Title

SECOND-HARMONIC GENERATION FROM SUB-MONOLAYER MOLECULAR ADSORBATES USING A CW DIODE LASER - MAUI SURFACE EXPERIMENT

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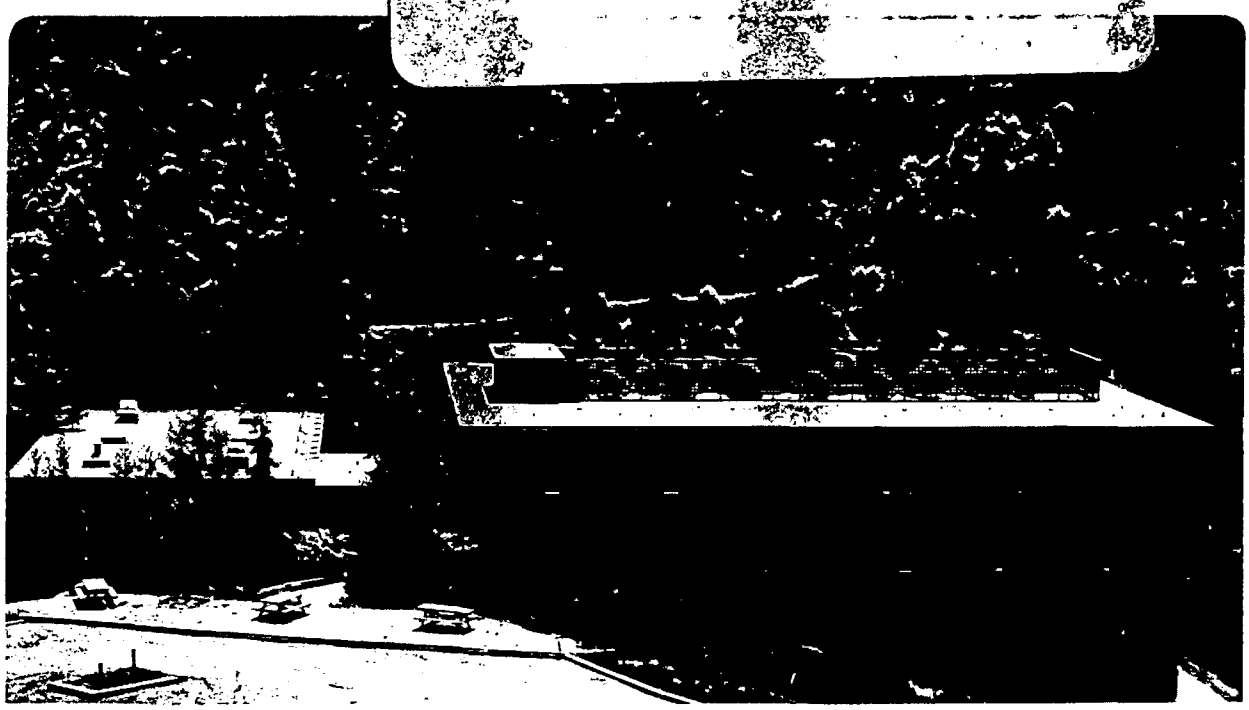

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DISCLAIMER

Second-Harmonic Generation from Sub-Monolayer Molecular Adsorbates Using a CW Diode Laser - Maui Surface Experiment

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Optical second-harmonic generation (SHG) can be an extremely sensitive tool for surface studies. The technique is capable of probing adsorbed molecules at various interfaces [1]. It is based on the idea that SHG is forbidden in a medium with inversion symmetry, but necessarily allowed at a surface. To see such a surface nonlinear optical effect, high laser intensity is often needed. Thus, in the experiments reported so far, pulsed lasers were used exclusively. From the consideration for practical applications, however, the technique would look much more attractive if the bulky pulsed laser can be replaced by a simple inexpensive CW diode laser. We demonstrate here at this conference that this is indeed possible. The work, described below, also constitutes the first experiment of surface SHG carried out with a CW laser.

The system we choose to probe is the surface of the silver electrode in an electrolytic cell containing a water solution of 0.1 M KCl and 0.1 M pyridine. Following appropriate electrolytic cycling, a sub-monolayer of pyridine can be adsorbed on or desorbed from Ag by applying proper biasing. It was shown earlier [2] that because of surface enhancement [3], such a system yields unusually strong SH signals. We therefore use it as our test system. We shall show, however, that with future improvement on the diode laser and the detection system, the surface enhancement will not be necessary.

The CW diode laser was purchased from Sharp (LT024MD). It emits 20 mW at 784 nm at room temperature. The laser beam is focused to a ~ 100 μm^2 spot on the Ag electrode and the diffuse second-harmonic light generated is collected by a photomultiplier with appropriate filtering. The laser is modulated at 500 Hz so that the signal can be processed by a lock-in amplifier.

