those high Q values. The weakness of the damping in this disordered system, even for large Q, is remarkable.

The authors wish to express their gratitude to Professor R. Blinc for several stimulating discussions and for providing the deuterated sample. They also wish to thank Mr. D. Glasenapp and Mr. W. Noack for their work on the computer hardware and software for the spectrometer, and Mrs. L. Schätzler and Mr. K. Wingerath for their assistance in adapting the computer programs to a time-sharing on-line system.

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Observation of a New Nonlinear Photoelectric Effect Using Optical Levitation

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(Received 28 October 1975)

We observe a new three-photon nonlinear photoelectric effect in glass with visible cw laser light using a method for measuring very low electron emission rates based on optical levitation of transparent particles. Electrons are pumped into the conduction band of glass by the absorption of two photons and subsequently ejected in a single-photon step.

Using optical levitation[1,2] we have observed that cw visible laser light causes emission of electrons from highly transparent dielectrics such as glass and liquids. We show that this unexpected effect in glass is due to a new three-photon nonlinear photoelectric process in which light pumps electrons into the conduction band by absorption of two photons and subsequently ejects some of them by single-photon absorption. This effect broadens our understanding of nonlinear photoemission effects[3-6] and is of importance for the study of linear and nonlinear absorption processes,[7] band energies,[8] and optical breakdown in highly transparent dielectrics[9] as well as for studies in other fields using levitated charged particles as in cloud physics.[2] Previous nonlinear photoelectric effects such as direct electron emission by two-photon absorption from the valence band of insulators[3] and semiconductors,[4] electron emission from the conduction band of metals by multiphoton absorption,[5] and two-photon-assisted thermionic emission[6] were observed with high-power pulsed lasers. In our experiments with cw lasers we used a new technique of observation based on the stable optical levitation and manipulation of transparent glass spheres and liquid drops in air and partial vacuum.[1,2] Indeed, we believe that nonlinear photoemission occurs from many insulators irradiated with cw visible lasers but was unobserved for want of detectors operable at atmospheric pressure, sensitive to emission rates of a few electrons a minute, and capable of long integration times. Our technique has similarities with the "oil-drop technique" for supporting charged particles in neutral equilibrium as used by Millikan and his students[10] and more recently Pope[11] to measure photoelectric thresholds and a nonlinear emission effect in the uv[12] in absorbing particles at low light intensities. Optical levitation, however, is most useful with cw laser intensities, low optical absorption, and long observation times.

The apparatus is basically the same as used before to levitate glass spheres[1] and liquid drops.[2] Soda lime silicate (SLS) glass spheres ~10 μm in diameter are launched into a ~20-mW 5145-Å cw argon laser beam by jiggling the glass base plate of a cell with a piezoelectric ceramic shaker. Oil drops are introduced with a spraying technique. Once trapped and levitated, particles are manipulated into a region of uniform vertical electric field located in a slot between two copper plates $\frac{1}{2}$ cm apart.[2] A microscope, viewing from the side, projects an image of the sphere on a screen in front of a camera. To measure the charge we photograph the shift in the position of the particle caused by a voltage pulse. With a trigger pulse we open the camera, start a motor-driven mirror to sweep the image of the sphere horizontally across the screen, and apply a $\frac{1}{4}$-sec pulse of up to 150 V to the plates. The shift thus recorded is proportional to the charge, for small shifts (up to 3 or 4 sphere diameters). It occurs with no vertical oscillations because of the air damping. The magnitude of the shift can be calibrated absolutely in terms of the percentage change in light power needed to restore the shifted particle to its original height.[2] Measurements were taken at atmospheric or reduced pressure. Figure 1 shows the typical charge variation of a 7.9-μm diam glass sphere taken with varying intensity and wavelength. The initial charge of the sphere is usually negative

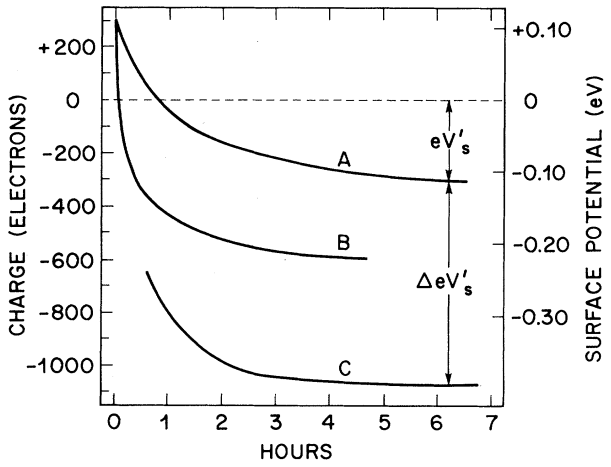

FIG. 1. Charge n (in units of e) and surface potential $eV_s=ne^2/a$ of a levitated 7.9-μm glass sphere versus time, observed at atmospheric pressure. Curve A is 5145-Å cw light. Curve B is pulsed 5145-Å light at 3.4 times the cw intensity but the same average power as A. Curve C is 4579-Å cw light.

