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Dynamics of second harmonic generation at the C_{60}/quartz interface

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Abstract

The dynamics of electronic excited states is studied for thin C_{60} films on quartz by second harmonic generation. Time resolved measurements show that for films thicker than 100 nm a single excited state is observed, which is occupied in faster than 45 ps and decays over 20 ns or longer. Spectroscopic studies reveal that the state can be excited over the entire visible range following the C_{60} absorbance down to 1.6 eV. This indicates that excitonic states below the band gap, most likely the lowest singlet and triplet states, determine the suppression mechanism. For thin films below 100 nm thickness a second excited state with a substantially reduced lifetime of 70 ps is observed. This state is attributed to the C_{60}/substrate interface and gives access to the coupling between C_{60} excitonic states and the immediate environment of the molecule.

Considerable interest has been shown recently in the photophysical and photochemical properties of fullerenes [1–6]. Many studies have demonstrated interesting fundamental and perhaps technologically relevant properties. Of particular interest are the optical properties in heterogeneous media. Understanding interactions at interfaces is a prerequisite for recognizing the opportunities for potential applications. Specifically, the lifetime of long-lived ($t > 1$ ns) electronic excitations in C_{60} is assumed to be determined by external and internal interfaces [7]. Non-linear optical methods, such as second harmonic generation (SHG) or sum frequency generation (SFG), are well known to be sensitive tools for the study of excitations at interfaces [8–10].

From the similarity of carbon bonding in C_{60} 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 C_{60} toluene solutions [11]. 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 C_{60} crystals [12] demonstrated that the SH signal significantly decreases on a picosecond timescale upon optical excitation by UV light pulses. In this Letter we present evidence, that the SHG quenching is an intrinsic effect of solid C_{60}. The study focuses on polycrystalline thin films where energy transfer processes become observable. In addition to the long-lived state observed at single crystal surfaces thin films exhibit a short-lived state which decays with a 70 ps time constant. The state is ascribed to excitons with reduced lifetime at the C_{60} / substrate

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interface. The study demonstrates that pump and SHG probe measurements can easily access the coupling between C_{60} molecules and their environment.

The experiments are performed at room temperature for thin C_{60} films evaporated in high vacuum (HV) onto polycrystalline quartz substrates. The substrates were cleaned by a dip in HF solution (concentration 5%), rinsing in deionized water followed by thorough rinsing in ethanol. The C_{60} powder (99.9% C_{60} purity) was cleaned from residual solvent by heating in vacuum to 550 K for 48 hs. The sublimation was made from a Knudsen cell at 680 K with a rate of less than 1 monolayer per minute onto a heated substrate (415 K). The thickness of each film was determined by edge profile measurements with nanometer resolution at the film edge and by spectrometric absorption measurements in the 900–200 nm wavelength region [13]. Samples with a thickness between 1200 and 20 nm were studied.

In the optical apparatus the fundamental wavelength of a 20 Hz Nd:YAG laser ($h\nu = 1.17$ eV) with 35 ps pulse duration was used for second harmonic generation (SHG) at the samples. The third harmonic of the laser radiation ($h\nu = 3.49$ eV) was used either as a direct pump pulse for the C_{60} sample or it was used to generate pump pulses tunable in the range 0.6 to 3.0 eV by means of an OPG/OPA set-up similar to the scheme described by Krause and Daum [14]. SHG measurements were performed in air and in a HV chamber in transmission through the sample. There was no significant SHG contribution from the amorphous quartz substrate.

The geometry of the experimental apparatus is shown in Fig. 1. Probe and pump pulses are incident at approximately 45° with respect to the surface normal. The pump pulse is reflected away from the detection unit of the SH signal thus reducing the

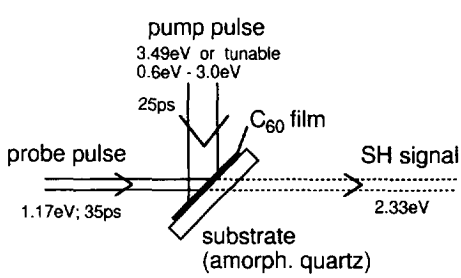

Fig. 1. Experimental geometry of the C_{60} film experiments.

