Ultrafast optical switching of second-harmonic generation at the C_{60} single-crystal surface

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The switching of second-harmonic generation (SHG) at a C_{60} single-crystal surface has been observed in a pump-and-probe experiment. The SHG signal from a picosecond 1.17 eV laser pulse is suppressed by one order of magnitude upon illuminating the crystal surface with a 3.49 eV pump pulse. The nonlinear optical response is faster than 45 ps and persists for longer than 20 ns. SHG suppression to $1/e$ occurs at pump densities as low as 2.8 $\mu J/cm^2$. We suggest that nonlocalized excited electronic states determine the change in the nonlinear optical behavior. © *1996 American Institute of Physics.* [S0021-8979(96)04106-3]

The physical and chemical properties of fullerenes, specifically of C_{60}, have been the subject of intense experimental and theoretical study in recent years. In view of potential applications much interest is due to their nonlinear optical properties like nonlinear absorption,[1] optical limiting,[2] optically induced absorption,[3,4] and the large values of third- and second-order nonlinear susceptibilities.[5–7] Detailed studies were recently performed for second-harmonic generation (SHG) from C_{60} thin polycrystalline films.[8–10] Not much work has yet been done on the nonlinear properties of C_{60} excited states and no SHG study from single-crystal surfaces has been reported. From the analogy to linear conjugated organic molecules it might be expected that nonlinear optical properties can be drastically changed by optical excitation.[11] The general importance of such an effect is related to the understanding and tailoring of fast switching elements for photonics which require a weak pump beam and a quasi-instantaneous and absorptionless response of an intense probe beam.

We report here on the first experiments of SHG at the C_{60} crystal surface and the changes in efficiency due to photoexcitation by picosecond UV light pulses. The azimuthal signal dependence demonstrates the influence of surface symmetry. A highly reproducible substantial change in SHG is observed for low pump densities of the order of $\mu J/cm^2$ under ambient experimental conditions. The response is faster than the experimental time resolution (45 ps), the pump information is integrated and remains accessible for times longer than 20 ns.

SHG has been measured for the hexagonal close-packed surface of C_{60} single crystals. The molecular crystals were grown by one of us (H.B.) from C_{60} powder (high grade S Hoechst; 99.6% C_{60} purity, further purified by sublimation) by the double temperature-gradient technique.[12] Grown above room temperature, they are known to have a fcc structure with a lattice parameter of 1.42 nm.[13] The largest crystal is about 3×6 mm^2 and 1 mm thick with a close-packed face exhibiting almost perfect optical reflections. In the optical setup the fundamental and the third harmonic from a Nd:YAG laser are used as a probe and a pump pulse, respectively. The laser generates 35 ps pulses at a 20 Hz repetition rate. The probe beam at 1.17 eV is focused to a 1.2 mm^2 spot. The pump pulse (3.49 eV) illuminates a much larger area. The measurements were performed at room temperature in air. C_{60} is transparent at the probe wavelength. The generated SH radiation lies in a region of small absorption above the optically forbidden band gap. The resonance conditions are thus the same as in a recent thin film study.[10] The pump beam is close to the second absorption maximum (3.56 eV) corresponding to the molecular $h_g \rightarrow t_{1u}$ transition.[14,15] In the reflection and transmission measurements the angle of incidence of the pump and probe beams with respect to the surface normal are 45°. The pump beam is incident at a small angle to the probe beam in the surface reflection geometry, while in the crystal transmission measurements the pump and probe beams are separated by about 90°. In both geometries a difference frequency generation between the pump and probe beams cannot occur in the direction of the detector.

Figure 1 shows the measured SH signal (circles) from the C_{60} crystal surface without a pump beam as a function of azimuthal angle for four polarization combinations. The azimuthal dependence of the signal was fitted to

$$S(\psi)=[a+s\ \sin(3\psi+\Phi)+c\ \cos(3\psi+\Phi)]^2. \qquad (1)$$

The parameters a, s, c, and Φ of the best fit (solid lines in Fig. 1) are given in Table I. One of the amplitudes s or c was set to zero in order to obtain a unique solution with a constant azimuthal phase Φ in all fits. We find isotropic and threefold contributions compatible with SHG at a fcc (111) surface.

