectra. Left panels, PNBA salt; right panels, PPNS polymer. At upper left is the spectrum of a water solution of Na-PNBA salt. At middle and lower left are SERS spectra of PNBA monolayers [experiment 2(a)] taken through a 200-Å Ag layer with 0- and 55-Å PMMA spacer thicknesses. At upper right is an ordinary Raman spectrum of 850-Å PPNS polymer. At middle and lower right are SERS spectra of different thicknesses of PPNS [experiment 2(b)]. The line under each spectrum represents the actual zero of intensity, and the maximum intensity (Raman scattering plus background) is listed for each spectrum in the figure.

with thin PPNS samples in experiment 2(b) for which calibration is done with use of unsilvered, thick PPNS layers. It is assumed in both cases that scattering from the entire layer is enhanced and the extinction coefficient of the Ag film is that of bulk silver.<sup>23,24</sup>

The results of the spacer and variable-thickness experiments are shown in Figs. 1(a), 1(b), 2(a), and 2(b), where the intensities of two Raman modes of the scatterer are plotted either as a function of spacer thickness  $d$  or scatterer thickness  $t$ . The SERS spectra of PNBA and PPNS in Fig. 3 resemble those of the carboxylate ion [Figs. 1(a) and 2(a)] or polymer [Figs. 1(b) and 2(b)], and reveal some interesting mode splittings and shifts.<sup>24</sup>

In order to make a definitive statement about the distance scale of SERS in the spacer experiments 1(a) and 2(a), it is crucial to determine whether or not there is actually any direct contact of the scatterer with the silver layer for  $d \cong 20\text{--}50 \text{ \AA}$ . To check for dissolution of the monolayer into the PMMA spacer, we carried out a series of experiments with structure-2(a) samples in which the rate of solution of PNBA mono-

layers in solvents was measured. The results<sup>24,25</sup> show that within the time of our Raman measurements ( $\sim 1\text{--}2 \text{ h}$ ), dissolution and diffusion of PNBA into the PMMA spacer layers is negligible. To check for pinholes in the PMMA layer, we ran a series of experiments in which water was used as a solvent to remove PNBA monolayers in type-2(a) samples with and without PMMA spacer layers. The results<sup>24,26</sup> show that a PMMA layer dramatically reduces the water dissolution of the PNBA and that its disappearance is far too slow to be caused by pinholes larger in size than molecular dimensions. Thus we can infer that SERS does not occur to any significant extent by direct contact of Ag and scatterer at the bottom of pinholes.

In each of our four experiments, SERS occurs over large silver-film-Raman-scatterer separations, decreasing by roughly a factor of 10 for 50 Å of separation. The additional signal due to an incremental thin PPNS layer below  $t = 100 \text{ \AA}$  in experiments 1(b) and 2(b) is consistent with the results of the spacer experiments 1(a) and 2(a). For  $t > 100 \text{ \AA}$ , the additional roughness of the PPNS may be causing more enhancement. We have ruled out enhancement mechanisms which require direct molecule-silver-film contact<sup>3-11</sup> in the spacer experiments 1(a) and 2(a). Both short-range<sup>3-11</sup> (molecule-silver-film separation  $d \sim 1 \text{ \AA}$ ) and long-range<sup>12-17</sup> ( $d \sim 10\text{--}30^3 \text{ \AA}$ ) enhancement mechanisms could possibly be at play at the same time in the variable-thickness experiments 1(b) and 2(b). We can set an upper bound of approximately a factor-of-10 enhancement for short-range mechanisms in these experiments.

The only experimental limitation on the systems which can be studied by SERS is that a known SERS enhancer must be brought within  $\sim 100 \text{ \AA}$  of the interface of interest. Amplification can be accomplished, for example, by direct contact with a rough silver film, or by spacing the film away from the surface in a number of possible geometries.<sup>24</sup>

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<sup>23</sup>In a calibration of the enhancements, the transmission (twice) through the rough  $\sim 200$ -Å silver layer on top of the scatterer must be taken into account. The quoted enhancements are with respect to the expected local Fresnel field intensity at the scatterer for smooth films. A uniform, smooth 200-Å-thick Ag film will transmit roughly 16% of the incident or scattered light.

<sup>24</sup>C. A. Murray, D. L. Allara, and M. Rhinewine, to be published elsewhere.

<sup>25</sup>A sample was fabricated with half the PNBA monolayer covered by a 50-Å PMMA layer for 20 h. Then all but 8 Å of the PMMA (and with it all dissolved PNBA) was removed by a chlorobenzene wash. The sample was then prepared with CaF<sub>2</sub> and Ag as usual. We discerned no change within our measurement accuracy of 4% in either the SERS intensity, or the IR absorption of the PNBA monolayer compared to half of the sample which had the PMMA washed off immediately after deposition.

<sup>26</sup>Soaking half a sample of PNBA monolayer on Al<sub>2</sub>O<sub>3</sub> in water for 5 min, then depositing CaF<sub>2</sub> and Ag as usual, reduces the SERS intensity on the water-soaked side by  $(60 \pm 8)$ %. However, on samples with a 50-Å layer of PMMA on top of the monolayer which were given the same treatment, the PNBA Raman intensity was only reduced after a 5-min water soak by  $(30 \pm 20)$ % on one sample and  $(4 \pm 5)$ % on another. If this reduction in PNBA Raman intensity is due to loss of PNBA by diffusion of H<sub>2</sub>O into and dissolved PNBA out of pinholes in the 50-Å PMMA layer, we can calculate an upper limit to the diffusion constant  $D$  of  $\sim 10^{-16}$  cm<sup>2</sup>/sec. The typical surface diffusion constants of small molecules through 100-Å-diam pores in a silica matrix are  $10^{-8}$ – $10^{-5}$  cm<sup>2</sup>/sec [H. Knozinger, in *The Hydrogen Bond*, edited by P. Schuster *et al.* (North-Holland, Amsterdam, 1976), Vol. 2, Chap. 27.] Thus the measured SERS intensity loss in our samples more closely resembles PNBA diffusion through a polymer network than removal of PNBA molecules at  $\geq 100$ -Å-scale pinholes.