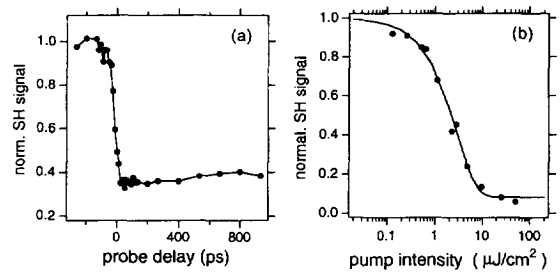

Fig. 2. UV pump–SHG probe transients for C_{60} single crystals with 3.49 eV pump beam and a 1.17 eV probe beam [12]. (a) Normalized SH signal transient with the pump beam incident at $t = 0$ ps. (b) Measured SH signal at 330 ps probe delay as a function of the pump energy per area (dots). The solid line is a single exponential fit with a 1/e decay at 3 $\mu J/cm^2$.

background and excluding detection of any frequency mixing. Typical probe pulse energies are 200 μJ on a 0.5 mm^2 spot. The spot illuminated by the pump beam is much larger than the spot illuminated by the probe beam.

We first give a short introduction to the observed quenching of the second harmonic (SH) signal for C_{60} single crystals [12]. Fig. 2a shows the response of the SH signal to the incidence of a UV pump beam (3.49 eV). The signal has been normalized to the SH signal without the pump beam. On the arrival of the pump pulse a sharp drop of the signal occurs within the experimental time resolution (45 ps). The SH signal stays at a low level for more than 20 ns. It has recovered completely after 50 ms when the next laser pulse arrives. Fig. 2b plots the SH signal at a probe delay of 330 ps as a function of the pump energy per area. A 1/e reduction is reached at pump densities of 3 $\mu J/cm^2$ which corresponds at this photon energy to an absorption density at the sample surface of 1 photon per 1000 C_{60} molecules demonstrating that essentially no depletion of the ground state occurs. The required pump density is more than five orders of magnitude smaller than for C_{60} 'linear' optical switching in solution [15]. The SH signal from the C_{60} crystal exhibits a threefold symmetry as expected for an fcc(111) surface plane. The signal reduction occurs independently of azimuth and is independent of the polarizations of probe beam, SH beam and pump beam. It corresponds to quenching of the SH signal and is not due to a destructive interference with an additional transient SH compo-

nent. The SH signal can typically be reduced to less than 10% of the original signal. The small excitation density required to quench the signal suggests that each excitation significantly reduces the second order non-linear susceptibility of C_{60} in a sphere of 5.5 nm radius. The exponential decrease of the signal with pump intensity reflects a Lambert–Beer type behavior. The SHG decrease can be explained by excited states perturbing the SH response of many molecules or may be due to electric fields resulting from charge separation.

The time and energy dependences of the SHG quenching observed for thick films of the order of 1 μm are similar to the ones of the C_{60} crystal. The azimuthal signal dependence observed for the crystals is not present for the films due to their polycrystalline nature on the quartz substrate. The curve for 3.49 eV in Fig. 3a shows the pump density dependent reduction of SHG for a thick film in good agreement with the result of the single crystal (Fig. 2b). The residual SH signal at maximum suppression by the pump pulse is slightly larger than in the case of the single crystal. The residual intensity becomes still larger if the films are not heated during C_{60} evaporation, indicating that unquenchable contributions are arising from structural defects.

