THREE-PHOTON PHOTOELECTRIC EFFECT IN GOLD*

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Two-photon absorption in solids has become a common phenomenon in the last few years. Two-photon photoelectric effects have also been reported.[1] With regard to higher order processes in solids, however, only a three-photon luminescence effect has been observed (in naphthalene).[2] In this Letter we report the observation and study of a three-photon photoelectric effect in gold at room temperature using a Q-switched ruby laser (photon energy 1.786 eV). Gold has a (photoelectric) work function $W = 4.8$ eV, much higher than the energy of two laser photons (3.57 eV), but lower than the energy of three laser photons (5.36 eV).

A TRG-104 Q-switched ruby laser generating light pulses of 1-J energy and 40-nsec duration was used. Before entering the photoelectric cell through a quartz window, the unfocused laser beam passed through two irises used to control the beam dimensions and through filters to eliminate the laser flashlamp light. The photoelectric cell was an evacuated brass cylinder used extensively here for the study of electron emission from solids under the influence of laser radiation and will be described elsewhere. The laser beam was incident on a stainless-steel mirror (on which a gold film was evaporated) at a 60° angle and was specularly reflected out of the cell through a second quartz window. The photoelectric current from the gold was multiplied with an electron multiplier which faced the mirror directly. The anode resistance of the electron multiplier was 51 Ω, and the voltage signal across it was displayed on a Tektronix 547 oscilloscope through a matched cable. A beam splitter was placed in front of the laser and a portion of the laser light was directed to two RCA-922 photodiodes. One diode served to monitor the laser intensity while the other supplied the trigger signal to the oscilloscope.

The gold films were evaporated on the stainless-steel mirror in an evaporation chamber existing in the laboratory and were transferred into the photoelectric cell within three minutes after evaporation. Only a very slight degree of contamination of the gold films is expected during their short exposure to the atmospheric air. Moreover, the gold films were probably somewhat annealed inside the photoelectric cell in allowing the full intensity of the laser to hit them. Experiments in this laboratory and others in the past have shown that surface heating to very high temperatures results when light intensities of the order of several megawatts per square centimeter are incident on a metal surface. The gold films were several thousand angstroms thick.

Figure 1 shows typical oscilloscope traces of the laser-light pulse and the resulting photoelectric pulse. Figure 2 shows the photoelectric current from gold as a function of laser intensity. The data points are the result of measurements on two different gold films. The laser intensity was controlled with Corning color filters and with neutral density filters. Both types of filters gave the same results, thus eliminating the possibility of any contriubtion from luminescence of the color filters. The transmission of the filters at the laser wavelength was measured in a Cary-14 spectrophotometer and also with the laser light itself using a TRG-100 thermopile. Both measurements gave the same results.

The plot of the photoelectric current versus laser intensity in Fig. 2 reveals two distinct processes. For intensities higher than about 1 MW/cm^2, the signal is very strongly dependent on the laser intensity. It is believed that this is because of thermionic emission resulting from heating of the metal surface. Results of these measurements will be reported elsewhere. For intensities lower than 1MW/cm^2, the signal follows a third-power dependence on the intensity, strongly indicating a three-photon effect. The shape of the photoelectric

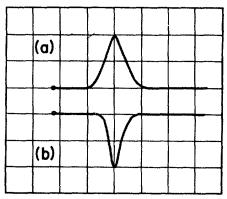

FIG. 1. (a) Laser pulse and (b) photoelectric pulse from the three-photon effect. The sketches are exact reproductions of oscilloscope pictures, traced here for clarity. Time scale is 50 nsec per division.

pulse is also consistent with a third-order process: The laser-light pulse is approximately Gaussian with a half-width T of about 40 nsec. If the photoelectric current is proportional to I^3, it should also have a Gaussian shape with a half-width $T' = T/\sqrt{3}$. Indeed, T' is shorter as seen in Fig. 1, with $T' \approx 22$ nsec.

