Effect of Adsorbed Surface Layers on Second-Harmonic Light from Silver*

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It has been found that atomically clean silver surfaces generate approximately four times as much harmonic light as those subjected to adsorption. Existing theories of the nonlinear optics of metals, which are based on bulk properties, must therefore be modified to account for the surface contribution. It is hypothesized that an electric dipole contribution to the nonlinear polarization may account for the present result.

IN previous studies of second-harmonic light from metals,[1–5] it has been assumed that the harmonics are generated by conduction-band and core electrons in the centrosymmetric metal regarded as a semi-infinite plane with abrupt boundary. No quantitative account has been taken of the possible contribution of electrons in surface states or of adsorbed layers. Even without such considerations, however, quite good agreement with theory has been achieved for the generation efficiency as a function of angle of incidence and as a function of the angle of incident polarization. Agreement is not as good, however, for the observed dispersion in the optical range or for the absolute generation efficiency. To examine the possibility that the surface conditions may in fact be important, we have measured the generation efficiency of atomically clean silver and find that fresh surfaces generate approximately four times more harmonic light than those subjected to surface adsorption. The pronounced sensitivity to surface condition suggests that previous experiments in the field should be reinterpreted.

Experiments were performed using a dye-switched mode-locked laser at 1.06 μ with peak power of about 3 MW as measured with an FT4000 photodiode and Tektronix 519 oscilloscope. The actual peak power was at least ten times higher. The experimental arrangement, as indicated in Fig. 1, was conventional except for the innovation of a high-vacuum chamber which permitted silver (99.99% purity) to be evaporated onto a glass optical flat substrate at the same time that measurements of the second-harmonic generation (SHG) were being made. The inner chamber was refrigerated to eliminate scattering of silver onto chamber windows. Signals from the silver mirror and from the KDP (potassium dihydrogen phosphate) reference monitor were integrated so as to include in the data harmonic photons occurring throughout the mode-locked pulse train. The experimental procedure was to take SHG data either during the evaporation of fresh silver at 2×10^{-7} Torr or, with equivalent results, for as long as one hour afterward. The vacuum was subsequently broken to 5×10^{-4} Torr (10^{-3} in some cases) and SHG efficiency was remeasured. The process could be repeatedly recycled with consistent results. In one experiment the pressure was maintained for 46 h at 2×10^{-7} Torr without redepositing fresh silver to discover the rate at which adsorption of background gases affected the response. Experiments were performed for incident polarization both parallel and perpendicular to the plane of incidence.

Designating the harmonic intensity in the "adsorbed" case as I_a, the intensity for fresh silver as I_f, and the ratio of I_a to I_f as R_{af} we find the following:

(1) For $\mathbf{E}_{\rm inc}$ parallel to the plane of incidence and including I_a data taken both at 5×10^{-4} Torr and at 10^{-3} Torr,

$$R_{af}=0.28\pm0.03.$$

(2) For $\mathbf{E}_{\rm inc}$ parallel to the plane of incidence and I_a determined after the silver had been kept for 46 h at 2.5×10^{-7} Torr,

$$R_{af}=0.25\pm0.04.$$

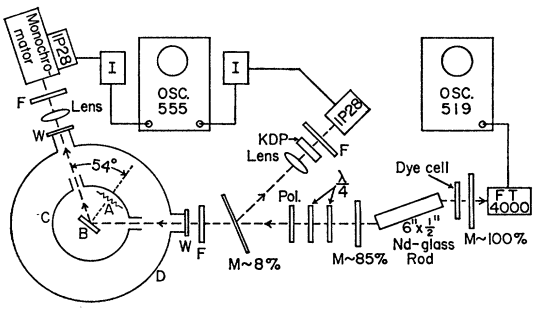

FIG. 1. Diagram of apparatus. A, evaporation source; B, target mirror; C, inner chamber at ~77°K; D, outer vacuum chamber; W, window; F, filter; I, integrating circuit. Data recorded with Tektronix type 555 oscilloscope, mode locking monitored on type 519. Beam polarization adjusted with mica $\frac{1}{4}\lambda$ plates and polaroid filter.