and is likely due to friction. In time this charge drops to zero, becomes positive, and finally reaches a nearly constant value n_{max} after several hours. This is just the behavior one expects from phtoemission. Initially the rate of emission is high since it is aided by the electric field of the negatively charged sphere. The emission slows and finally stops as the charge reverses and the sphere of radius a reaches an equilibrium retarding potential at the surface with a value $eV_s'=n_{max}e^2/a$ equal to the maximum kinetic energy of the emitted electrons. Thus using no external voltage, we have the equivalent of the classic retarding-potential experiment. We assumed above that the charge redistributes itself uniformly over the sphere during emission since the electrons are not emitted uniformly. This occurs either by the residual conductivity of the glass or the photoconductivity of the photoemission process as discussed later. This problem of nonuniform local surface potentials which we avoid simply is one of the drawbacks to clean photoemission data in insulators[13] with cw light. Application of *external* electric fields to a particle perturbs (increases) the photoemission by the Schottky effect.[14] For the $\frac{1}{4}$-sec voltage pulses used this contribution was negligible.

We established that the observed charge variation on the time scale of minutes or hours is due to photoemission from the sphere and not the apparatus. With 5145-Å light, substituting an oil drop for a glass sphere results in no photoemission. Changing 5145- to 4579-Å light with oil drops initiates photoemission. Thus the particle type and the wavelength determine the photoemission, as expected. Also, with 6328-Å light, a charged glass sphere which gave no apparent photoemission after ~10 h gradually lost charge after ~3 days and stayed at zero as might be expected from background ions. We do not believe that the electrodes contribute charge since low-intensity scattered visible light should not eject electrons from copper. uv from the laser discharge was filtered out. Furthermore, putting the copper electrodes external to the cell makes no difference.

To probe the origin of photoelectrons from glass with 5145-Å light we studied the intensity dependence of the photoemission. With a levitated sample one cannot increase the intensity by just increasing the cw laser power because the particle rises to a new equilibrium where the intensity is the same. We can however chop a beam of higher power rapidly, with a duty cycle

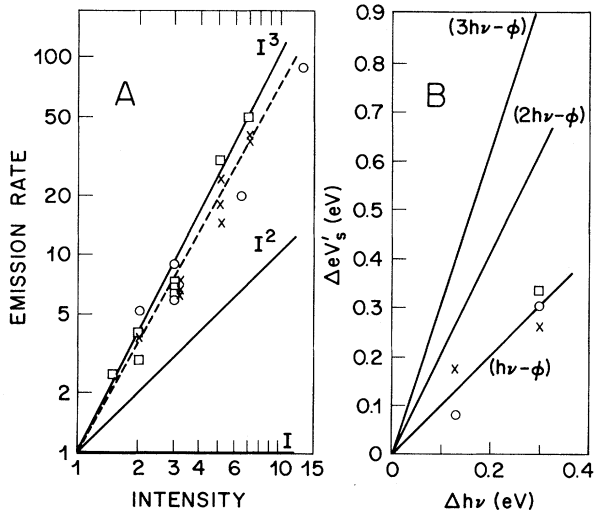

FIG. 2. (a) Emission rate versus light intensity I for constant average light power. The origin is the rate for I_{cw}, the cw intensity. Data from different spheres are plotted with different symbols. Solid lines show rates varying at I, I^2, and I^3. The experimental curve (dashed) is closely I^3. Typically $I_{cw} \cong (1-2) \times 10^4$ W/cm^2. (b) Change in kinetic energy of emitted electrons versus change in photon energy expressed as $\Delta(eV_s')$ versus $\Delta(h\nu)$. The origin is the emitted energy for $h\nu = 2.4$ eV (5145 Å). Solid curves show a one-, two-, or three-photon change in energy.

that keeps the average power constant. In this case the particle does not respond to the rapid high-intensity pulses but remains at the same height. Curve B of Fig. 1 taken in this way shows a more rapid emission rate than the cw case (curve A). Figure 2(a) plots the emission rate measured at zero charge versus the peak intensity. The observed rate shown dashed is highly nonlinear, increasing with a slope that is closely I^3 indicating a three-photon process. It does not distinguish, however, between simultaneous absorption of three photons through virtual levels, stepwise absorption of three photons involving real levels, or some combination of these processes involving three photons.

In this regard we studied the change in maximum kinetic energy of photoelectrons as the photon energy was varied. The maximum kinetic energy equals the equilibrium value of the surface potential eV_s' and depends on the photon energy $h\nu$ and the work function φ in three possible ways as given below with $n = 3$, 2, or 1:

$$E_{Kmax} = eV_s' = nh\nu - \varphi. \quad (1)$$

n is the number of photons simultaneously absorbed in the *final* emission process. Figure 2(b) shows the three possibilities and the experimental data in terms of the increments $\Delta(eV_s')$ versus $\Delta(h\nu)$ for several particles, taking eV_s' for $h\nu = 2.42$ eV (5145 Å) as reference. Curves A and C of Fig. 1 show $\Delta(eV_s')$. Figure 2(b) compares data at 5145, 4880, and 4579 Å in a way which removes the effect of any changes of φ from particle to particle. The results, including data taken at reduced pressures as will be discussed below, agree with the $n = 1$ possibility within experimental error. Thus emission occurs by the absorption of a single photon from a final, fixed, real energy level which can be populated by light of various energies (5145, 4880, 4579 Å). This indicates that this final level is the bottom of the conduction band. The picture then of the overall three-photon process first requires the absorption of two visible photons to inject electrons into the conduction band. Electrons then relax quickly to the bottom of the conduction band from which level they eventually relax back down or are ejected by single-photon absorption. The photoconductivity of the two-photon step causes the charge redistribution mentioned above. Our data give no detail on the initial two-photon step. Recent work by Stolen and Lin[7] on two-photon absorption effects in glass fibers shows that two-step absorption via real levels dominates over simultaneous two-photon absorption. This suggests that the observed photoemission should be sensitive to the impurities in the glass. Indeed, experiments[15] show that Na impurities in SiO_2 generate a band of states 0.5 eV wide located ~2.4 eV below the conduction band. When these states were populated, electrons could be photoexcited to the conduction band with visible light. Our spheres were of commercial SLS glass,[16] and thus the bulk impurity content was unknown. Attempts to interpret our data as due to absorbed surface impurities fail to account simultaneously for the intensity and wavelength dependence of the photoemission.

A surprising feature of the data is that much of it was taken at atmospheric pressure where one might not expect to see photoemission. This is a result of the small size of the particle relative to the electron mean free path in the gas, i.e., electrons make relatively few collisions in escaping the retarding field. The mean free path of an electron at one atmosphere is ~0.5 μm compared to a particle radius $r \sim 4$ μm. Since the sticking probability and energy loss per collision are negligible at these energies, collisions

mainly reduce the average radial velocity component of the electrons. Although this causes a reduction, significant emission still occurs. Collisions make an absolute measurement of eV_s', the so-called equilibrium value of surface potential, difficult by attenuating the high-energy tail of the electron distribution. It is still possible to obtain accurate values of $\Delta eV_s'$, the *change* in emitted energy, due to a change $\Delta h\nu$ in photon energy, and to observe the effects of intensity on the emission rate. Thus in curves A and C of Fig. 1, values of eV_s' are quite low but $\Delta(eV_s') \cong 0.3$ eV for $\Delta h\nu \cong 0.3$ eV in agreement with $n=1$. Also comparing points of maximum curvature of A and C shows that the *change* in energy of the maximum of the electron energy distribution is again ~0.3 eV. Evidence of difficulties in measuring eV_s' comes from the pulsed high-intensity data where emission rates are increased to where a 7 h run at $I=8I_{cw}$ is equivalent to a $7(8^2)=448$ h run at cw intensity.[17] With $I=8I_{cw}$ we find that eV_s' increases steadily from the cw value of ~0.12 to ~0.26 eV for 5145 Å. This increase comes from the occasional electrons escaping with fewer collisions. In addition data taken at reduced pressure (down to ~100 Torr)[18] show a further increase in eV_s' to ~0.65 eV. At 100 Torr, $\lambda \cong 3.8$ μm is comparable with $r \cong 4$ μm. We therefore expect 0.65 eV to be close to the maximum electron kinetic energy $E_{K\,max}$. Using 0.65 eV and Eq. (1) with $n=1$ gives a value of φ of our glass sample of $2.42-0.65 \cong 1.8$ eV. In our case this is also the electron affinity χ. Recently χ for fused silica was determined[8] indirectly to be ~1.7 eV in agreement with our value which supports our assignment of 0.65 eV as $E_{K\,max}$. It is known that φ varies with surface treatment. Experimentally φ varied $\sim \pm 0.05$ eV from sphere to sphere indicating fairly uniform surfaces.[19] We often removed this variable from the data by discharging a sphere on the glass base plate and using it again. Another way of getting φ would be to levitate with a tunable laser and find the threshold photon energy for photoemission.

In conclusion, we find the study of photoemission using optical levitation to be a sensitive way of studying excitation processes in transparent dielectrics. It gives information on absorption effects, band energies, and photoelectric thresholds which is useful in understanding linear and nonlinear optical effects. Such studies in glass could help clarify the role of specific impurities in absorption.[7,15] Our experiments relate to optical breakdown[9] where only a few electrons trigger the process. In cloud physics experiments using levitation[2] one can fortunately avoid photoemission by using longer wavelength light. This permits experimentation with particles of arbitrary fixed charge.

The authors thank J. P. Gordon, J. E. Rowe, R. H. Stolen, and J. Tauc for helpful discussions.

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[17]The equivalence of pulsed and cw operation is seen in Fig. 1, curves A and B where the charge after 0.6 h at $I=3.4I_{cw}$ is closely equivalent to $0.6(3.4^2) \cong 7$ h at I_{cw}.

[18]At lower pressures increased radiometric forces cause instabilities (Ref. 1). Recently levitation down to 10^{-6} Torr was achieved with lower glass spheres (to be published).

[19]Spheres were cleaned with distilled water and NH_4Cl and sat on a glass plate cleaned with "Mr. Clean."