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OPTICAL SECOND-HARMONIC GENERATION FROM A MONOLAYER
OF CENTROSYMMETRIC MOLECULES ADSORBED ON SILVER

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ABSTRACT

An increase in the optical second-harmonic signal arising from an electrochemically treated silver surface upon adsorption of a monolayer of the centrosymmetric molecule pyrazine is reported and an effective second-order nonlinear polarizability for the adsorbed species is deduced. These investigations illustrate the potential of second-harmonic generation in the elucidation of the character of interfaces on an atomic scale.

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In centrosymmetric media, no optical second-harmonic generation (SHG) can occur within the electric-dipole approximation.¹ As a consequence, the weak second-harmonic (SH) signal produced by such materials may be strongly influenced by surfaces, regions where the inversion symmetry of the bulk material breaks down. We have previously determined that the adsorption of a monolayer of pyridine onto an electrochemically reformed silver surface causes a marked growth in the SH intensity.² Lacking inversion symmetry, the free pyridine molecule has an electric-dipole contribution to the second-order nonlinear polarizability $\chi^{(2)}$. Therefore, a simple alignment of molecules upon adsorption could explain the increase in SHG. For the adsorption of centrosymmetric molecules, however, such an alignment alone cannot account for a change in the SH intensity. In this paper, we report on the augmented SH signal associated with the adsorption of a monolayer of the centrosymmetric molecule pyrazine on an electrochemically treated silver surface. We interpret this effect in terms of the broken inversion symmetry of the adsorbed molecules interacting with the metal. Our work underscores the sensitivity of SHG to the details of surface structure.

The experiment was carried out with an electrochemical cell consisting of a mechanically polished polycrystalline silver plate and a platinum working electrode in an electrolyte of 0.1M KCl in doubly distilled water. A saturated calomel electrode (SCE) was also present, with respect to which all potentials are quoted. Pulses of 10 nsec duration from a Q-switched Nd:YAG laser operating at a wavelength of 1.06 μ and a repetition rate of 10 Hz illuminated the silver sample. This fundamental beam, which had a cross-sectional area of 0.2 cm² and an energy

of 0.3 mJ/pulse, was p-polarized and incident on the silver surface at a 45° angle. A significant fraction of the angularly diffuse .53 μ SH radiation generated at the interface of the roughened silver was collected by f/1 optics aligned along the direction of the specular reflection. Relying on color and interference filters to block light of undesired frequencies, we detected the SH signal with a photomultiplier and gated electrometer.

The principal results of these investigations are given in Fig. 1. The plot represents the SH intensity from generation at the silver surface as a function of the reverse bias applied between the silver and platinum electrodes, registered by the silver-SCE potential, $V_{\text{Ag-SCE}}$. The silver sample was prepared by completing three oxidation-reduction cycles, each with a charge transfer of 90 mC/cm². Through this procedure, the silver surface was reformed and an appreciable roughening on the scale of 100 nm resulted, as we confirmed with the aid of a scanning electron microscope. The SH signal in Fig. 1 does not exhibit a pronounced dependence on the voltage applied following the third cycle in the presence of just the pure electrolyte. Upon introduction of pyrazine to form a 0.05M solution, however, we observe an increase in SH intensity and a characteristic voltage dependence of the signal. It should be noted that we recorded the SH signal while making the silver electrode more negative at each step, since irreversible changes in the surface chemistry or structure seem to be induced for large reverse biases.³ In the pyrazine solution, the maximal SH intensity was found to be ~ 10 times as great as that originating from the roughened silver surface in the pure electrolyte. By way of comparison, the adsorption of pyridine gave

rise to a ~ 50 -fold increase in SHG.² The SH radiation was angularly diffuse and unpolarized, as one would expect in view of the rough profile of the silver surface on the scale of an optical wavelength. That the signal was, in fact, SH was verified by checking its monochromaticity and its quadratic variation with the intensity of the fundamental excitation.

The dependence of the SH intensity on the silver electrode potential depicted in Fig. 1 can be compared to that obtained by Raman scattering measurements.^{3,4} In the latter case, strong signals have been observed from what is taken to be a monolayer of adsorbed pyrazine under experimental conditions similar to ours for $V_{\text{Ag-SCE}} \sim -0.4\text{V}$. The increase in SHG that we have attributed to the adsorption of pyrazine also reaches a peak in the vicinity of $V_{\text{Ag-SCE}} = -0.4\text{V}$. The Raman spectra of the adsorbed pyrazine molecules were notable for the appearance of infrared-active bands, which for the centrosymmetric free pyrazine molecule are not Raman active. The observed comparable intensity of these otherwise forbidden transitions was attributed to the lowering of the symmetry of the adsorbed pyrazine molecules by a strong molecule-metal interaction. The same conclusion follows from our SHG measurements: if pyrazine adsorption occurred with only a minimal redistribution of electronic charge in the molecules and in the metal, such adsorption would not cause an appreciable change in the SH signal, since the undistorted pyrazine molecules have a vanishing second-order polarizability in the electric-dipole approximation.

In this experiment, we dealt with particularly strong SH signals, which can be understood⁵⁻⁹ as stemming from a significant enhancement

of the optical fields near the rough structures formed on the silver surface by the electrolytic cycling. At a fundamental wavelength of 1.06μ , such a surface enhancement of $\sim 10^4$ in SH intensity of a cycled silver surface compared with a flat one has been established.⁹ Even for the relatively low intensity excitation ($\sim 100 \text{ kW/cm}^2$) utilized in this experiment, we observed $\sim 10^6$ photons/pulse of SHG. This suggests that under favorable conditions,² detection of such surface sensitive SH signals should also be practical in the absence of surface enhancement effects.