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[1] F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters **14**, 1029 (1965); F. Brown and R. E. Parks, *ibid.* **16**, 507 (1966).
[2] N. Bloembergen, R. K. Chang, and C. H. Lee, Phys. Rev. Letters **16**, 986 (1966); N. Bloembergen and Y. R. Shen, Phys. Rev. **141**, 298 (1966).
[3] S. S. Jha, Phys. Rev. Letters **15**, 412 (1965); Phys. Rev. **140**, A2020 (1965); S. S. Jha and C. S. Warke, *ibid.* **153**, 751 (1967).
[4] H. Sonnenberg and H. Heffner, J. Opt. Soc. Am. **58**, 209 (1968).
[5] C. C. Wang and A. N. Duminski, Phys. Rev. Letters **20**, 668 (1968).

(3) For the ratio M of generation efficiencies with $\mathbf{E}_{\text{inc}}$ parallel and perpendicular to the plane of incidence, fresh silver case,

$$M=I_f(\mathbf{E}_{\text{inc}}\perp)/I_f(\mathbf{E}_{\text{inc}}||)=0.046\pm0.010.$$

(4) Since the harmonic efficiency is low at 1.06 μ when $\mathbf{E}_{\text{inc}}$ is perpendicular to the plane of incidence, a significant value of M could not be assigned for the adsorbed case. We estimate, however, that $R_{af}<1$ in this case.

Clearly, the adsorption of gas causes a pronounced drop in harmonic efficiency. If the adsorbed layer is assumed to be less than a few monolayers thick, direct optical absorption of harmonic light by the layer cannot be responsible for the reduction. Furthermore, since several hours are required at 2×10^{-7} Torr for noticeable adsorption, it is probable that the effect is due to chemical adsorption involving an activation energy, rather than to physical adsorption. In the latter case a monolayer would form in a matter of seconds at the above background pressure.

We may attempt to explain the above effect in terms of changes in the parameters of the theory of Bloembergen[2] and of Jha and Warke[3] for second-harmonic generation in centrosymmetric materials. For example, from photoelectric studies it is well known that adsorption alters the surface-barrier potential of metals by ~1 eV, a change which occurs in a distance ~1 Å. The adsorbed molecular layer may thus produce an electric field of 10^8 V/cm at the surface, changing the dielectric constants $\epsilon(\omega)$ and $\epsilon(2\omega)$, as in the case of electroreflectance.[6-8] The corresponding effect on SHG is found most easily from the expression for generation efficiency in the form used by Sonnenberg.[9] It is found that a 50% increase is needed in both $\epsilon(\omega)$ and $\epsilon(2\omega)$ in order to give the factor-of-4 drop in harmonic efficiency which we observe in the present experiments. According to Buckman and Bashara,[8] a negative bias applied to silver causes a change in the surface dielectric constant $\epsilon_s=\epsilon_1-i\epsilon_2$ such that $|\epsilon_1|$ and $|\epsilon_2|$ both increase. The magnitude of the effect observed by these authors is quite small, however (they measure changes $\delta\epsilon_1$ and $\delta\epsilon_2\sim10^{-2}$–$10^{-3}$ for fields of 10^5–10^7 V/cm), so that it is questionable whether a surface field of 10^8 V/cm, as in the present case, could produce the whole of the required 50% increase in ϵ. If it is assumed that $\epsilon(\omega)$ and $\epsilon(2\omega)$ are only altered in the region of the surface, rather than throughout the bulk, a still larger change is needed to explain our results.

It is also possible that the nonlinear coefficients α, β, and δ, which are thought to govern the nonlinear polarization at a centrosymmetric boundary,[10] may be affected. All three parameters are derived in the theory as bulk constants even though terms involving β and δ are only effective at the boundary where $\nabla\cdot\mathbf{E}\neq0$. In this region β and δ may in fact differ significantly from the bulk values, and Bloembergen *et al.*[10] take them as $\tilde{\beta}=\frac{1}{2}\beta$ and $\tilde{\delta}=\frac{1}{2}\delta$, assuming that both change abruptly to zero at the boundary. In any case, both β and δ may be sensitive to the surface potential and thus depend, in a way not yet derived, on the conditions of adsorption. The nonlinear coefficient α governs harmonic light produced throughout the optical skin depth of the surface (~100 Å) and is therefore little affected by potential changes within ~1 Å of the boundary.