Figure 1 shows the second-harmonic intensity and the electrolytic current as a function of time. We began with an SH signal from a monolayer of pyridine adsorbed on Ag with a negative bias potential, -0.78V, on Ag (relative to a standard calomel electrode). The signal corresponds to ~ 4000 photons/second at the photodetector. At $t = 0$, the bias potential is switched from -.78 to +0.08V, and the SH signal drops abruptly as pyridine is desorbed from Ag. The residual signal at $t > 0$ arises from AgCl layers formed on Ag [2]. Since SHG is only sensitive to the first one or two surface AgCl layers, the signal does not vary appreciably with the multilayer formation or reduction of AgCl on Ag. At $t = 2$ min, the bias potential is switched from +0.08 to -0.01V, and the AgCl layers start being reduced. The reduction is complete at $t \sim 5$ min when the bias potential drops to -0.78V and the monolayer of pyridine again gets adsorbed on Ag. The process is readily repeatable. The signal is confirmed to be from SHG by its quadratic power dependence and spectral purity. The dominant noise source in the present case is the dark current in the photodetector.

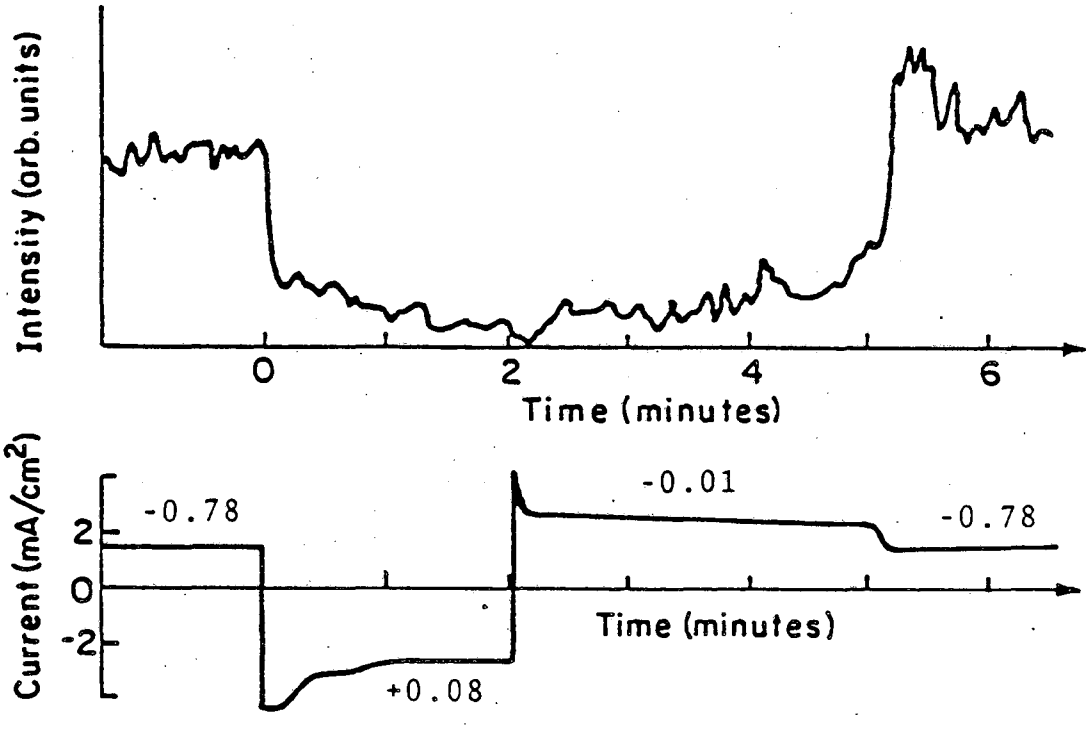

Fig. 1 SH intensity (top) from the Ag electrode and cell current (bottom) vs time. Ag bias potentials are relative to a standard calomel electrode

The above results indicate that one can indeed monitor the adsorption of a monolayer of molecules on an electrode in an electrolytic cell by SHG using a single diode laser. If 100-mW diode lasers become available and focusing of the laser beam to 10 μm^2 is possible, then a signal of $\sim 4 \times 10^6$ photons/sec from pyridine on a Ag electrode could be obtained. With such a setup, even monolayer adsorbates on smooth substrates (without surface enhancement) would be easily detectable. Further improvement could be made by using a diode array and a photon counting detection system.

In conclusion, we have demonstrated that surface SHG using a CW diode laser to study surfaces and interfaces is feasible. Compactness of the setup could make this system an extremely attractive and useful surface tool. Among the many applications of such a system, we only mention here the possibility of an optical second-harmonic surface microscope, capable of displaying surface structure and morphology with sub-micron resolution.

This experiment was conceived at the Maui Surf Hotel, Kaanapali Beach, Maui, Hawaii. We wish to thank the Hotel for its hospitality in accomodating the preparation of this experiment in its Queen Suite and the subsequent demonstration in its conference hall. GTB and YRS acknowledge partial support from the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and TWH acknowledges partial support from the U.S. Office of Naval Research under Contract No. ONR N00014-C-78-0304.

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