When the crystal surface is optically pumped at 3.49 eV the generated SH signal is substantially affected. As shown in Fig. 2(a) it falls off with the pump–probe correlation time

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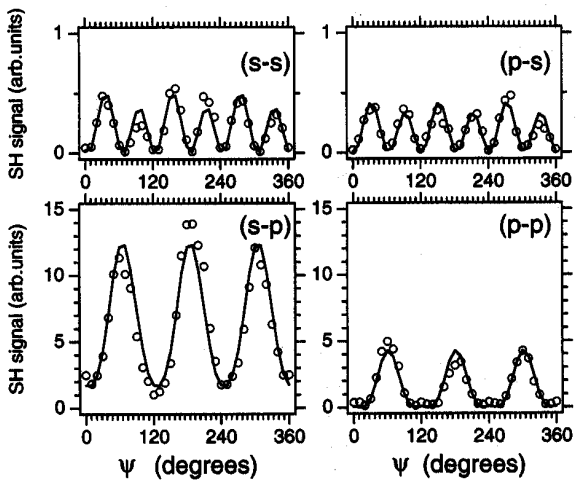

FIG. 1. Azimuthal scans for different polarizations of the incident fundamental (20 mJ/cm^2) and the observed second-harmonic beam. The open circles are the measured points, the lines are best fits to Eq. (1) with the parameters given in Table I. In the short notation the first and second letters indicate the polarizations of the incident fundamental beam (1.17 eV) and the polarization of the generated second-harmonic beam (2.33 eV), respectively.

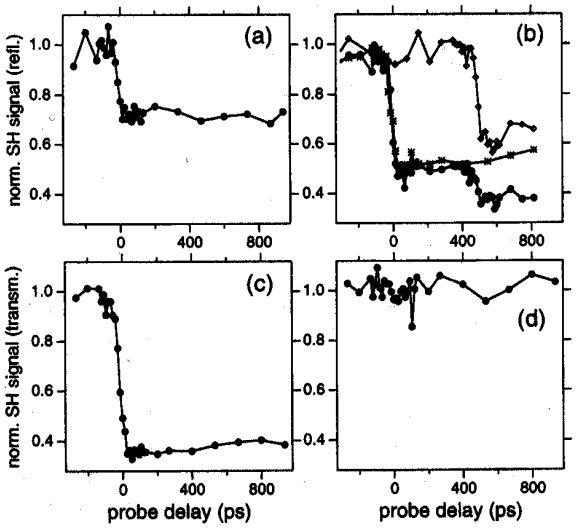

FIG. 2. Ultraviolet pump and SH probe transients at an azimuthal angle of ψ=60°. The SH signal is normalized to the signal without pump pulse. SH in reflection from the crystal surface (p-p polarization): (a) single pulse, pump density 1.3 μJ/cm^2; (b) response to two separate pump pulses of approximately 1.5 μJ/cm^2 each (stars: pulse incident at $t=0$ ps, diamonds: delayed pulse at $t=500$ ps) and response to the succession of the two pulses (full circles). SH signal in transmission through the crystal (containing p-p plus p-s contributions): (c) pump beam incident on the back of the crystal, pump density 6.4 μJ/cm^2; (d) pump beam incident on the front of the crystal, pump density 4.6 μJ/cm^2.

(45 ps) and stays constant over the accessible delay time of 1 ns. The response is thus faster than 45 ps and the lifetime of the observed state is longer than 20 ns. When the following laser pulse arrives after 50 ms the signal has completely recovered. The lifetime τ is thus 20 ns$<\tau<$20 ms. We found equivalent pump-and-probe transients for different azimuthal angles and other polarization combinations of the fundamental, SH, and pump beams. The SH signal is quenched in any case without indication of the creation of an additional isotropic or threefold component. In transmission through a 1-mm-thick crystal the observed SH signal is generated near the exit face. Signal reduction occurs when the exit face is pumped [Fig. 2(c)] while it does not occur if the entrance face is pumped [Fig. 2(d)]. Thus no remarkable transient absorption occurs for the fundamental beam. Also for the SH frequency the transient absorption change[16] cannot explain the observed decrease in the SH signal. The observed decrease is thus based on a true change of nonlinear susceptibility.

