Spectroscopy of Molecular Monolayers by Resonant Second-Harmonic Generation

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(Received 7 December 1981)

Spectra of the $S_0 \rightarrow S_2$ electronic transition of rhodamine dyes adsorbed at submonolayer coverages on a fused silica substrate have been obtained by resonant second-harmonic generation. Polarization dependences of the second-harmonic signal have been studied and are used in the construction of a model for the orientation of the adsorbates. A value for the molecular second-order nonlinear polarizability at resonance is deduced.

PACS numbers: 42.65.Cq, 07.60.-j, 78.40.Ha, 68.20.+t

Third-order nonlinear optical effects have proved to be of considerable advantage for a wide variety of spectroscopic studies.[1] On the other hand, the second-order processes of sum- and difference-frequency generation have found less use because they are forbidden in media with inversion symmetry.[2] Just this attribute, however, may make these processes particularly valuable in investigations of interfaces, since it implies a discrimination against signals from the bulk media and, hence, an intrinsic surface sensitivity. In previous experiments, the sensitivity of second-harmonic generation (SHG) to the condition of surfaces[3] and, notably, to the presence of adsorbates has been demonstrated.[4-7] In this Letter, we report on the first application of a second-order nonlinear optical process in measurements revealing spectral features of adsorbates at submonolayer coverages. We have obtained the position and line shape of the electronic transition for rhodamine-dye molecules adsorbed onto a fused silica substrate by optical second-harmonic (SH) spectroscopy. In addition to the method's potential for identifying the quantity and nature of adsorbates, the polarization dependences of the signal may provide some information about the structural properties of the adsorbate and of the surface, as we shall illustrate in the discussion below.

As a model for SHG by a layer of an adsorbate, let us consider a light wave of frequency ω incident on a thin slab of a nonlinear medium at an angle θ from the surface normal. An induced current at twice the driving frequency is established, leading to forward and reflected SH radiation. If the incoming light has polarization $\hat{e}_\omega$, then the intensity of the forward or reflected harmonic light of polarization $\hat{e}_{2\omega}$ is given by[8]

$$I_{2\omega} = 32\pi^3(\omega^2/c^3)\sec^2\theta\,|\hat{e}_{2\omega}\cdot\overleftrightarrow{\chi}_s^{(2)}(2\omega=\omega+\omega):\hat{e}_\omega\hat{e}_\omega|^2 I_\omega^2 \tag{1}$$

(in cgs units). In this equation the linear susceptibility of the material has been neglected, and I_ω is the incident pump intensity. The third-rank tensor $\overleftrightarrow{\chi}_s^{(2)}(2\omega=\omega+\omega)$ represents the second-order surface nonlinear susceptibility, which, without local-field corrections, is simply the sum of the second-order nonlinear polarizabilities of the adsorbate molecules over a unit area.

The polarizability for SHG displays a resonant enhancement when either the fundamental or the SH frequency coincides with that of a transition from the ground state of the molecule to an excited state. Treating the molecular levels as inhomogeneously broadened and working in the electric-dipole approximation, we can express the nonlinear polarizability tensor for a resonance of the SH frequency with the transition from the ground state $|g\rangle$ to the excited state $|n\rangle$ as[2]

$$\alpha_{ijk}^{(2)}(2\omega=\omega+\omega) = (\alpha_{ijk}^{(2)})_{\mathrm{NR}} - (1/\pi\hbar^2)\tilde{\alpha}^{(1)}(2\omega)\langle g|p_i|n\rangle \times \sum_{n'} \frac{\langle n|p_j|n'\rangle\langle n'|p_k|g\rangle + \langle n|p_k|n'\rangle\langle n'|p_j|g\rangle}{\omega - \omega_{n'g}}. \tag{2}$$

Here $(\alpha_{ijk}^{(2)})_{\mathrm{NR}}$ is the nonresonant part of $\alpha_{ijk}^{(2)}$; $\langle n'|\vec{p}|n\rangle$ and $\omega_{n'n}$ denote, respectively, the dipole-matrix element and the frequency for a transition from state $|n\rangle$ to state $|n'\rangle$; and $\tilde{\alpha}^{(1)}(2\omega)$ represents the linear molecular polarizability at frequency 2ω, normalized so that integrating over the resonance yields $\int \mathrm{Im}[\tilde{\alpha}^{(1)}(2\omega)]\,d(2\omega) = 1$. The factor $\tilde{\alpha}^{(1)}(2\omega)$ arises from the summation of the resonant energy denominator over the broadened transition from state $|g\rangle$ to state $|n\rangle$. Since the SH conversion efficiency is proportional to $|\alpha_{ijk}^{(2)}(2\omega)|^2$, the observed spectra, $I(2\omega)$ versus 2ω, will have resonant contributions from both the real and the imaginary parts of $\tilde{\alpha}^{(1)}(2\omega)$.

