Detection of Molecular Monolayers by Optical Second-Harmonic Generation

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Second-harmonic generation is shown to be sensitive enough to detect molecular mono-layers adsorbed on a silver surface. Adsorption of AgCl and pyridine on silver during and after an electrolytic cycle can be easily observed.

Detection of molecular monolayers at an interface is a subject of great importance in surface science.[1] Various techniques have been invented for this purpose. Recently, we have been interested in developing nonlinear optical techniques for detecting adsorbed molecules.[2] The second-order nonlinear optical effects are particularly interesting. In a medium with inversion symmetry, the second-order nonlinear susceptibility vanishes in the bulk in the electric-dipole approximation.[3] The surface layers of atoms or molecules, however, do not possess inversion symmetry. In addition, the molecules may be aligned, or they may interact with the neighboring medium, or both. Then, the electric-dipole contribution of a surface molecular layer may contribute as much to the second-harmonic generation (SHG), for example, as the electric-quadrupole and magnetic-dipole contribution of several hundred molecular layers in the bulk. In this respect, a monolayer of adsorbed molecules on a surface could generate as much second harmonic (SH) as a molecular film of several hundred angstroms thick. It was often believed that SHG from monolayers of adsorbed molecules would be difficult to detect. In this Letter, we show that this is a wrong conception; SHG by adsorbed molecular monolayers on a metal surface is in fact easily observable. This is particularly true in the presence of a surface enhancement due to the local-field correction resulting from surface roughness.[4,5]

The theory of SHG from a thin slab of nonlinear material has been worked out by Bloembergen and Pershan.[6] Applying their result to a uniform monolayer of adsorbed molecules at a metal-dielectric interface, we find that the generated SH signal is given by

$$S \simeq (128\pi^3\omega/\hbar c^3)|N_a\alpha^{(2)}|^2 I_1^2 AT$$

$$\text{photons/pulse,} \qquad (1)$$

where N_a is the number of molecules per unit area, $\alpha^{(2)}$ is the second-order nonlinear polariza-bility, I_1 is the intensity of the fundamental pump beam incident at 45°, A is the beam cross section, T is the pulse duration, and ω is the second-harmonic frequency. If $\alpha^{(2)} \sim 1 \times 10^{-29}$ esu, $N_a \sim 4 \times 10^{14}$ cm^{-2}, $I_1 \sim 1$ MW/cm^2 at 1.06 μm, $A = 0.2$ cm^2, and $T = 10$ nsec, we have $S \simeq 1.5 \times 10^3$ photons/pulse. This signal is distinguishable from that generated by the metal surface, ~ 20 photons/pulse for silver, with the same input.[7] Thus, even without surface enhancement, SHG from a monolayer of adsorbed molecules with $|N_a\alpha^{(2)}| \gtrsim 10^{-15}$ esu should be easily detectable.

We study here SHG by adsorbed molecules on silver in an electrolytic process. The experiment was carried out with use of a Q-switched Nd:YAlG (neodymium-doped yttrium aluminum garnet) laser operating at 1.06 μm, 10 pulses/sec, and a 10 nsec pulse width. The laser beam was incident at 45° on a bulk silver sample with TM polarization. The sample was mechanically polished and then, together with the platinum working electrode and the reference saturated calomel electrode (SCE), was submerged in an electrolytic cell containing 0.1M KCl in doubly distilled water. The silver surface was initialized by two or three electrolytic cycles with a charge transfer of ~ 65 mC/cm^2 per cycle. Formation of AgCl at the silver electrode and the subsequent reduction of AgCl back to silver resulted in substantial roughening of the sample surface.

Second-harmonic reflection from the silver surface was easily detected, even with a laser energy of < 0.6 mJ/pulse over 0.2 cm^2. The signal was recorded with a photomultiplier and gated integrator, with use of spatial filtering, color filters, and a monochromator or interference filter to reject the pump laser. By monitoring the SH signal during the electrolytic cycle, the change in the signal resulting from the appearance and disappearance of AgCl could be observed, as shown in Fig. 1. With a current of 500 μA/cm^2, the signal rose and fell rapidly at the beginning and end
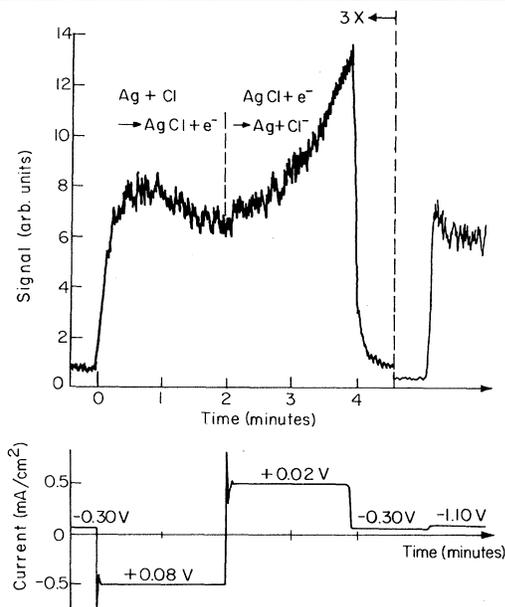
FIG. 1. Current and diffuse second-harmonic reflection as functions of time during and after an electrolytic cycle. The voltages listed on the lower curve are V_{Ag-SCE}. $0.05M$ pyridine was added to the $0.1M$ KCl solution following the completion of the electrolytic cycle.

