Molecular adsorbates under high pressure: a study using surface-enhanced Raman scattering spectroscopy

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Abstract. Molecules adsorbed on metal surfaces were studied in a diamond anvil cell with Ar pressure-transmission medium up to several GPa pressure using Raman spectroscopy. The problem with studying molecules on surfaces is the small number density. This problem was overcome using photonic substrates to amplify the Raman intensity by factors of $10^6$ in the case of self-assembled monolayers on Ag-coated nanoarrays, where the probed region contained $\sim 10^9$ molecules, and $>10^9$ in the case of the dye Rhodamine 6G on Ag nanoaggregates, where $<10^6$ molecules were probed. Pressure effects on the adsorbate vibrations and on the underlying nanostructures are discussed.

1. Introduction
Molecules adsorbed on metal surfaces often assume unique conformations and possess unique chemical reactivity compared to their bulk counterparts. Studies of molecular adsorbates under pressure are relevant to applications such as lubrication, tribology and heterogeneous catalysis. One of the most interesting features of such systems is that the adsorbates exist at interfaces between metal surfaces and the pressure-transmitting medium, and the molecular species are much more compressible than the underlying metal medium. However such measurements must overcome a major obstacle: the number density of surface molecules is small. For instance a molecular crystal small enough to fit into a diamond anvil cell (DAC) may contain $10^{16}$ molecules, whereas the surface of the crystal will have only $\sim 10^9$ molecules at full-surface coverage, and even fewer molecules at lower coverages. Therefore, highly sensitive spectroscopic techniques are required for such studies.

Vibrational spectra reveal detailed information about the state of molecules, and for this reason, Raman scattering has been frequently used to study molecules in DACs. Raman is an insensitive spectroscopic method, but it is possible to amplify Raman spectra by factors of $10^6$ or more using surface-enhanced Raman scattering (SERS) [1]. In SERS, the analyte molecules are adsorbed on nanotextured metal surfaces. The noble metals Au and Ag work best. An incident laser beam excites localized surface plasmon resonances (LSPR) of the nanotextured metal. Optimal SERS enhancement occurs when the LSPR is in resonance with both the incoming laser and the outgoing Stokes-Raman photons [2]. In such cases, the surface plasmons act like resonant cavities that cause the electric fields of both the incident laser beam and the outgoing Raman-shifted light to build up, enhancing both local field strengths by a factor $\eta$. The Raman intensity is then proportional to $\eta^4$, so a plasmonic enhancement of 30, which is readily attainable, is enough to amplify the Raman intensity by $10^6$. The LSPR can be tuned by varying parameters such as nanoparticle sizes, geometries, state of aggregation.
and dielectric environment [3]. So in our experiments, pressure can affect both the adsorbate vibrations and the SERS intensities by pressure-tuning of the LSPR. An additional mechanism for Raman enhancement of several orders of magnitude occurs when the adsorbate has an electronic transition in resonance with the laser. This resonantly-enhanced SERS process provides the ultimate in sensitivity, so that even single molecule Raman spectra can be obtained [4, 5].

In this study we describe the use of SERS to study two kinds of adsorbate systems in DACs that are depicted in figure 1. The system in figure 1a consists of a fully-dense monolayer formed from benzenethiol (BT) on Ag. This is a highly-ordered adsorbate lattice termed a self-assembled monolayer (SAM). The average SERS enhancement was provided by a crystalline array of polymer nanospheres coated with Ag was measured to be 9(±4)×10^7, underlying which is a distribution ranging from 2.8×10^4 to 4.1×10^10 [6]. The system in figure 1b consists of Ag nanoparticle aggregates precipitated from solution, with a small amount of absorbed Rhodamine 6G dye (R6G). The combination of the surface and the resonance Raman effect leads to 10^{14} ~ 10^{15} fold increase in R6G Raman scattering [7]. The R6G/nanoparticle aggregate structure was stabilized by embedding it in a polymer, poly-vinyl alcohol (PVA).

2. Sample preparation

2.1. Self-assembled monolayers on Ag-coated nanoarrays

The nanoarray substrate was a 15 μm Mylar® film whose surface was made hydrophilic with a sputtered coating of 25 nm of SiO₂. A drop of aqueous suspension of 320 nm polystyrene spheres (Thermo Scientific) was evaporated on the surface to form a close-packed nanosphere lattice, and 200 nm of Ag were sputtered onto the nanospheres. The sphere diameter and Ag thickness were those that optimize the array for 532 nm laser Raman scattering. The SAM was deposited by soaking the array in a 1mM solution of BT in ethanol for several hours. A scalpel was used to slice a tiny piece of the array that fit into the anvil.