Monolayer samples of rhodamine 110 and rhodamine 6G adsorbed on a fused silica surface were used for our measurements. They were prepared by placing a few drops of a $3\times10^{-4}M$ ethanolic solution of the dye on the clean, optically flat substrate, and spinning at 2000 rpm for 2 min. Through a direct determination of the optical density of the strong $S_0\rightarrow S_1$ transition in the adsorbate, we deduced an average surface density of dye molecules of 5×10^{13} cm^{-2}. A dye laser pumped by a Q-switched Nd^{3+}-doped yttrium aluminum garnet laser provided tunable pulses of approximately 10 ns duration, 1 cm^{-1} linewidth, and 1 mJ energy. The output of the dye laser, focused to an area of 10^{-3} cm^2, fell on the sample at an angle of 45°. The reflected SH light, which amounted to ~ 10^4 photons per pulse for the peak signal, was detected by a photomultiplier and a gated integrator after it passed through low-frequency blocking filters and a monochromator. A thin quartz plate, always adjusted to the peak of a Maker fringe,[2] served as a nonlinear reference signal. The observed signal at the SH frequency was well-defined spectrally, reproduced the temporal profile of the exciting pulse, and manifested a quadratic power dependence on the pump-laser power when normalized against the quartz reference. Further, by continuously monitoring the SHG from the monolayer as time elapsed, we determined that no laser-induced damage or molecular desorption occurred at the surface.

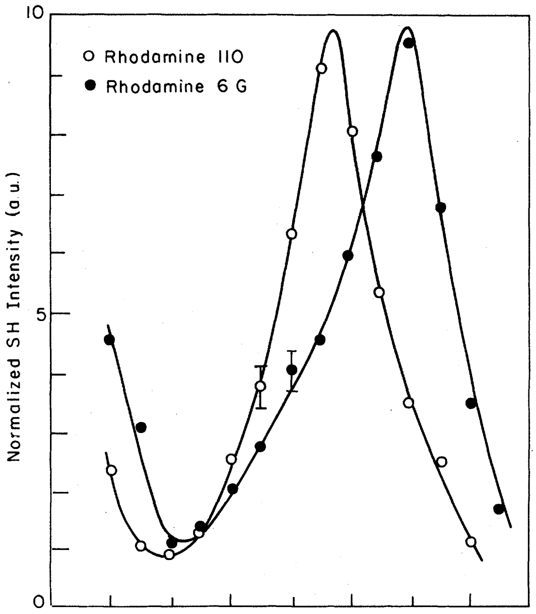

FIG. 1. Normalized SH intensity for p-polarized excitation of monolayer samples of rhodamine 110 and rhodamine 6G on fused silica as a function of the SH wavelength in the region of the $S_0\rightarrow S_2$ transition.

Figure 1 displays the observed SH spectra for the monolayer samples of rhodamine 110 and rhodamine 6G in the region of the $S_0\rightarrow S_2$ electronic transition. The resonant SHG process is described in Fig. 2, which also shows the transition energies of the relevant states for the two dyes dissolved in ethanol. It was noted that the contribution to the SHG from the fused silica plate was a few orders of magnitude smaller than that from the monolayer of dye molecules. While a detailed study of the line shape could provide insight into the structure of the adsorbed molecules and their interaction with the substrate, for the present, let us just remark that the frequency of the peak in the SHG is sufficiently similar to that of the molecules in solution so that such spectra could be useful in identifying adsorbed molecules. The data also suggest that the nonresonant part of $\overleftrightarrow{\alpha}^{(2)}$ is relatively unimportant. The somewhat skewed appearance of the spectrum for rhodamine 6G on the short-wavelength side can be understood as a resonant enhancement as the fundamental frequen-