An alternative explanation may be to recognize that a metallic boundary is actually a composite structure consisting of an underlying centrosymmetric metal and a noncentrosymmetric surface region. This region includes the adsorbed molecular layer and the first few atomic layers of the metal. These metal layers near the boundary may lack a center of inversion because the adsorbed layer causes a distortion of the boundary potential and/or because surface states are involved. For such a composite structure the effective nonlinear polarization includes a new dipole term, which represents the net effect of the entire noncentrosymmetric surface, in addition to the usual quadrupole terms derived for the bulk material.

We thus write

$$\mathbf{P}^{\text{NL}}(2\omega)=\alpha(\mathbf{E}_L\times\mathbf{H}_L)+\beta\mathbf{E}_L(\nabla\cdot\mathbf{E}_L)+(\delta-\beta)(\mathbf{E}_L\cdot\nabla)\mathbf{E}_L+\chi^{(2)}(\mathbf{E}_L\mathbf{E}_L), \quad (1)$$

where $\chi^{(2)}$ has the $C_{\infty v}$ symmetry of the surface. ($\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}$, $\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}\neq\chi_{zzz}^{(2)}$, and other elements are zero.) We discuss below two possible contributions to $\chi^{(2)}$: (a) the part contributed by the adsorbed layer itself and (b) the part contributed by the underlying layer of metal when the boundary potential is distorted by the presence of adsorbed molecules. The contribution to $\chi^{(2)}$ of surface states cannot be evaluated without a knowledge of surface-state wave functions.

The contribution (a) of the adsorbed layer alone, ignoring for the moment the underlying metal, may be estimated from the formula[11] for SHG in a thin nonlinear layer. If the layer is assumed to consist of adsorbed molecules on a perfectly reflecting substrate, Z axis normal to surface, we may take $|\epsilon_T|\gg1$ and make the assumption that $P_z^{\text{NLS}}(2\omega)\gg P_x^{\text{NLS}}(2\omega)$. The latter is reasonable since the total laser field is nearly normal to the surface for E_{inc} parallel to the plane of incidence; and, unless $\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}\gg\chi_{zzz}^{(2)}$ in the noncentrosymmetric adsorbed layer, a possibility which seems unlikely in view of the nonlinear properties of crystals of the related C_{4v} class, $P_z^{\text{NLS}}(2\omega)$ will be

[6] J. Feinleib, Phys. Rev. Letters **16**, 1200 (1966).
[7] A. Prostak and W. N. Hansen, Phys. Rev. **160**, 600 (1967).
[8] A. B. Buckman and N. M. Bashara, Phys. Rev. **174**, 719 (1968).
[9] See Ref. 4, Eq. (1).
[10] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968).
[11] N. Bloembergen and P. S. Pershan, Phys. Rev. **128**, 606 (1962).

dominant. The reflected harmonic field is then

$$E_{||}{}^{R}=-i8\pi P_z{}^{\mathrm{NLS}}(2\omega)\omega d c^{-1}[\epsilon_a(2\omega)]^{-1}\tan\theta, \quad (2)$$

where θ is the angle of incidence and $\epsilon_a(2\omega)$ refers to the adsorbed layer of thickness, d. An estimate of the electric field inside the layer is difficult. For a layer which is thin compared to the Thomas-Fermi shielding distance, the field in the layer is the same as that of the incident beam. On the other hand, for a layer of macroscopic dimensions, both Fresnel's law and Snell's law apply. Since the layer in question may be of intermediate dimensions, we have used for the electric field in the layer the geometric mean of values found for the two limiting cases. The harmonic efficiency then becomes

$$\frac{I_{2\omega}}{I_\omega{}^2}=\left(\frac{8\pi}{c}\right)^3\left(\frac{4\chi_a{}^{(2)}\omega d\sin^2\theta\tan\theta}{\epsilon_a(\omega)\epsilon_a(2\omega)}\right)^2, \quad (3)$$