If J is the photoelectric current density, then $J = cI^3$, where c is a constant containing all the information on the three-photon effect in the material, i.e., the probability for three-photon absorption (of total energy 5.36 eV) and the escape probability of the electrons. From the data, we obtain $c = 1.02\times10^{-7}$ (A/MW)/(MW/cm^2)^2. If we define the quantum yield η_3 as the number of emitted electrons per incident photon, then η_3 (electrons/photon) $= 1.8\times10^{-6}cI^2$ MW/cm^2. For example, for an intensity $I = 0.77$ MW/cm^2, the quantum yield η_3 is 1.1×10^{-13} electrons per incident photon. In the absence of data concerning the escape probability of the electrons, it is not possible to calculate exactly the three-photon effect in terms of a more familiar quantity, the absorption constant $\alpha_3(I) = \gamma I^2$. However, we may estimate α_3 from our measurements if we assume that the escape probability function is given by $p(x) = \exp(-x/D)$. Taking into consideration the strong attenuation of the light beam with distance x into the metal due to one-photon absorption,[3] we obtain an approximation formula: $\eta_3 = \alpha_3/(3\alpha_1 + 1/D)$ or $\alpha_3 = 1.8\times10^{-6}(3\alpha_1 + 1/D)cI^2$, where α_1 is the absorption constant of the one-photon effect and α_3 the three-photon absorption constant at the surface ($x = 0$) for the incident intensity I. Using reasonable values $D = 5\times10^{-7}$ cm and $\alpha_1 = 10^6$ cm^{-1}, we calculate $\alpha_3 = 5.5\times10^{-7}$ cm^{-1} for a laser intensity[4] $I = 0.77$ MW/cm^2 at 5.36 eV.

For comparison we report some results on a two-photon photoelectric effect observed in

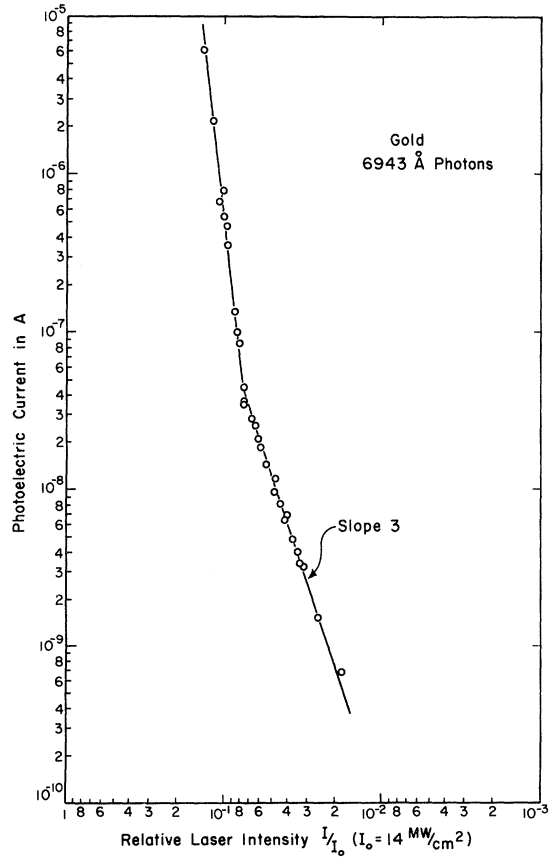

FIG. 2. Photoelectric current versus relative laser intensity of the first harmonic of the ruby laser. $I_0 = 14$ MW/cm^2. The light-beam diameter was 4.6 mm.