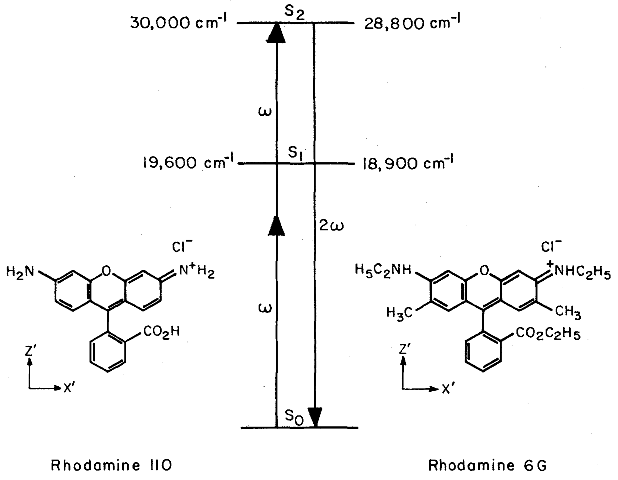

FIG. 2. Energy-level diagrams for rhodamine 110 and rhodamine 6G with the line centers for the linear absorption of the dyes dissolved in ethanol given in units of inverse centimeters. The structure of the dyes and the molecular axes referred to in the text are indicated.

cy approaches that of the $S_0 \rightarrow S_1$ transition.

Measurements of the SHG by the adsorbed monolayers were taken for both p- and s-polarized excitation. In either case, only p-polarized light was observed at the SH, the s component being at least one order of magnitude less intense. These results suggest that the monolayer has reflection symmetry about x-z and y-z planes, where x and y are coordinates in the plane of the monolayer, parallel and perpendicular to the plane of incidence, respectively, and z is the coordinate in the direction normal to the surface. With such symmetries, the only nonvanishing components of $\overleftrightarrow{\chi}_s^{(2)}$ are those of the form $(\chi_s^{(2)})_{zii}$, $(\chi_s^{(2)})_{izi}$, and $(\chi_s^{(2)})_{iiz}$. Furthermore, the SH intensity was found to be independent of the rotation of the sample about its surface normal, indicating a fully isotropic configuration in the plane of the monolayer. The presence of a SH signal then implies that the interface must not have reflection symmetry with respect to the x-y plane, either because there is a net average orientation of the molecules along the surface normal or because the electronic charge distributions of the adsorbate and of the substrate are distorted through their mutual interaction. In view of the substantial strength of the SHG, the former seems more reasonable.

Since the optical properties of the rhodamine dyes are governed primarily by the π electrons in the system of three adjoining phenyl groups, the molecules can be treated as being planar and exhibiting mirror symmetry about the plane perpendicular to the molecule passing through the oxygen atom and the oppositely located carbon atom in the central phenyl group.[9] Consequently, the transition dipole matrix elements must always lie in the plane of the molecule, either along the line of symmetry (say, the z' direction) or perpendicular to it (x' direction). It has been deduced that the S_0 and the S_2 states are even under the reflection operation, while the S_1 state is odd. Hence, the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transition dipole moments must be directed along the x' axis, and the $S_0 \rightarrow S_2$ moment must be parallel to the z' axis. Then, making the reasonable assumption that in our experiment the S_1 level dominates as an intermediate level in Eq. (2), we see that the only nonvanishing component of the resonant second-order polarizability is $\alpha_{z'x'x'}^{(2)}$. This single coefficient determines the surface nonlinear susceptibility $\overleftrightarrow{\chi}_s^{(2)}$ and, consequently, the ratio of the various tensor elements must depend only on the geometrical factors associated with the molecular orientation. We have measured a ratio $r \sim 2$ for the strength of the SH signal arising from p-polarized excitation to that for s-polarized light.

One simple model for the molecular orientation consists of the assumption that the x' axes of the adsorbates lie in a randomly distributed fashion in the plane of the surface. In this case, one expects the ratio r of the SH signal strengths for the two polarizations to be $\frac{1}{4}$, regardless of the directions assumed for the molecular z' axes. An alternative scheme in which the molecular y' axes (the directions normal to the plane of each molecule) are oriented randomly in the plane of the surface leads to $r = (2\langle\cos\theta'\rangle/\langle\cos^3\theta'\rangle - \frac{3}{2})^2$, where θ' is the angle between the z' axis of a molecule and the surface normal, and averages are to be extended over the distribution of this angle for all of the adsorbed molecules. For $r = 2$, we infer that $\langle\cos^3\theta'\rangle/\langle\cos\theta'\rangle = 0.69$ or, if molecules all make the same angle, $\theta' = 34°$.