where $\chi_a{}^{(2)}$ is the nonlinear coefficient of the adsorbed layer, the magnitude of which may be estimated using Miller's rule.[12] Assuming that $\epsilon_a(\omega)=\epsilon_a(2\omega)\sim 3$ and $d\sim 1$ Å for the adsorbed layer, the efficiency is $I_{2\omega}/I_\omega{}^2\sim 2.6\times 10^{-30}$ esu or 2.6×10^{-23} W^{-1} cm^2. Comparing this with the absolute efficiency measured by Sonnenberg and Heffner[4] at 6943 Å ($I_{2\omega}/I_\omega{}^2\sim 9\times 10^{-19}$ W^{-1} cm^2), Eq. (3) confirms[13] that the adsorbed molecular layer by itself cannot radiate sufficient harmonic light to interfere appreciably with the quadrupole radiation from the underlying silver.

The contribution (b) of the underlying metal when the boundary potential is distorted may be estimated using Eq. (3) again but with $\chi_a{}^{(2)}$ replaced with the effective nonlinear susceptibility of the metal layer, $\chi_m{}^{(2)}$. We assume that the distortion is produced by an equivalent dc field $\mathbf{E}_0$ normal to the boundary, so that $\chi_m{}^{(2)}$ may be found from the third-order susceptibility of the metal, $\chi^{(3)}$, using $\chi_m{}^{(2)}\sim\chi^{(3)}\mathbf{E}_0$. Here $\chi^{(3)}$ is related to the constants γ and γ' of Lee *et al.*[10] [Eq. (3)] appropriate to isotropic symmetry. Equation (3) above then determines the required magnitude of $\chi_m{}^{(2)}$ (and thus of $\chi^{(3)}$ if a value of $\mathbf{E}_0$ is assumed) in order that dipole radiation from the distorted region of the metal be comparable in magnitude to the observed SHG in silver. In making the estimate we have assumed that α, β, and δ in (2) are unchanged. For $\mathbf{E}_0\sim 10^8$ V/cm, we have $I_{2\omega}/I_\omega{}^2\sim 9\times 10^{-19}$ W^{-1} cm^2 as before, and substituting the metal dielectric constants $\epsilon_m(\omega)\sim -50$ and $\epsilon_m(2\omega)\sim -10$ for $\epsilon_a(\omega)$ and $\epsilon_a(2\omega)$, we find the required third-order susceptibility for silver to be $\chi^{(3)}\sim 3\times 10^{-10}$ esu. In the absence of theoretical or experimental knowledge of $\chi^{(3)}$ for metals, it is impossible to evaluate this requirement conclusively. For III-V compounds,[14] however, $\chi^{(3)}\sim 10^{-10}$–10^{-8} esu with the bound-electron contribution comparable to that of conduction electrons at $n\sim 10^{16}$ electrons/cm^3 in the conduction band. One may thus speculate that $\chi^{(3)}$ for silver will also be at least of this magnitude and therefore large enough for an adsorption-dependent dipole term in $\mathbf{P}^{\mathrm{NLS}}(2\omega)$ to be responsible for the effect seen here.

We have shown that second-harmonic light generation in metals is significantly modified by foreign atoms on the surface. Since theories so far developed deal only with the case of the pure metal, experimental comparisons to date are open to reinterpretation. It seems unlikely that the entire adsorption effect can be due to a modification of the dielectric constants entering essentially in the centrosymmetric theory. Little is known, however, about the nonlinear coefficients β and δ in the region near the surface, or of the way they are affected by the shape of the surface potential. Changes in these, therefore, might conceivably account for the facts. On the other hand, it is hypothesized here that an adsorption-induced dipole layer at the surface could radiate enough harmonic light to account for the observed factor-of-4 reduction in generation efficiency provided the third-order susceptibility of the metal, $\chi_m{}^{(3)}$, is comparable to that of III-V semiconductors.

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[12] R. C. Miller, Appl. Phys. Letters **5**, 17 (1964).

[13] C. H. Lee, R. K. Chang, and N. Bloembergen, Phys. Rev. Letters **18**, 167 (1967).

[14] S. S. Jha and N. Bloembergen, Phys. Rev. **171**, 891 (1968). The authors wish to thank Professor Bloembergen for calling their attention to this work.