2.2. Rhodamine 6G adsorbed on Ag nanoaggregates

The Ag nanoparticle aggregates were prepared according to Lee and Meisel’s method [8]. Five milliliters of the suspension were mixed with 50 μL of 10⁻³ M R590 chloride (Exciton) in water, and vortexed for 30 s. Afterwards 5 ml of 20 mM NaCl solution were added to assist nanoparticle aggregation [9], following by another 30 s vortexing. The 10 ml suspension was incubated for 1.5 hour. To remove the free R6G in the solution phase, the suspension was centrifuged at 10⁴ rpm for 15 minutes. The precipitate was mixed with 0.01% sodium citrate solution and redispersed by vortexing. Replacing the supernatant with Milipore water resulted in nanoparticle flocculation. This process was repeated until the R6G concentration of the supernatant fell below 1nM. The precipitate from the final centrifugation was mixed with 1.6 g 5% poly vinyl alcohol (PVA) in 0.01% sodium citrate solution. The mixture was drop-coated onto a 2”×2” glass plate cleaned with Piranha solution (H₂SO₄: H₂O₂ =
and air-dried to form a greenish yellow film, and a small chip of the film peeled off, cut to size and inserted into the DAC. The total number of R6G molecules added to the solution was $10^{14}$ R6G. However, due to the repeated washing process and the scale of laser spot (0.03 mm in diameter) compared to the original sample ($2'' \times 2''$), the number of R6G molecules in the probing volume was estimated to be $\sim 10^6$. However, many, or possibly even most of the R6G molecules were not located at nanoparticle junctions where the SERS enhancement factors are the largest [10], so the total number of molecules contributing to the SERS signals may be much smaller.

3. Experimental

The DAC was a Merrill-Basset cell, and Ar was the pressure transmission medium. The gaskets were BeCu. Spectra were acquired 30 min after each pressure adjustment. The Raman apparatus used a 30 mW, 532nm laser (doubled Nd:YVO₄). Ruby chips in the DAC were excited by the same laser. Raman and fluorescence spectra were detected by a Shamrock 303i spectrograph (Andor) with a PIXIS 256 CCD camera (Princeton instruments). The reflectance spectra of the nanosphere arrays and the extinction spectra of the nanoaggregates were used to determine the LSPR spectra. The samples were illuminated by a Tungsten-Halogen lamp (Ocean optics, HL-2000), and the spectra were acquired with an Ocean Optics USB4000 spectrometer.

4. Results and discussion

Some SERS spectra of BT SAM in the DAC are shown in figure 2. We had previously studied the pressure-induced shifting of Raman transitions of the BT and other SAMs in a DAC. We found the adsorbate shifts were quite similar to molecules in a bulk solid [11, 12] and there was little hysteresis in the shift with increasing and decreasing pressures. Now we have studied pressure effects on the LSPR spectra of the nanosphere array, as shown in figure 3. The LSPR has a broad resonance in the 450-675 nm range, with a peak at 620 nm (figure 3a). Upon application of a small amount of pressure (0.7 GPa), dramatic changes in the LSPR spectra were observed, but these changes had little effect on the SERS intensities (figure 2). The LSPR resonance split into two peaks, at 500 nm and 750 nm, and neither peak was as intense as the original peak. Increasing the pressure to 6 GPa caused the two peaks to redshift, but continued pressure increase up to 6.9 GPa had minimal effect on the LSPR. The structures near 900 nm in figure 3 were artifacts caused by low grating efficiency.

![Figure 2](image-url)

**Figure 2.** The SERS spectra of benzenethiol self-assembled monolayers on Ag-coated nanosphere arrays in a DAC.

![Figure 3](image-url)

**Figure 3.** The LSPR spectra of Ag film coated nanosphere arrays. The green dashed line indicates the laser wavelength.
The LSPR will redshift when the nanoparticle size is increased \cite{13}. The redshift has been attributed to increased separation of image charges on opposite surfaces of the nanoparticles, which weakens the restoring force and lowers the LSPR frequency. In our case, where the sample was under compression, a reasonable explanation for the redshift is that the forces exerted by the pressure medium on the Ag-coated polymer spheres deforms the spheres anisotropically because only one-half of each sphere is in contact with the more incompressible Ag. The anisotropic compression breaks the radial symmetry, causing the LSPR to split into two bands. The higher-energy band, which shifts from 620 to 500 nm, fortuitously remains in resonance with the laser and the Stokes photons, so the SERS signal intensities were not significantly weakened with increasing pressure.

![Figure 4](image1.png)

**Figure 4.** The SERS spectra of R6G adsorbed on Ag nanoaggregates. Blue arrows point to that two Raman bands analyzed in figure 6.