The quenching of the SH signal is a true effect of the non-linear polarizability. Transient absorption changes for the fundamental (1.17 eV) and the second harmonic (2.33 eV) 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 $\Delta T = 1$ K. The low excitation density which is sufficient to quench the SH signal might indicate the involvement of impurities. However, the pump density necessary to reduce the SH signal to $1/e$ was found to be similar for a wide variety of differently prepared samples. In particular, it was verified that the efficiency does not change when the concentration of the main impurity, C_{70}, is increased by a factor of ten. The suppression is not due to the presence of oxygen as the same behavior is observed in air and in a high vacuum cell (10^{-6} mbar). Finally, it must be taken into consideration that the use of strongly absorbed pump radiation can result in a slow photo polymerization. However, the identical

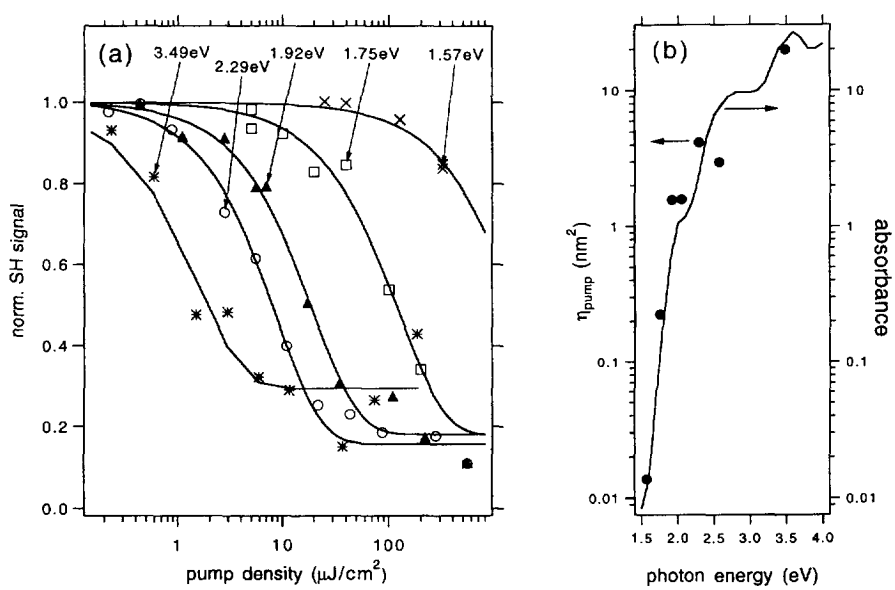

Fig. 3. (a) Quenching of the normalized SH signal of a thick film (250 nm) as a function of pump density for different photon energies at 300 ps probe delay. Compare to the single crystal result in Fig. 2b. The solid lines are best fits to a single exponential, Eq. (1). From the fit parameters the SHG quenching cross section is calculated. (b) SH quenching cross section η_{pump} (definition see Eq. (2)) as a function of photon energy (dots) compared to the film absorption (solid line) taken from Ref. [17]. A scaling factor was used to overlay the two curves.

observation of SH quenching in air and vacuum suggests that a polymer is not involved as the presence of oxygen is known to inhibit polymerization [16]. Moreover, in comparison to the doses required for a measurable polymerization the energy deposited by the pump pulse is negligible: we observe SH quenching already in a 7 min measurement with a 2.5 eV pump beam from a freshly prepared thin film. After this measurement the sample which was transferred to the experiment under dark room illumination has been exposed to a total pump energy of only 0.004 J/mm^2 compared to a dose of 55 J/mm^2 at the same wavelength necessary to obtain detectable polymerization [16]. Raman spectroscopy from one of our samples which was irradiated by 3.49 eV photons at an energy density of 30 μJ/cm^2 over 150 000 laser shots did not indeed show any indications of polymerization.

In Fig. 3 the pump density (energy per area) dependence of the SH quenching is plotted for different photon energies. For decreasing photon energy larger pump densities are necessary to achieve the same SH signal reduction. In order to quantify the efficiency the experimental data at each photon energy have been fitted by a single exponential (solid lines in Fig. 3a)