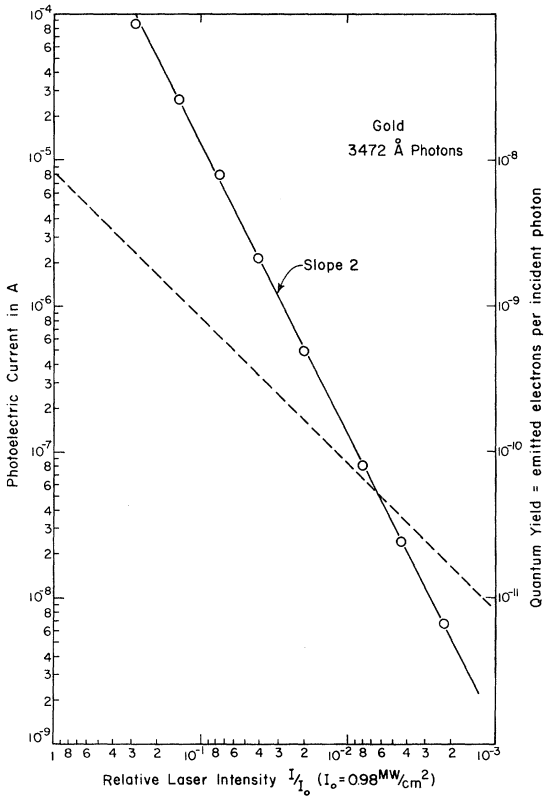

FIG. 3. Photoelectric current versus relative laser intensity of the second harmonic of the ruby laser (solid line). $I_0 = 0.98$ MW/cm^2. The light-beam diameter was 6 mm. The quantum yield for the two-photon photoelectric effect is also plotted as a function of the light intensity (dotted line).

gold, using the second-harmonic radiation from the ruby laser. The photon energy of this radiation is 3.57 eV, which is lower than the work function W of gold. Two such photons, however, have total energy of 7.14 eV, much higher than W. Figure 3 shows the photoelectric current versus intensity and reveals a two-photon photoelectric effect. We may write $J = bI^2$ for the current density, where b has a physical meaning similar to c in $J = cI^3$. From the data we obtain $b = 2.35 \times 10^{-3}$ (A/MW)/(MW/cm^2). The quantum yield is plotted also as a function of intensity in Fig. 3. A calculation similar to that for the three-photon effect gives an estimate of the absorption constant of the two-photon effect at the surface: $\alpha_2 = 3.6 \times 10^{-6}(2\alpha_1 + 1/D)bI$. For an incident laser intensity $I =$ 0.77 MW/cm^2, for example, we obtain $\eta_2 = 6.5 \times 10^{-9}$ electrons/photon and $\alpha_2 = 2.6 \times 10^{-2}$ cm^{-1} at 7.14-eV total photon energy.

We are presently working on a theoretical calculation of the three-photon photoelectric effect.

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[1]H. Sonnenberg, H. Heffner, and W. Spicer, Appl. Phys. Letters 5, 95 (1964); M. C. Teich, J. M. Schroeer, and G. J. Wolga, Phys. Rev Letters 13, 611 (1964).

[2]S. Singh and L. T. Bradley, Phys. Rev. Letters 12, 612 (1964).

[3]A possible two-photon absorption is neglected since its contribution to the attenuation of the light with depth into the metal is negligible compared with the one-photon absorption.

[4]The effect of reflectivity is neglected in this estimate of the absorption constant.

NOTE ON TRANSIENT CURRENT MEASUREMENTS IN LIQUID CRYSTALS AND RELATED SYSTEMS

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The purpose of this note is to present the results of some measurements of transient currents in nematic liquid crystals and some structurally related non-nematic compounds of ultrahigh purity.

The experimental procedure consisted of melting the nematic substance between two pieces of glass possessing evaporated metal electrodes on their surfaces. The area of these cells was typically 1.3 cm^2. The thickness of the cell was determined by Mylar spacers and ranged from 6 to 25 μm in our experiments. Provisions were made for maintaining the cell at constant temperature within its nematic liquid crystalline range. Currents were observed through a series load resistor by means of an oscilloscope. The applied voltage step was generated by means of a mercury relay and a variable dc supply. The materials which we have investigated include p-azoxyanisole (nematic range 120-136°C), and azobenzene, a structurally similar but nonmesomorphic compound which melts at 69°C. Although the data presented are for p-azoxyanisole, similar behavior was found for azobenzene.

Figure 1 shows a typical current transient. The initial portion of the curve is due to the normal charging current. The secondary peak is striking and is the subject of our investigation. We note that this type of transient has been frequently observed for space charge injection into insulators.[1]

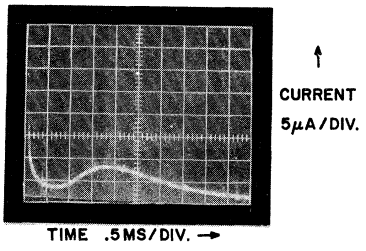

FIG. 1. Typical current transient—nematic p-azoxyanisole.