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C_{60} excited state energy transfer to metal surfaces across distances below 3 nm

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Abstract

The light-induced instantaneous quenching of second harmonic generation at C_{60} interfaces is employed to measure the decay rate of C_{60} excitons at various interfaces. While at C_{60} surfaces a state with a life time longer than 20 ns is observed the C_{60} /quartz interface exhibits a short lived state (70 ps) ascribed to a decreased life time of C_{60} excitonic states due to the proximity of the dielectric. The coupling between excitonic C_{60} states and a metal surface can be varied by employing C_{60} /alkanethiol/Au sandwich structures with alkanethiols of different chain length. For spacer layers from 2.4 to 1.0 nm a decrease of the life time from 520 to 44 ps is observed.

Keywords: Energy dissipation; Fullerenes; Non-linear optical methods; Polycrystalline thin films; Second harmonic generation

1. Introduction

The transfer of energy near surfaces and interfaces is of fundamental interest for the understanding of the coupling between different parts of heterogeneous systems. The quantitative determination of the coupling strength gives valuable information on the transfer processes [1]. Of interest with respect to interface characterization and surface active sensors [2] is the transfer of energy between two media which are in contact at an interface.

Energy transfer taking place on the sub-ns time scale can be investigated by pump-and-probe techniques employing ultra-short laser pulses. The modification generated by the pump pulse is monitored by a probe pulse after a variable delay time.

Apart from transient absorption measurements [3] an important probe technique is sum frequency generation (SFG) [4] and second harmonic generation (SHG). The energy transfer between two coupled systems can be determined by probing the state which is primarily excited and deriving the coupling to the second system from the life time changes in varied geometries.

In this paper we present results of a pump-and-probe investigation employing optical second harmonic quenching at C_{60} interfaces. We reported recently that the SH signal generated at a C_{60} sample is temporarily quenched by a light pulse [5]. We present here results from C_{60} films on quartz and show that this effect is well apt to probe the coupling of C_{60} electronic transitions to the surface of another solid. The technique is then applied to study the coupling of C_{60} to a metal surface over small adjustable distances. It is known

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that upon direct contact with a metal the electronic properties of a C_{60} monolayer are strongly modified due to charge transfer or covalent bonding [6]. Employing insulating spacer layers these drastic effects can be avoided although an efficient excitation transfer can still occur. The deexcitation of excited electronic states can occur due to near field radiation effects or due to electron and hole tunneling.

A detailed identification of the transfer process requires a careful control of the C_{60} -metal distance with ångström precision. We describe a sandwich system in which C_{60} is separated from a Au surface by a thiol spacer layer which provides a well defined spacing due to the perfect substrate wetting and the ordering in the self-assembled monolayers. Samples prepared in this way allow a precise determination of the distance dependence of the excitation transfer rate at extremely short distances.

2. Experimental

For the first set of experiments C_{60} films are prepared by evaporation in high vacuum on thin quartz substrates. The pure (99.9%) C_{60} powder is preheated in vacuum to 550 K for some 50 h prior to evaporation at 680 K from a Knudsen cell onto the heated (415 K) quartz substrate. The C_{60} /alkanethiol/Au sandwich structures are prepared in the following way: A Au film is evaporated onto a freshly cleaved mica surface. The front side is glued to a silicon substrate and the mica removed thus exposing an ultra-flat Au surface [7]. In a 1 mM ethanolic thiol solution a thiol monolayer self-assembles on the Au surface. In order to obtain a well ordered layer the sample is left in the solution for more than 10 h. Finally a thin C_{60} film (<20 nm) is evaporated in vacuum from the Knudsen cell onto the thiol layer. C_{60} molecules are physisorbed on the $-CH_3$ tail group of the thiol as evidenced by the C_{60} mobility seen by STM at 300 K and complete removal by rinsing in chloroform [8]. A well-prepared thiol layer is compact [9,10] and prevents any penetration of C_{60} into the spacer layer thus exactly defining the C_{60} -Au distance. The samples are transferred to a

high vacuum chamber in which the pump-and-probe measurements are carried out at room temperature.

In the experimental set-up 35 ps light pulses at 1064 nm (1.17 eV) are employed as a probe beam which generates the second harmonic (SH) signal at the sample. A 25 ps pump pulse at 355 nm (3.5 eV) is used to create the excitation of the sample. Pump and probe beams are derived from the pulses of a Nd:YAG laser operating at 20 Hz repetition rate. The geometries of the experiments are shown in Fig. 1. The SH photons are emitted from the sample in a narrow beam and are detected