Within the framework of the second model for the molecular orientation, we can estimate the value of nonlinear polarizability of the adsorbates. For s-polarized excitation, the only relevant component of the surface susceptibility tensor is $(\chi_s^{(2)})_{zyy} = (N/2)\langle\cos^3\theta'\rangle\alpha_{z'x'x'}^{(2)}$. With $\langle\cos^3\theta'\rangle \sim \cos^3 34°$, we deduce from Eq. (1) that $|\alpha_{z'x'x'}^{(2)}| \sim 3\times10^{-29}$ esu for rhodamine 110 at the peak of the resonant SHG. In the calculation, the observed SH signal strength of $I_{2\omega}/I_\omega^2 \simeq 7\times10^{-29}$ esu was used; this value was obtained by comparing with the signal from an evaporated silver film, for which an absolute calibration has been established.[10] With the measured values of 8×10^{-18} and 3×10^{-18} esu for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition dipole moments and a figure for the $S_1 \rightarrow S_2$ transition of 1.1×10^{-17} esu derived from a free-electron model for the dye,[11] Eq. (2) yields $|\alpha_{z'x'x'}^{(2)}| \sim 2\times10^{-28}$ esu for resonant SHG, in rough agreement with the value deduced above. In this estimate, the linear absorption band $\tilde{\alpha}^{(1)}(2\omega)$ was treated as having a triangular profile of width 40 nm.

In summary, we have measured spectra of transitions in molecules adsorbed at a surface at submonolayer coverage by means of resonant SHG. The polarization dependence of the signal allowed us to propose a model for the orientation of the adsorbates, with the aid of which we deduced a rough value for the previously unknown molecular nonlinear polarizability. Being applicable to interfaces between two dense media and being capable of providing high-resolution measurements, the second-order nonlinear optical processes share the advantages of other optical techniques for surface study. Yet unlike optical methods, these processes can exhibit the high degree of intrinsic surface sensitivity characteristic of the techniques relying on the absorption, emission, or scattering of electrons and other massive particles.

One of the authors (T.F.H.) acknowledges financial assistance under a National Science Foundation graduate fellowship. One of us (Y.R.S.) acknowledges a research professorship from the Miller Institute of the University of California. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. W-7405-ENG-48.

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Stability of Electron Vortex Structures in Phase Space

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(Received 13 October 1981)

The stability of one-dimensional, solitary vortex structures in the electron phase space (electron holes) is investigated. A linear eigenvalue problem is derived in the fluid limit and solved exactly, assuming that the normal mode is well represented by the lowest eigenstate of a properly chosen field operator. A new dispersion relation is obtained which exhibits purely growing solutions in two dimensions but only marginally stable solutions in one dimension. This explains the numerically well-known fact that vortex structures disappear in going from one to two dimensions.

PACS numbers: 52.35.Py, 52.35.Fp, 52.35.Mw, 52.55.Dy

Phase-space vortices, best known from particle simulations,[1] are saturated trapped-particle states of beam- or wave-driven plasmas. Only recently they have been observed experimentally[2] and described analytically.[3] The analytic solution in terms of a specially tailored Bernstein-Greene-Kruskal (BGK) wave shows a characteristic positive potential hump in which a finite number of electrons is trapped. For its existence there has to be a deficit of deeply trapped particles in accordance with the ring-shaped pattern of a vortex structure in phase space. Its characteristic speed is of the order of the electron thermal velocity or less. Being thus an entirely kinetic phenomenon, little information is available about its stability behavior. Stability theories[4] presented up to now deal with idealized periodic BGK equilibria.

This paper is devoted to the stability of a solitary, localized one whose physical existence has been proven experimentally. Guided by the general framework of Lewis and Symon,[5] I first derive an eigenvalue problem for two-dimensional perturbations adapted to localized BGK waves and then solve it under two assumptions.

An equilibrium phase-space vortex is described[3]