

NONLINEAR OPTICAL DYNAMICS AT SOLID C₆₀ INTERFACES

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The optical quenching of second harmonic generation (SHG) at surfaces of solid C₆₀ is characterized: A fast decay (<45ps) of the signal is followed by a slow recovery (>20ns and <20ms). The efficiency of SH suppression traces the absorbance of the C₆₀ solid for photon energies between 3.5eV and 1.6eV. In this range the same intensity reduction is observed for the same number of photons absorbed per unit of volume. This identifies the lowest states leading to SH quenching to be excitonic states below the band gap. For films thinner than 100nm an additional state with a lifetime of 70ps is observed. It is ascribed to excitons at the C₆₀/quartz interface.

1 Introduction

From the similarity of carbon bonding in C₆₀ and conjugated chain molecules it was assumed that non-linear optical properties may change significantly on electronic excitation. A strong increase was indeed reported for degenerate four wave mixing (DFWM) in C₆₀ toluene solutions [1]. Due to the different properties of the tensors involved these results cannot be transposed to three wave mixing experiments like second harmonic generation (SHG). In fact recent UV pump - SHG probe experiments for C₆₀ crystals [2] demonstrated that the SH signal significantly decreases on a ps time scale upon optical excitation by UV light pulses. Due to this result and due to its surface sensitivity, SHG can be employed to study the dynamics of C₆₀ electronic excitations at interfaces as will be shown in this contribution.

2 Experimental

The experiments are performed at room temperature for thin C₆₀ films evaporated from a Knudsen cell at 680K in high vacuum onto a heated (415K) polycrystalline quartz substrate. Before, the C₆₀ powder (99.9% purity) had been cleaned from residual solvent by heating in vacuum to 550K for 48 hours. The fundamental wavelength of a 20Hz Nd:YAG laser ($h\nu = 1.2\text{eV}$) with 35ps pulse duration are employed for second harmonic generation (SHG) in transmission through the samples (Fig.1). The third harmonic of the laser radiation ($h\nu = 3.5\text{eV}$) is used either

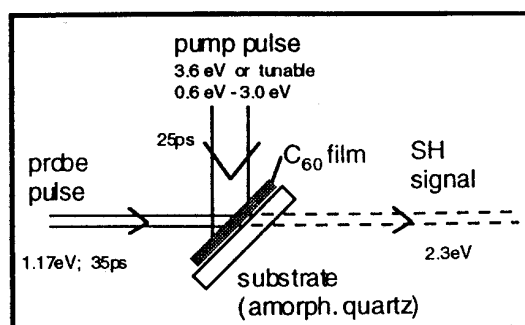


Figure 1 : Geometry of the film experiments

as a direct pump pulse for the C_{60} sample or it is used to generate pump pulses tunable in the range 0.6eV to 3.0eV by means of an optical parametric generator/amplifier (OPG/OPA) set-up [3]. SHG measurements are made in a high vacuum chamber. There is no significant SHG contribution from the amorphous quartz substrate. The spot illuminated by the pump beam is much larger than the spot illuminated by the probe beam.

3 Results and Discussion

3.1 Thick films

Fig.2a shows the transient response of the SH signal from a thick film to a UV pump pulse (3.6eV) incident at $t=0$ ps. The signal has been normalized to the SH signal without pump beam. A sharp drop of the signal occurs within the experimental time resolution (45ps). The SH signal stays low for 20ns or more. It has recovered completely after 50ms when the next laser pulse arrives. The dependence of the reduced SH intensity on the pump intensity (energy per area) is shown in the 3.49eV curve in Fig.3. The experimental data (symbols) can be well fitted by single exponentials (solid lines)

$$I_{SH}(p) = A + (1 - A)e^{-\gamma p} \quad (1)$$

with the unquenchable SH contribution A , the pump density p and the efficiency parameter γ . We define the quenching cross section $\eta_{pump} = h\nu\gamma$ and obtain $1/\gamma = 3\mu\text{J}/\text{cm}^2$ and $\eta_{pump} = 19 \text{ nm}^2$ for 3.5eV pump photon energy. This cross section is large compared to the C_{60} lattice parameter.

