Title
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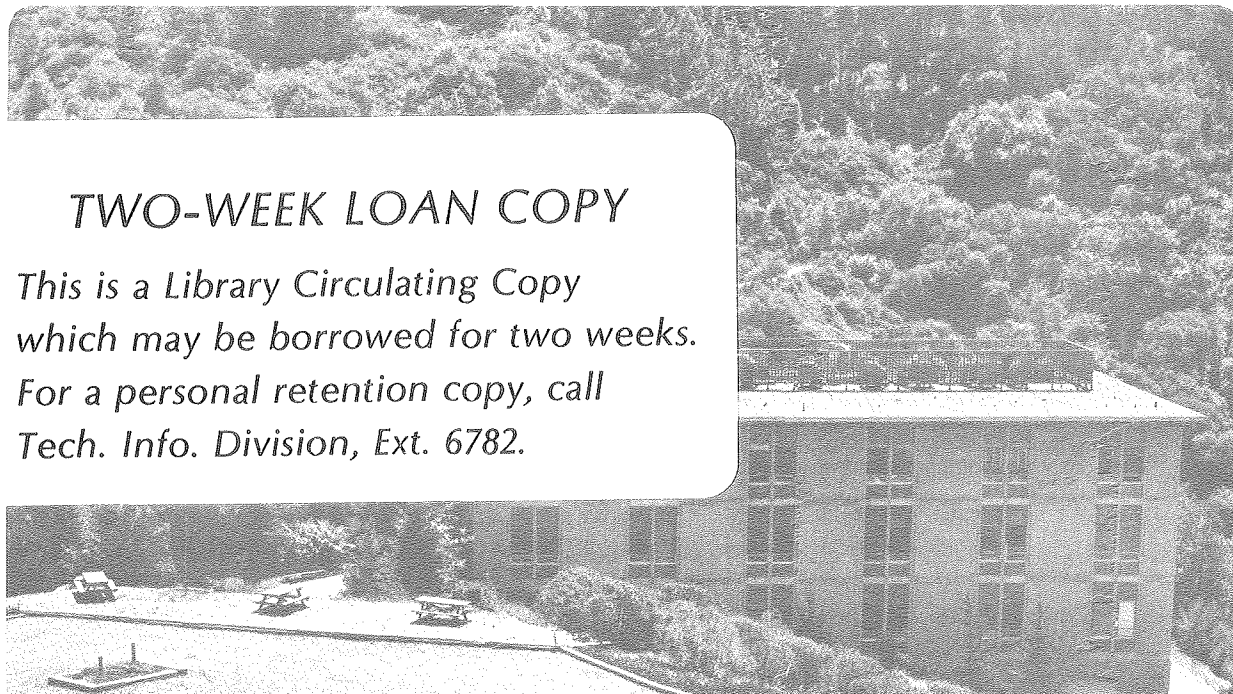DETECTION OF MOLECULAR MONOLAYERS BY OPTICAL
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C.K. Chen, T.F. Heinz, D. Ricard, and Y.R. Shen

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DISCLAIMER

DETECTION OF MOLECULAR MONOLAYERS BY OPTICAL
SECOND HARMONIC GENERATION

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ABSTRACT

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

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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 Å 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

$$S \simeq \frac{128\pi^3\omega}{\hbar c^3} \left| N_a \alpha^{(2)} \right|^2 I_1^2 AT \quad \text{photons/pulse} \tag{1}$$

where N_a is the number of molecules per unit area, $\alpha^{(2)}$ is the second-order nonlinear polarizability, 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 $S \simeq 1.5 \times 10^5$ 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 $\left| N_a \alpha^{(2)} \right| \gtrsim 10^{-15}$ esu should be easily detectable.

We study here SHG by adsorbed molecules on silver in an electrolytic process. The experiment was carried out using a Q-switched Nd:YAG laser operating at 1.06 μm, 10 pulses/sec, and a 10 nsec pulsewidth. 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 0.1 M KCℓ in doubly distilled water. The silver surface was initialized by two or three electrolytic cycles with a charge transfer of ~ 65 m Coul/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 de-

tected, 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, using

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 ap-

pearance and disappearance of AgCℓ could be observed, as shown in Fig.