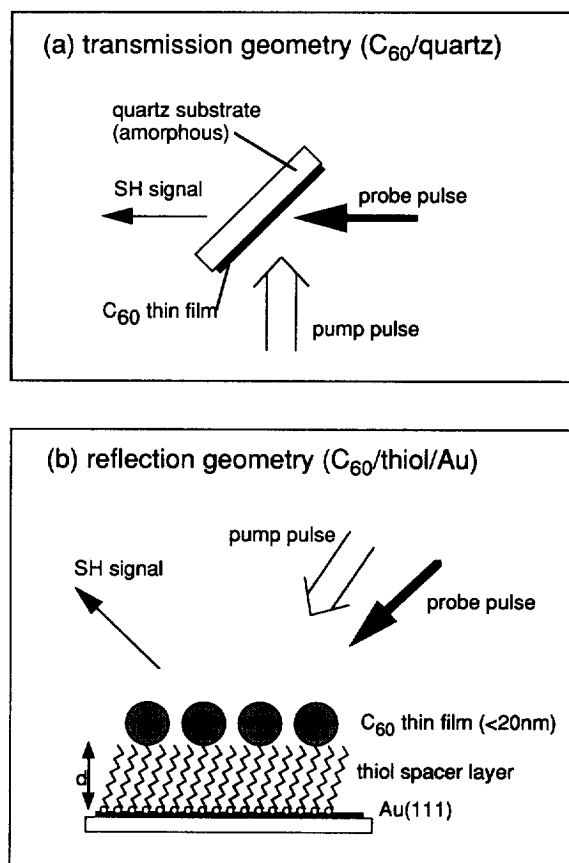


Fig. 1. Geometries used in the pump-and-SH-probe experiments: (a) transmission geometry used in the C_{60} /quartz experiment, (b) reflection geometry employed to study the C_{60} /thiol/Au sandwich structures. In both experiments the incident probe beam and the pump beam have wavelengths of 1064 and 355 nm, respectively.

by a standard photomultiplier mounted on a monochromator. The probe beam is p-polarized, the detected SH photons are not polarization selected. The polarization of the pump beam is arbitrary and does not contribute to the experimental result.

3. Results/discussion

3.1. C_{60} /quartz interface

SH quenching of electronically excited C_{60} was observed for C_{60} single crystals and for thin films on amorphous quartz substrates. Fig. 2 shows

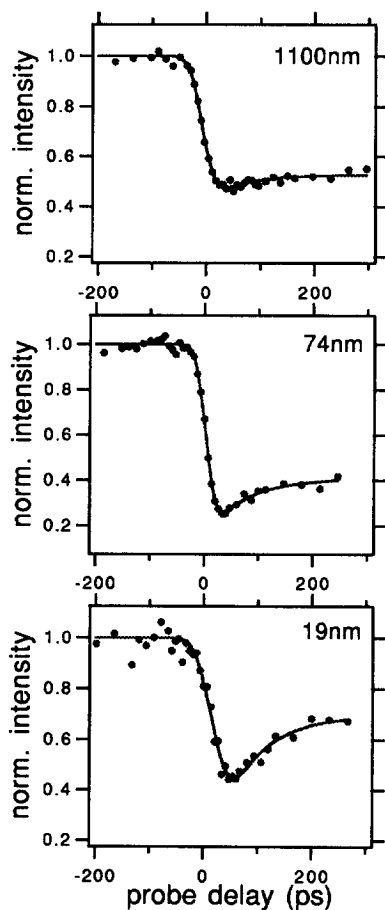


Fig. 2. Pump-and-SH-probe transients for C_{60} films of different thickness on an amorphous quartz substrate. The normalized SH signal is plotted as a function of probe pulse delay time.

typical transients for films of different thicknesses. The SH signal is normalized to the signal generated in the absence of a pump beam. The time scale represents the delay of the probe pulse with respect to the pump pulse. Thick films (Fig. 2 top) exhibit a quenching of the SH signal upon arrival of the pump pulse. It is important to note that very low pump densities of a few $\mu\text{J cm}^{-2}$ are sufficient to substantially reduce the SH probe signal. The missing recovery of the signal in Fig. 2 top demonstrates that the probed state has a long life time (>20 ns). The response of the system to the pump beam is instantaneous and efficient SH quenching is possible over a wide spectral range (350 to >650 nm). The high efficiency at 650 nm indicates that excitonic states located below the C_{60} band gap are responsible for SH quenching. It has been shown that the lowest singlet exciton is a likely candidate with an appropriate life time [11].

In addition to the long lived state observed for thick films, thin films exhibit a state with a reduced life time. It becomes more prominent with decreasing film thickness (Fig. 2 top to bottom). The life time is 70 ps independent of the film thickness. The short lived state is due to energy transfer at the C_{60} /quartz interface. In transmission geometry the interface will be excited by the pump beam only when the film thickness is of the order of or smaller than the extinction depth of the pump beam in solid C_{60} (30 nm [12]). The reduced life time of the excitonic state can be ascribed to the C_{60} environment which is modified at the interface by the quartz substrate. The C_{60} exciton lifetime may be modified, e.g. due to the presence of polar Si-O species at the interface.