Figure 3 shows in a semilogarithmic plot the decrease of the SH signal at 330 ps delay with increasing pump intensity. Fluorescence contributions arising from the pump beam have been subtracted. The best-fit single exponential to the data is obtained as

$$S(P)/S(0)=0.08+0.92\ \exp(-0.36P), \qquad (2)$$

where P is the pump energy density in μJ/cm^2. The $1/e$ value is reached at a pump density of 2.8 μJ/cm^2. A weak beam is thus sufficient to control the SHG efficiency over at least one order of magnitude. As the optical properties change for times longer than 20 ns in response to the absorption of UV photons the crystal surface constitutes a storing detection device which can be read by an IR light pulse. The effect of two successive pump pulses is shown in Fig. 2(b). The first pulse reduces the SH signal to 54%, the second to 62%. The decrease measured after the two pulses is 37% and

TABLE I. Fit parameters of the azimuthal scans in Fig. 1. The fit function is given by Eq. (1).

Polarization: fund.-SH	a	s	c	ϕ (deg)
s-s	0.04	0.66	0	6
s-p	2.40	0	−1.14	6
p-s	0.04	0.61	0	3
p-p	0.90	0	−1.17	2

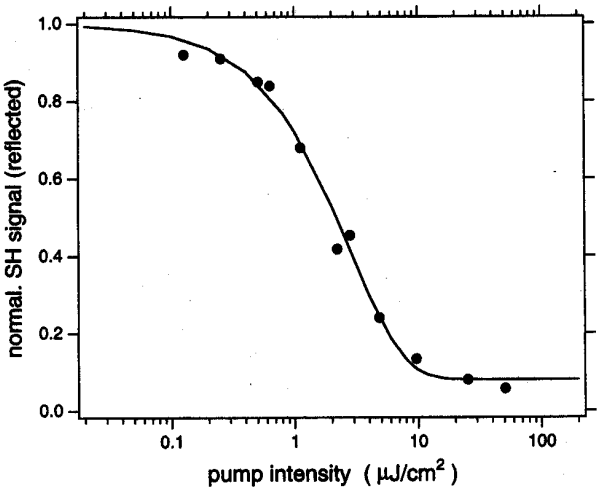

FIG. 3. Normalized SH signal at 330 ps probe delay as a function of pump intensity at 3.49 eV. The full circles and the line represent the measured values and the exponential fit of Eq. (2), respectively.

agrees with the product 54%×62%=33% indicating that the decrease is a function of the time integrated intensity and does not primarily depend on pulse power.

One reason for the high efficiency of SH switching is the limitation of excitation to the surface region where in the case of a thick crystal the reflected SH signal is generated. There is no evident transport of excitation into the bulk on a ns time scale. The change in optical properties occurs due to excitation of the electronic system and is not due to the pump-induced heating of less than 0.9 K.[17] We can also exclude that the presence of oxygen, C_{70} impurities, or photopolymerization by the UV pulses plays an essential role in the described effect.[18] Photoexcitation of solid C_{60} above 1.5 eV results in the creation of singlet Frenkel excitons, which can decay via intersystem crossing to triplet excitons. They can dissociate to charged polarons or even free carriers.[19] A SH contribution from trapped excitons at isolated chemical impurities does not explain an overall quenching of the SHG efficiency in which the crystal symmetry is reflected. With the extinction depth for the pump pulse in C_{60} of $\alpha^{-1}=43$ nm (Ref. 15) an energy density of 2.8 μJ/cm^2 corresponds at the surface to a ratio of absorbed photons to C_{60} molecules of only 8×10^{-4}. Even if all excitations would rapidly migrate to the surface the excitation density in the top layer would remain below 5%. The low excitation density suggests that each excitation quenches the SH signal generated by a large number of molecules. Indeed, at photon energies above 2 eV the excitation has been found to result in an increased creation of molecularly nonlocalized states and free carriers.[20] Whereas the SHG from solid C_{60} in the ground state and at room temperature can be described by molecular transitions, the presence of electronic excitation even at low densities tends to include intermolecular coupling effects. Both, extended electric fields due to charge separation (polarons and free carriers) and delocalized electronic states will affect the nonlinear optical properties. Currently we cannot unequivocally assign the operative mechanism. Spectroscopic studies are in progress in order to further clarify the origin of the induced change in SHG. These studies will provide information on the spectral range over which the susceptibility can be controlled and reveal the dependence of efficiency on the wavelength of the pump beam.

In summary, we have reported on the efficient control of SHG at C_{60} single-crystal surfaces under ambient conditions due to pump pulses in the UV of only a few μJ/cm^2. The response of the nonlinear optical properties of the system is faster than 45 ps and persists for times longer than 20 ns. The surface behaves as a storing UV detector which can be read by an IR pulse. We suggest that nonlocalized excited electronic states play an important role in the change of nonlinear optical behavior.

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