The quenching of the SH signal is a true effect of the nonlinear polarizability. Transient absorption changes for the fundamental (1.2eV) and the second harmonic (2.3eV) beams are too small to explain the observed decrease. The effect is not due to local heating by the pump pulse of the order of $\Delta T=1\text{K}$. The low excitation density which is sufficient to quench the SH signal might indicate the involvement of impurities. However, the quenching cross section was found to be very similar for a wide variety of differently prepared samples. The suppression is not sensitive to the

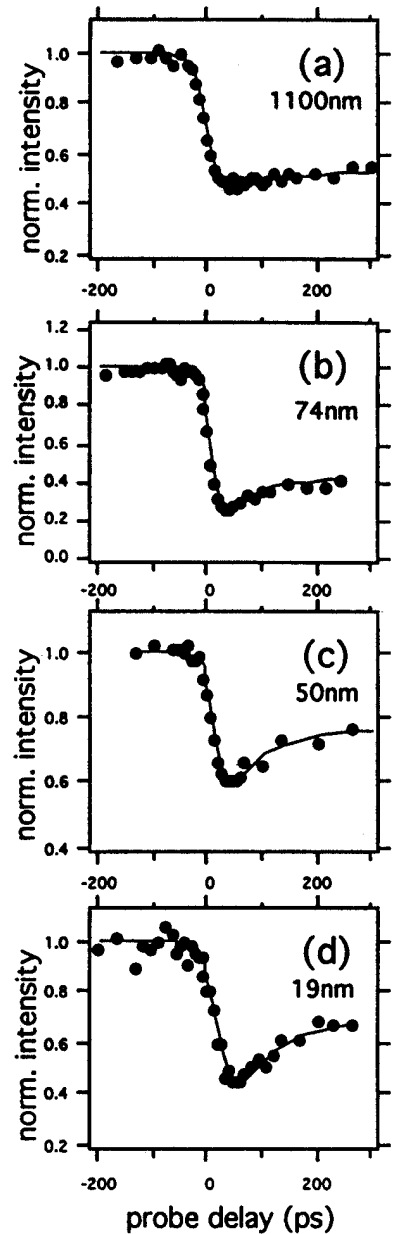


Figure 2: 3.6eV-pump-SHG-probe transients for C_{60} films of decreasing thickness (a-d). The appearance of a short lived state (70ps) is observed.

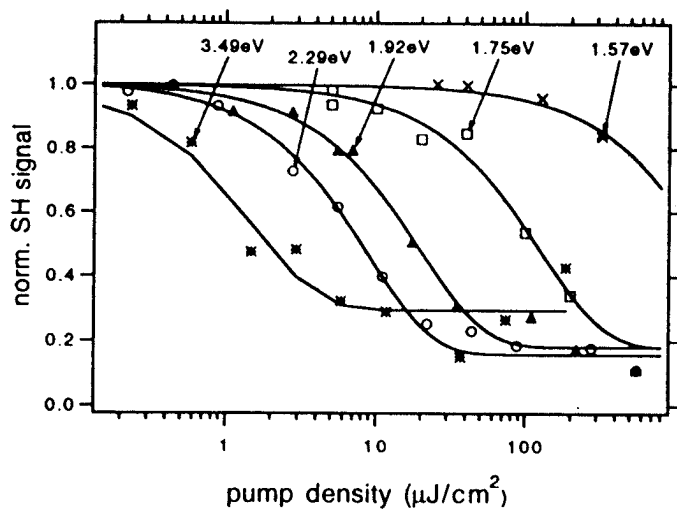


Figure 3: Pump density dependence of SH quenching for different photon energies. Film thickness 250nm, probe delay 300ps.

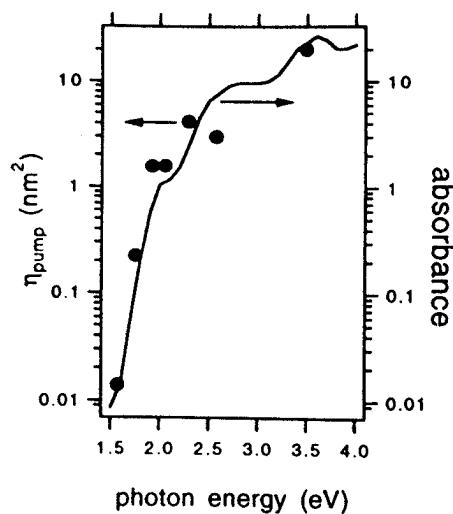


Figure 4: SH quenching cross section (dots) and thin film absorbance [4] (line) as a function of photon energy.

presence of oxygen as the same behavior is observed in air and in high vacuum. Also, Raman spectroscopy from one of our samples did not show any indications of polymerization after irradiation by 3.5eV photons at an energy density of $30\text{mJ}/\text{cm}^2$ over 150,000 laser shots (which is much more than in a typical measurement).