3.2. C_{60} /thiol/Au sandwich structure

From the preceding discussion one can conclude that the coupling of C_{60} excitons to their environment can be studied by means of pump-and-SH-probe measurements. We apply the technique to the sandwich layers shown schematically in Fig. 1b. Samples with thiols $\text{CH}_3(\text{CH}_2)_n\text{SH}$ of different chain lengths n were prepared and investigated. Transients for thiols between $n=5$ and $n=17$ are shown in Fig. 3. Similar to the case of C_{60} /quartz a short lived state is observed. Its life

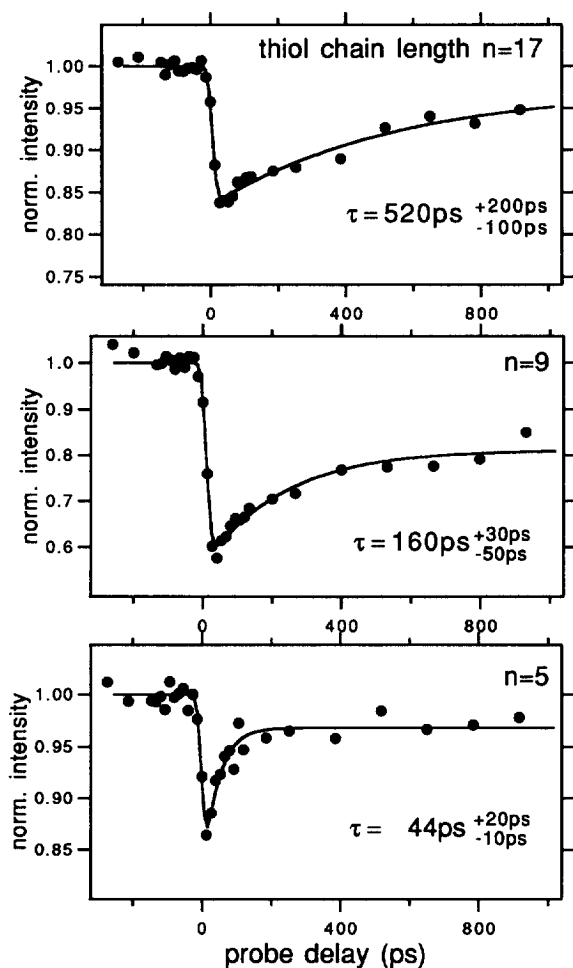


Fig. 3. Pump-and-SH-probe transients for C_{60} separated from a Au surface by alkanethiols of different chain length n in reflection geometry. The errors in life time are determined from the scattering of a large number of individual measurements.

time is, however, not constant but depends on the thickness of the spacer layer, i.e. the thiol chain length. The dots in Fig. 3 represent the measured data while the lines represent a fit according to,

$$\frac{S(t)}{S_0} = \left(\left(1 - \theta(\tilde{t}) \left[\frac{\Delta\chi_{\text{long}}^{(2)}}{\chi_0^{(2)}} + \frac{\Delta\chi_{\text{short}}^{(2)}}{\chi_0^{(2)}} \right] \times \exp \left\{ -\frac{\tilde{t}}{\tau} \right\} \right) \right)^2 R(\tilde{t}-t), \quad (1)$$

where θ is the Heaviside function ($\theta(t)=1$ for $t>0$ and $\theta(t)=0$ for $t<0$) and R is a Gaussian repre-

senting the time resolution function of the experiment. The formula is based on the following model: At $t=0$ the pump beam excites a long lived and a short lived state which both reduce the second order non-linear susceptibility $\chi_0^{(2)}$ associated with the sample without excitation. $\chi^{(2)}$ is assumed to return to its original value $\chi_0^{(2)}$ by a single exponential decay for the short lived state plus a decaying long lived state, here approximated by a constant. This amplitude function is convoluted with the experimental time resolution and then squared to obtain the SH intensity presented in Fig. 3.

The life time τ of the short lived contribution obtained from the best fit is printed in Fig. 3 for each measurement. It decreases with decreasing spacer thickness d . The life time depends still on d at the largest separations. As the coupling of the exciton to the thiol will be independent of the thiol chain length, we can attribute the observed life time reduction essentially to the C_{60} -Au energy transfer. The spacer layer thickness d can be derived from the formula $d=5.1 \text{ \AA} + 1.1 \text{ \AA} \cdot n$ based on known bondlengths and a tilt angle of 25° of the thiol chains with respect to the surface normal [13]. The life time follows a d^3 behavior which is characteristic of energy transfer between an electric dipole and a metal bulk [14]. No indication of an additional transfer channel like electron or hole tunneling is observed down to a separation of 1 nm. In a pure electronic transition from the lowest singlet exciton of T_{1g} symmetry to the ground state of A_g symmetry no electric dipole field would be generated. Our result thus suggest the participation of C_{60} vibrations in the transition similar as in the absorption and emission spectra where Hertzberg-Teller activity is found to be essential [15].

4. Conclusion

We demonstrated that light-induced SH quenching of C_{60} can be employed to study the exciton coupling at heterogeneous C_{60} interfaces. The long life time (>20 ns) observed at the surfaces of solid C_{60} is found to be reduced at interfaces. The reduction to 70 ps at the quartz interface is

assigned to the interaction with the Si–O groups at the interface. In the proximity of a Au surface the life time reduces with decreasing C₆₀–Au distance. Such type of measurements can be performed with high accuracy for C₆₀/alkanethiol/Au sandwich structures.

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