FIG. 2. Diffuse second-harmonic signal vs V_{Ag-SCE} following an electrolytic cycle, with $0.05M$ pyridine and $0.1M$ KCl dissolved in water.

of the cycle, and changed relatively slowly during the cycle. This result suggests that the SH signal mainly originated from a few layers of AgCl at the surface. This is expected since bulk AgCl has inversion symmetry. To determine more quantitatively how the surface AgCl layers contributed to the SHG, we time resolved the sharp decrease in the SH signal at the end of a cycle by limiting the current there to 60 μA/cm². The observed amount of charge transferred during the fall of the signal corresponded to an average of three to four monolayers of AgCl. In fact, the deposition and removal of AgCl on silver were not expected to be uniform. The rise and fall of the SH signal were probably related to the fractional coverage of the silver surface by AgCl.

Because of the rough silver surface, the observed SHG from the surface was angularly diffuse and unpolarized, with or without adsorbed molecules. That the signal was indeed SHG was verified by its quasimonochromatic character at 0.53 μm. It also had a pulse shape closely resembling that of the pump pulse. With the electrolytic cycle interrupted to prevent further formation or reduction of AgCl, the SH signal showed a quadratic dependence on the incident la-

ser power. The magnitude of the increase in the second-harmonic signal resulting from AgCl was somewhat sensitive to the initial sample preparation and the incident laser fluence. At higher laser fluences, e.g., 30 mJ/cm², the SH signal versus time during the electrolytic cycle was also qualitatively different, even though the characteristic sharp rise and fall at the beginning and end of the cycle remained the same. This is presumably due to laser heating, and to desorption and readsorption of molecules on silver. With identical conditions, however, the SH signal versus time was reproducible. Depending on the exact experimental parameters, the maximum SH signal during a cycle was found to be 5–25 times larger than the signal before and after the cycle.

In surface-enhanced Raman scattering,[5,8] it has been established that approximately a monolayer of pyridine molecules can be adsorbed on silver by a negative bias in an electrolytic solution following an electrolytic cycling. The maximum Raman signal of pyridine appeared in the range -0.6 V $> V_{Ag-SCE} > -0.9$ V, where V_{Ag-SCE} is the voltage between the silver and the reference SCE.[8] From our result on SHG from adsorbed AgCl, we anticipated that a monolayer of adsorbed pyridine molecules on silver could also yield a detectable SH signal. Indeed, with pyridine $(0.05M)$ added in the previous electrolytic solution, the SH signal rose rapidly immediately following the electrolytic cycle when $V_{Ag-SCE} < -0.6$ V. This is shown explicitly in Fig. 1. The maximum increase of ~ 50 times in the SH signal was obtained with $V_{Ag-SCE} \sim -1.0$ V. Figure 2 shows the SH signal versus V_{Ag-SCE} immediately after the electrolytic cycle

with and without 0.05M pyridine in the electrolytic solution. The results clearly indicate that SHG from a monolayer of pyridine is easily observable. We also observed SHG associated with a monolayer of CN^- adsorbed to silver. The relative increase of as much as 40–50 times in the SH signal due to adsorbed pyridine was not very sensitive to the strength of electrolytic cycling and hence the resulting surface roughness, even though the absolute magnitude may be different. This is consistent with the picture that adsorption of pyridine on Ag is responsible for the increased SH signal. With an input of ~ 0.2 mJ/pulse in 0.2 cm^2 at the sample, the maximum SH signal from adsorbed pyridine corresponded to a total of $\sim 8 \times 10^5$ photons/pulse, integrated over the 2π sr emission solid angle. Assuming a 10^4 local-field enhancement due to surface roughness in the SH signal,[4] we estimate $\alpha^{(2)} \sim 2 \times 10^{-29}$ esu for adsorbed pyridine from Eq. (1). For comparison, $\alpha^{(2)}$ for monosubstituted and disubstituted benzene molecules is typically $\sim 10^{-30}$ esu.[9]

We found that when the 0.05M pyridine was dissolved into the electrolytic solution a few minutes after the completion of an electrolytic cycle, an increase of only ~ 20 times in the SH signal occured at $V_{\text{Ag-SCE}} = -1.0$ V. The time delay had apparently led to a partial coverage of the cleaned Ag surface by other molecules that prevent the adsorption of pyridine.

Adsorption of pyridine molecules to the Ag surface appears necessary for the strong SH signal from pyridine, and electrolytic cycling is necessary for cleaning the surface in order for pyridine to be adsorbed. For example, using a 1000-Å freshly evaporated Ag film in the electrolytic solution with 0.05M pyridine, we observed, before electrolytic cycling, no increase in the SH signal from adsorbed pyridine molecules with a negative $V_{\text{Ag-SCE}}$. But, following a weak electrolytic cycle with a charge transfer of only ~ 2 mC/cm^2 corresponding to an average removal of only eight layers of silver, an increase of ~ 10 times in the angularly diffuse SH signal was readily seen at $V_{\text{Ag-SCE}} = -1.0$ V. When the incident pulsed laser energy was increased to 30 mJ/cm^2 (at 10 Hz), the SH signal from adsorbed pyridine decreased to an intermediate value with a ~ 15 sec decay time. This relaxation to a new steady state presumably results from competition between laser desorption and electrically driven molecular adsorption.

During and after a weak electrolytic cycling of 2 mC/cm^2, the evaporated silver film remained optically smooth, and showed very little change in its specular-reflection property. The collimated SH signal also remained nearly unchanged, while the diffuse SH signal changed drastically as described earlier. This is consistent with the picture of a nonuniform polarization resulting from the adsorbed molecules. Through the local field effect, the diffuse SH signal could be strongly enhanced. This was confirmed by scanning electron micrographs which showed a very non-uniform coverage of AgCl on the silver film.

In conclusion, we have demonstrated that a single monolayer of adsorbed molecules can give rise to an easily observable second-harmonic signal. Extension to sum and difference frequency generation should allow us to do spectroscopy on adsorbed molecules via resonant enhancement. This should then provide a sensitive high-resolution probe of various interfaces. Work is presently in progress along this line.

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