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

with the unquenchable SH contribution A, the pump density p and the efficiency parameter γ. We define the quenching cross section

$$\eta_{pump} = \hbar\omega\gamma \quad (2)$$

and obtain $\eta_{pump} = 19$ nm^2 for the above case of 3.49 eV pump photon energy and $1/\gamma = 3$ μJ/cm^2. This result for the thick film agrees within experimental uncertainty with the result obtained for the single crystal. In Fig. 3b we have plotted the quenching cross section as a function of photon energy together with the absorbance of a C_{60} film. The suppression efficiency decreases by three orders of magnitude between the near UV and the near IR nicely following the C_{60} film absorption measured by photothermal deflection spectroscopy [17]. The absorbance of a film is proportional to the fraction of photons absorbed per unit length at its surface. It is also proportional to α, the inverse of the penetration depth of the pump beam. The measurement thus demonstrates that the ratio η_{pump}/α is constant. In the entire range of measurements (Fig. 3) the same number of absorbed photons per volume results in the same SH reduction. The observed cut-off at 1.85 eV proves that states below the band gap (2.3 eV) [18] play a decisive role in SH suppression. The observation demonstrates that free carriers do not determine the SH suppression as else a cut-off at 2.4 eV [19] would be expected. Photoexcitation 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. Carrier relaxation was observed to occur on a timescale of 1 ps and is thus much faster than the observed transients [20]. Due to the spin states of the electron and hole immediately after their creation a singlet exciton at 1.8 eV is formed at first. It then undergoes an intersystem crossing in 1.2 ns [7] to a triplet exciton (1.55 eV [21]) with a lifetime of the order of 100 μs. The observed decrease of the SH signal (see Fig. 2a) on a picosecond timescale thus demonstrates that the singlet exciton causes the SH quenching in agreement with the spectroscopic result. The absence of any decay of SH quenching within 1 ns suggests that the triplet state may also be involved in the late stage of the process. The SH signal may respond similarly to the excitation of the singlet and triplet excitons.

With respect to the described observations it is interesting to note that a similar SH quenching effect was observed for C_{60} films protected by a SiO_2 capping and exposed to corona poling fields at 140°C [22]. Corona poled films were reported to exhibit a substantial increase in SHG efficiency. The quenching of SHG upon excitation by a UV pump pulse was interpreted as a generation of free carriers compensating for the effect of the exposure to the poling field. Our results, however, 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.

In the following we discuss the results for films below 100 nm thickness. In addition to the long-lived state observed for crystals and thick films a short-lived state appears for decreasing film thickness (Figs. 4b–4d). A fit taking into account the instrumental time resolution (45 ps) indicates a decay time

of this state of about 70 ps. The short lifetime is likely to be due to the influence of the interface between C_{60} and the substrate. This interface is not

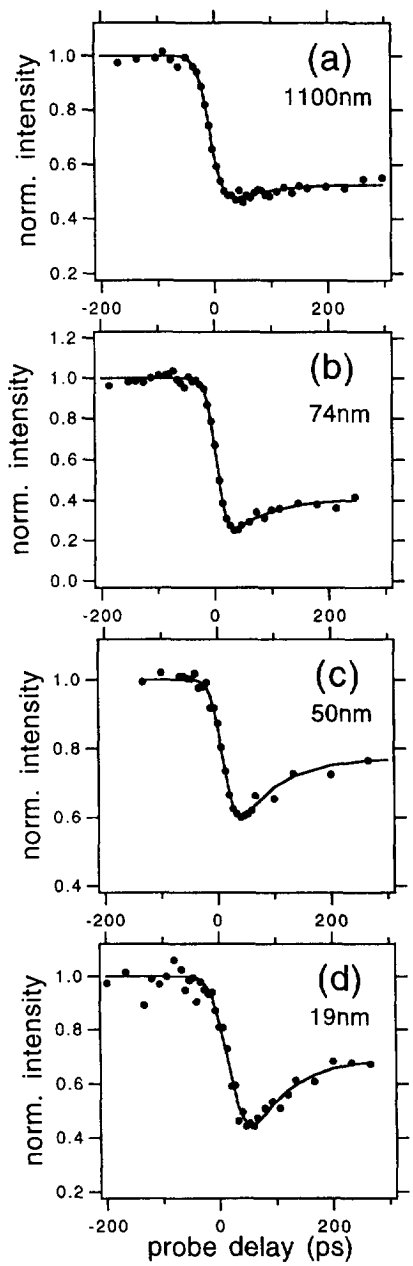

Fig. 4. 3.49 eV pump and SHG probe transients for C_{60} films of decreasing thickness, (a)–(d). The 1100 nm thick film exhibits a response similar to the single crystal (see Fig. 2a). With decreasing film thickness a short-lived state (70 ps) becomes prominent.