1. With a current of 500 $\mu A/cm^2$, the signal rose and fell rapidly at

the beginning and end of the cycle, and changed relatively slowly dur-

ing the cycle. This result suggests that the SH signal mainly origin-

ated 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 $\mu A/cm^2$. 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 sur-

face was angularly diffuse and unpolarized, with or without adsorbed

molecules. That the signal was indeed SHG was verified by its quasi-

monochromatic character at 0.53 μm. It also had a pulse shape closely

resembling that of the pump pulse. With the electrolytic cycle inter-

rupted to prevent further formation or reduction of AgCℓ, the SH signal

showed a quadratic dependence on the incident laser power. The magni-

tude of the increase in the second harmonic signal resulting from AgCℓ
was somewhat sensitive to the initial sample preparation and the inci-
dent laser fluence. At higher laser fluences, e.g. 30 mJ/cm^2, 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 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 elec-
trolytic 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
(.05 M) 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
$\sim$ 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 0.05 M pyridine in the electrolytic solution.
The results indicate clearly 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 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 mono and disubstituted benzene molecules is typically $\sim 10^{-30}$ esu.[9]

We found that when the 0.05 M 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_{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 0.05 M pyridine, we observed, before electrolytic cycling, no increase in the SH signal from adsorbed pyridine molecules with a negative V_{Ag-SCE}. But, following a weak electrolytic cycle with a charge transfer of only ~ 2 m Coul/cm^2 corresponding to an average re-

moval of only eight layers of silver, an increase of ~ 10 times in the

angularly diffuse SH signal was readily seen at $V_{Ag-SCE} = -1.0$ 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 m Coul/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 non-uniform 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 ad-

sorbed molecules can give rise to an easily observable second harmonic

signal. Extension to sum and difference frequency generation should al-

low us to do spectroscopy on adsorbed molecules via resonant enhance-

ment. This should then provide a sensitive high-resolution probe of

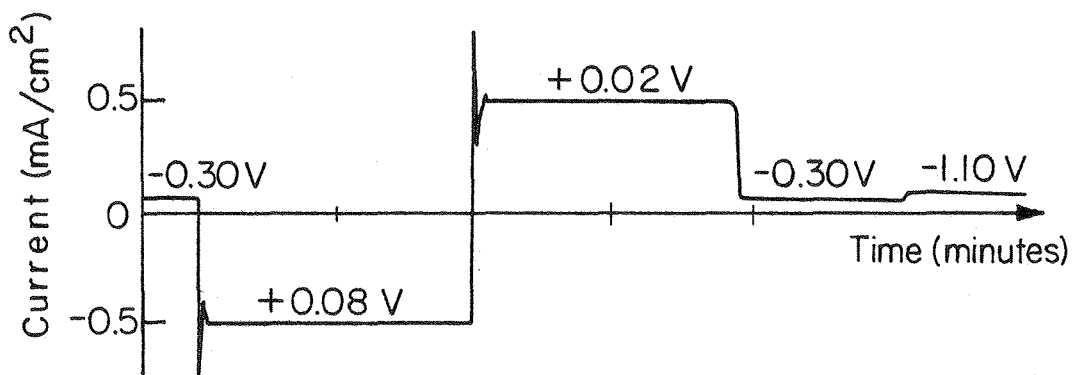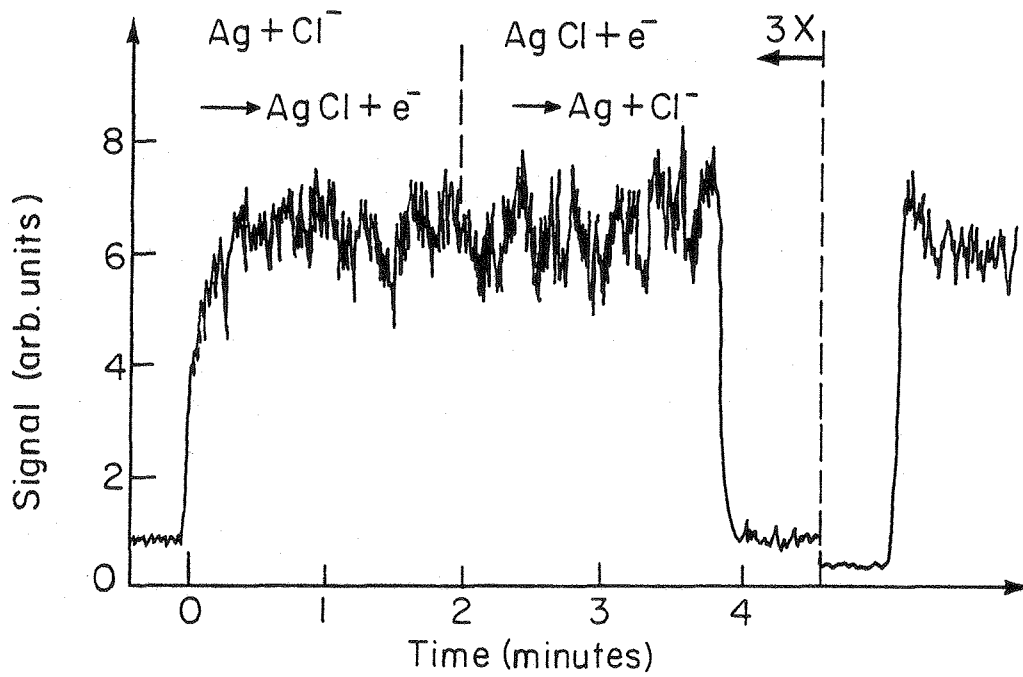various interfaces. Work is presently in progress along this line.