Fig.3 shows the pump energy dependence for photon energies between 3.5eV and 1.6eV. The quenching cross section calculated from these data is plotted in Fig.4 (dots). The cross section nicely follows the thin film absorbance demonstrating that the reason for reduced quenching efficiency at long wavelengths is the reduced absorption. In the entire range the same number of absorbed photons per volume results in the same SH reduction. The cut-off at 1.85eV (Fig.4) proves that states below the band gap (2.3eV [5]) play a decisive role in SH suppression. Free carriers do not determine the SH suppression as else a cut-off at 2.4eV [6] would be observed. Photo excitation of C_{60} results in the creation of an electron-hole pair which rapidly relaxes to the band gap where it binds to form an exciton. A singlet exciton at 1.8eV is created at first which then undergoes an intersystem crossing in 1.2ns [7] to a triplet exciton (1.55eV [8]) with a life time of the order of 100ms. The instantaneous decrease of the SH signal (Fig.2a) suggests that the singlet exciton causes the SH quenching in agreement with the spectroscopic result.

With respect to the described observations it is interesting to notice that a similar SH quenching effect was observed for corona poled C_{60} films [9]. Our results demonstrate that if the quenching mechanism in the two experiments should be similar the effect is more general and does not rely on the enhancement of SHG induced by a poling field.

3.2 Thin films

In addition to the long lived state observed for C₆₀ crystals and thick films a short lived state appears for decreasing film thickness (fig.2.b,c,d). A fit taking into account the instrumental time resolution (45ps) yields a decay time of this state of 70ps. The short life time is due to the interface between C₆₀ and the substrate. This interface is not equivalent to the film surface because C₆₀ molecules are situated close to a dielectric. The dynamic dipole coupling to the dielectric can result in energy transfer to the substrate [10] or induce additional decay channels by breaking the symmetry of the sites. Both mechanisms will lead to a reduced life time. The observed appearance of the short lived interface state below 100nm film thickness can be explained by increased transmission of the pump pulse through the film. The pump intensity transmitted to the C₆₀ quartz interface increases exponentially with decreasing film thickness (penetration depth 30nm for at 3.5eV photon energy [11]) in agreement with the experimental observation. We thus ascribe the short lived state to excitons located at the C₆₀/quartz interface.

4 Conclusion

The observation of the short lived state at the C₆₀/quartz interface shows that the pump-SHG-probe technique described in this contribution gives access to detailed studies of even weak coupling of the molecular solid to its immediate environment. It will also be applicable to the observation of the exciton decay in C₆₀ molecules which are separated from a metal by a spacer layer.

5 References

1. F. Li, et al., in: Proceedings of SPIE ,Vol. **2284**, Fullerenes and Photonics, Z. H. Kafafi, Eds. (1994), pp. 169.
2. K. Kuhnke, *et al.*, J.Appl.Phys. **79** (1996) 3781.
3. H.-J. Krause, *et al.*, Appl.Phys.Lett. **60** (1992) 2180.
4. A. Skumanich, Chem.Phys.Lett. **182** (1991) 486.
5. R. W. Lof, *et al.*, Phys.Rev.Lett. **68** (1992) 3924.
6. S. Kazaoui, *et al.*, in: Physics and Chemistry of Fullerenes and Derivatives; H. Kuzmany, J. Fink, M. Mehring and S. Roth, Eds. (World Science, New York, 1995), pp. 242.
7. H. J. Byrne, *et al.*, Chem.Phys.Lett. **204** (1993) 461.
8. A. Lucas, *et al.*, Phys.Rev.B **45** (1992) 13694.
9. X. K. Wang, *et al.*, Thin Solid Films **257** (1995) 244.
10. K. H. Drexhage, in: Progress in optics; **XII**, E. Wolf, Eds. (North-Holland, Amsterdam, 1974), pp. 163.
11. A. F. Hebard, *et al.*, Appl.Phys.Lett. **59** (1991) 2109.