equivalent to the film surface because the C_{60} molecules are situated close to a dielectric. The dynamic dipole coupling to the dielectric results in a changed radiative rate constant [23]. Moreover, additional decay channels can arise due to the breaking of site symmetry at the interface. Both mechanisms will lead to a reduction of observed lifetime. Another mechanism might be the quantum confinement of the excitonic states. In a study of multiple quantum wells of crystalline organic semiconductors a continuous reduction of exciton lifetime with decreasing film thickness was reported which results from the squeezing of the exciton volume [24]. Even though the layer thickness in the present case is of the same magnitude (< 100 nm) the fact that we see a second state with a lifetime which is independent of film thickness suggests that this model, although appealing, is not compatible with our observation. The short-lived state can thus be assigned to an excitonic state located at the interface.

In fact the observed appearance of the short-lived interface state below 100 nm film thickness can be explained by a simple calculation. For decreasing film thickness, the ratio of the amplitude of the short-lived state A_{short} and the amplitude of the long-lived state A_{long} increases. We compare this ratio to the ratio of the pump intensities present at the film surface and the pump intensity at the film/substrate interface. The latter is calculated from the extinction depth of C_{60} for the 3.49 eV pump light of 30 nm [13,25]. The absorption of the fundamental and SH photons can be neglected in this estimate. The two ratios are found to be proportional to each other, supporting the assignment of the short-lived state to the C_{60}/quartz interface. It is likely that the SH quenching by the short-lived state and by the long-lived state are due to a similar type of excitation. Further efficiency measurements are necessary to prove an equivalent spectral behavior. It appears, however, reasonable to assume that C_{60} excitons below the band gap exhibit a reduced lifetime at the interface. One may speculate about the role of internal interfaces in polycrystalline films. If the lifetime of the exciton decreases far below our experimental time resolution (45 ps) the short-lived state will not be observable. At the same time the long-lived state will only exhibit a small amplitude even for large pump intensities. This situation is

exactly found in the transients measured for films with small grain sizes. Internal grain boundaries may thus act similarly to external interfaces resulting in a reduced lifetime quite in contrast to the surface which does not exhibit a short-lived state.

The observation of the short-lived state at the C_{60}/quartz interface gives access to detailed studies of the coupling of the molecular solid to its immediate environment. The small difference between absorption spectra of isolated molecules and the molecular crystal is regarded as an indication of the weakness of interaction within the C_{60} solid resulting in rather localized electronic ground states. Studies on the C_{60} adsorption on metals [26–28] and semiconductors have demonstrated a strong interaction leading to covalent bonding and charge transfer. In these cases the electronic properties of the C_{60} layer at the interface are substantially altered. The coupling at a C_{60}/quartz interface will be much weaker. The technique described in this Letter proves to be sensitive to these comparatively weak interactions. The technique may also be applicable to the observation of exciton decay in C_{60} molecules which are separated from a metal by a spacer layer [23].

In summary, we have shown that the SH quenching for films thicker than 100 nm is similar to the quenching observed for C_{60} crystals: a decay within less than 45 ps is followed by a recovery time of 20 ns or longer. The efficiency of SH suppression traces the absorbance of the C_{60} solid for photon energies between 3.5 and 1.6 eV. 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 (the singlet state at 1.8 eV and the triplet state at 1.55 eV). For films thinner than 100 nm an additional state with a lifetime of 70 ps is observed. With decreasing film thickness this state becomes more and more prominent; its lifetime is independent of thickness. The short-lived state is ascribed to the C_{60}/quartz interface, where the coupling to the dielectric induces a reduction of the C_{60} exciton lifetime.

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