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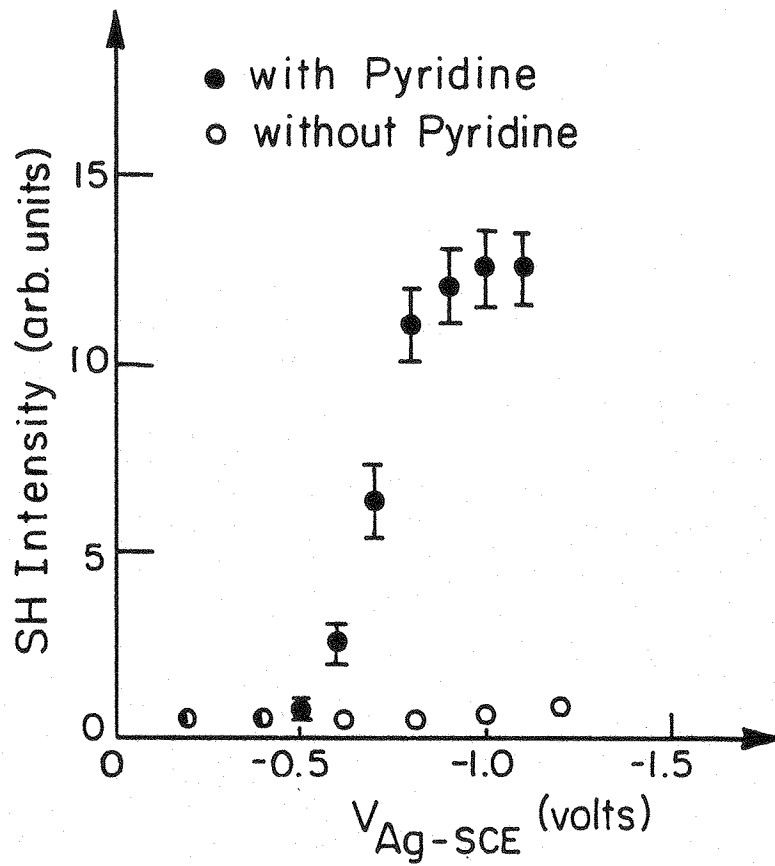
References:

1. See, for example, G. A. Somorjai and M. A. Van Ho e, Adsorbed Mono-
    layers on Solid Surfaces (Springer-Verlag, 1979); G. Ertl and J.
    Küppers, Monographs in Modern Chemistry, Vol. 4, series ed. H. F.
    Ebel (Verlag Chemie, 1974).

2. C. K. Chen, A. R. B. de Castro, Y. R. Shen, and F. DeMartini, Phys.
    Rev. Lett. 43, 946 (1979).

3. See, for example, N. Bloembergen, Nonlinear Optics (W. A. Benjamin,
    1977) p. 9.

4. C. K. Chen, A. R. B. de Castro, and Y. R. Shen, submitted to Phys.
    Rev. Lett.

5. See T. E. Furtak and J. Reyes, Surf. Sci. 93, 351 (1980) and refer-
    ences therein for a recent review of surface enhanced Raman spectros-
    copy.

6. N. Bloembergen and P. S. Pershan, Phys. Rev. 128, 606 (1962).

7. N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev.
    174, 813 (1968).

8. D. L. Jeanmaire and R. P. Van Duyne, J. Elec. Chem. 84, 1 (1977);
    M. Fleishmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett.
    26, 163 (1974).

9. J. L. Oudar and H. LePerson, Opt. Comm. 15, 258 (1975); J. L. Oudar,
    Ph.D Thesis, Université Pierre et Marie Curie, Paris (1977).

Figure Captions

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 $V_{Ag\text{-}SCE}$. 0.05 M pyridine was added to
the 0.1 M KCℓ solution following the completion of the electro-
lytic cycle.

Fig. 2 Diffuse second harmonic signal versus $V_{Ag\text{-}SCE}$ following an elec-
trolytic cycle, with 0.05 M pyridine and 0.1 M KCℓ dissolved in
water.

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