![Figure 5](image2.png)

**Figure 5.** The LSPR spectra of Ag nanoparticle aggregates under different pressures.

The SERS spectra of R6G adsorbed on Ag nanoaggregates at various pressures are shown in figure 4, and the LSPR spectra of the nanoaggregates are shown in figure 5. The peak shifts of two of the more intense R6G Raman bands (610 cm$^{-1}$ and 1647 cm$^{-1}$) are plotted at a few pressures in figure 6a. The magnitudes of the pressure-induced vibrational blueshifts were unremarkable. There was a small amount of hysteresis in the shift behavior with pressure increasing or decreasing. The hysteresis was attributed to the slow relaxation of the PVA polymer, and this attribution was strengthened when we noticed the pressure blueshift could increase a few cm$^{-1}$ if the sample were held at constant high pressure overnight.

In figures 6a and 6b we also plot the integrated areas of these two SERS transitions versus pressure. Between zero pressure and 1 GPa, there was a significant loss of SERS intensity, but above 1 GPa the intensity varied little. When the pressure was gradually decreased to <1 GPa, some of the intensity recovered, but it never returned to its original level. These responses of the SERS intensities to high pressure were consistent with what was observed with the nanoparticle aggregate LSPR spectra in figure 5. The LSPR resonance was broad due to inhomogeneity in the nanoaggregate suspension, and it did not shift much with pressure. But when pressure was first applied the intensity dropped significantly, and only partially recovered when the sample was unloaded, even if we waited hours.

We were concerned about using LSPR intensities to interpret the R6G SERS intensities, due to the small number of R6G molecules being detected. Pressure-induced changes in the LSPR spectra, representing an average over the nanoaggregate ensemble, may not be representative of the R6G
molecules being detected by SERS. The R6G signals preferentially arise from R6G molecules that happen to be near nanoparticle junctions, and due to the low R6G concentration, many or even most nanoaggregates may not have R6G at such junctions. However the seemingly close correlation between the pressure-dependence of the SERS intensities and LSPR intensities appears to obviate this concern. Such concerns would not be expected to be an issue for the SAM experiments, since the SAM uniformly coats the entire Ag surface of the nanoarray, and the nanoarray itself has a highly-ordered structure with minimal inhomogeneity.

The mechanism that led to the irreversible loss of SERS intensity in the nanoaggregates, but not in the nanoarrays is not understood yet. We do note that the arrays consist of polymer spheres with an Ag coating, whereas the aggregates consist of Ag nanoparticles, and Ag nanoparticles are known to have a phase transition at 2 GPa that has been observed by X-ray diffraction [14]. Another possibility is that high pressure caused a mechanical distortion of the interparticle sites that had adsorbed R6G molecules and were responsible for most of the R6G SERS signal. The mechanical distortion reduced the local field enhancement at those sites, and lead to significant changes in the SERS intensity. For this to be the case we would have to postulate that other, less favorable sites were not improved by high pressure.

![Figure 6](image)

**Figure 6.** (a) Peak shifts and integrated peak areas of R6G 1647 cm\(^{-1}\) in-plane CH bending mode plotted against pressure. (b) Peak shifts and integrated peak areas of 610 cm\(^{-1}\) ring deformation mode plotted against pressure. The samples were allowed to equilibrate for 30 minutes at each pressure. In each figure there is a pair of solid blue circles that represent measurement at the same pressure, where the sample was allowed to equilibrate overnight. The longer equilibration time led to a small redshift, which was attributed to slow relaxation of the PVA polymer matrix.

5. Conclusions
We studied the effects of pressure on the SERS spectra of two types of molecular adsorbates, and the LSPR spectra of the nanotextured Ag substrates that supported the adsorbates and provided the SERS enhancements. The pressure vibrational blueshifts of both the BT and R6G adsorbates were unremarkable, but pressure effects on the LSPR spectra and the SERS enhancement factors (as judged by the SERS intensities) were significant. The nanoarray LSPR spectrum split into two peaks, presumably due to pressure-induced deformations of the polymer nanoparticles. However, the splitting was such that the SERS intensities were not affected much. The LSPR spectra of the nanoaggregates lost intensity when pressure was applied, which resulted in a diminishment of SERS signals, and the intensity loss only partially recovered when pressure was released. Both of these SERS materials were fabricated using well-known procedures that optimized the ambient-pressure SERS intensity at the excitation wavelength of 532 nm. It might be possible to develop methods to fabricate SERS materials that are suboptimal at ambient pressure, but improve as pressure is increased. A remarkable feature of these studies was the small number of molecules contributing to the Raman
spectra, and in fact with the R6G-nanoaggregate system it might someday be possible to study single-molecule Raman spectra at high pressure.

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