We can deduce from our measurements an approximate value for the effective second-order nonlinear polarizability of a pyrazine molecule adsorbed to a silver surface. The term effective polarizability is used advisedly, as the SH radiation may well arise largely from the metallic conduction electrons in the distorted distribution induced by the interaction with the adsorbed pyrazine, rather than from the perturbed distribution of the electrons in the adsorbed molecules themselves. Let us suppose for the purpose of estimating the nonlinear polarizability that the ratio R of the SH intensity from the pyrazine-silver system to that of the clean silver surface is independent of the degree of roughness of the silver. Since the absolute SH signal strength arising from a flat silver surface can be readily determined,^{2,10} the SH conversion efficiency for pyrazine molecules adsorbed on a smooth silver surface can be inferred from the known ratio R . Modeling the system as a monolayer of aligned, noninteracting,¹¹ polarizable molecules positioned directly in front of a reflecting plane, we can then determine the second-order polarizability of the molecules by an elementary analysis.^{2,12} With $R \sim 10$ and a

surface density of adsorbed molecules of $\sim 4 \times 10^{14} \text{ cm}^{-2}$ for a full monolayer coverage, we obtain for the effective second-order nonlinear polarizability of pyrazine adsorbed on silver, $\alpha_{\text{eff}}^{(2)} (\text{pyrazine/silver}) \sim 4 \times 10^{-30} \text{ esu}$.^{13,14} Following the same procedure for pyridine with the adsorbate surface density given above, but with the experimental ratio $R \sim 50$, we infer $\alpha_{\text{eff}}^{(2)} (\text{pyridine/silver}) \sim 8 \times 10^{-30} \text{ esu}$.

In the environment of the electrochemical cell, static electric fields in excess of 10^6 V/cm are found in the double charge layer,¹⁵ and one cannot dismiss out of hand the possibility that the SH signal arises, at least in part, from a third-order nonlinear process involving the static electric field. This mechanism, however, does not appear to be dominant in these measurements, since there is only a weak variation of the SH signal with applied voltage in the absence of pyrazine, while in the presence of pyrazine the Raman scattering and SH signals show similar voltage dependences.

The detection of SH associated with the adsorption of the centrosymmetric molecule pyrazine to silver described here exemplifies the high degree of surface sensitivity afforded by SHG. The results obtained also substantiate the idea of a strong adsorbate-metal interaction, as previously suggested by Raman scattering measurements. SHG, or its extension to resonant sum-frequency generation, appears to hold promise as a new probe of surface structure, one that is useful for the difficult study of interfaces between two dense media.

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References

1. C. Flytzanis, in: Quantum Electronics, Vol. 1, part B, ed. H. Rabin and C. L. Tang (Academic Press, New York, 1975) p.23.
2. C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. 46 (1981) 1010.
3. R. Dornhaus, B. M. Long, R. E. Benner, and R. K. Chang, Surface Sci. 93 (1980) 240.
4. G. R. Erdheim, R. L. Birke, and J. R. Lombardi, Chem. Phys. Lett. 69 (1980) 495.
5. S. McCall, P. Platzman, and P. Wolff, Phys. Lett. 77A (1980) 381.
6. J. Gersten and A. Nitzan, J. Chem. Phys. 73 (1980) 3023.
7. M. Kerker, D.-S. Wang, and H. Chew, Appl. Opt. 19 (1980) 4159.
8. J. E. Rowe, C. V. Shank, D. A. Zwemer, and C. A. Murray, Phys. Rev. Lett. 44 (1980) 1770.
9. C. K. Chen, A. R. B. de Castro, and Y. R. Shen, Phys. Rev. Lett. 46 (1981) 145.
10. N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. 174 (1968) 813.
11. This calculation neglects local-field effects from interactions between adsorbed molecules, a potentially significant correction.
See B. F. Levine, C. V. Shank, and J. P. Heritage, IEEE J. Quantum Electron. QE-15 (1979) 1418.
12. N. Bloembergen and P. S. Pershan, Phys. Rev. 128 (1962) 606.
13. Here, as in Ref. 2, we define the second-order polarizability under the convention in which the real electric field $\vec{E}(t)$ associated with a Fourier component $\vec{E}_\omega$ is $\vec{E}(t) = 2\text{Re } \vec{E}_\omega e^{-i\omega t}$. See Ref. 1.

14. Because of the distortion of the optical fields near the rough structures of the silver surface, we cannot identify our nonlinear polarizabilities with any specific component of the tensor, but we must consider it as an averaged quantity corresponding to various polarizations of the fundamental and second harmonic radiation.
15. A. W. Adamson, Physical Chemistry of Surfaces, 3rd ed. (John Wiley and Sons, New York, 1976).

Figure Captions

Fig. 1 SH intensity from the cycled silver surface as a function of its potential $V_{\text{Ag-SCE}}$ for an electrolytic solution of 0.1M KCl with and without 0.05M pyrazine present. The error bars are indicative of the uncertainty in the relative shape of the voltage dependence; the overall ratio of the signal in the two cases is possibly subject to a somewhat larger error.

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