Second-harmonic spectroscopy of fullerenes

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Abstract

Optical second-harmonic generation spectra of C_{60} and C_{70} films are presented for the fundamental energy range 1.0–2.3 eV. The linewidths of the observed resonances are around 0.1 eV and thus much narrower than in linear absorption spectra of fullerene solids. We discuss the assignment of the resonances. Allowed and electric dipole forbidden transitions are observed for C_{60}. The resonances observed for C_{70} are very weak. Efficient quenching of the signal by the population of excitonic states is observed only for the lowest observed resonance of C_{60} at 1.18 eV. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Fullerenes are known to have large non-linear polarizabilities, which have been attributed to the delocalization of π electrons on the carbon shell. Even though the initial hopes of extraordinarily large efficiencies have not become true, the non-linear properties of the fullerenes remain a field of substantial interest. Second-harmonic generation (SHG) spectroscopy can contribute to the spectroscopy of solids with a dipole-forbidden band-gap. Due to its resonance enhancement, one can observe signal maxima in SHG spectra, which can be due to electronic transitions at the fundamental photon energy (the frequency of the incident laser beam) or at the doubled energy (the emitted, frequency-doubled light). The symmetry of the C_{60} solid and the selection rules of the SHG process forbid the observation of electric dipole (ED) transitions in the bulk so that the intensity of these transitions will be strongly

reduced due to a restriction of the generation process to the surface. This facilitates the observation of forbidden transitions which can generate a SHG signal also in the bulk region. Theoretical studies [1,2] have elucidated different aspects of SHG from C_{60} and C_{70}. The relative importance of forbidden transitions and allowed transitions is, however, rarely addressed [3,4] and still requires experimental studies.

In this Letter we present SHG spectra of C_{60} and C_{70} thin films over a wide spectral range employing a tunable OPG/OPA apparatus. Between the fundamental photon energies of 1.0 and 2.3 eV, we find four resonances for C_{60} and two for C_{70}. We discuss the assignment of the observed peaks and their strengths. A second subject of this Letter is the study of transient suppression of the non-linear signal by excitation of the electronic system. A similar change of non-linear efficiency is known for third-order non-linear effects [5,6]. We demonstrated earlier for the resonance at a fundamental frequency of 1.18 eV, an efficient suppression by visible and UV pump

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pulses for pristine C_{60} samples [7]. In this Letter we investigate the response to electronic excitation for other SHG resonances.

2. Experimental

Fullerene thin-film samples are prepared by evaporation of C_{60} (> 99.9% pure, MER) or C_{70} (> 99% pure, MER) on amorphous quartz discs. C_{60} and C_{70} were evaporated from a graphite crucible at 670 and 715 K, respectively, after having been degassed at 500 K for more than 24 h. Evaporation times of 10 h give a film thickness of ∼ 100 nm. During evaporation, the substrate is heated to 415 K in order to increase the crystallinity of the film. A typical absorption spectrum is shown in Fig. 1. The SH measurements were performed at room temperature in a high-vacuum chamber. Tunable 35 ps pulses of 10–100 µJ are generated by an optical parametric generator and amplifier (OPG/OPA) based on LBO nonlinear crystals [8]. The pulses are focused by a lens to a spot smaller than 1 mm² on the sample. Displacement of the lens allows the energy density to be adjusted so that the beam stays safely below the damage threshold. The spectral width of the 30 ps pulses in the scanning range is < 0.01 eV. Only between 1.70 and 1.80 eV does the spectral width of the tunable beam exceed 0.02 eV, reaching a sharp maximum of ∼ 0.13 eV at 1.75 eV. The detector resolution of 2 nm corresponds to < 0.02 eV over the entire scanning range.
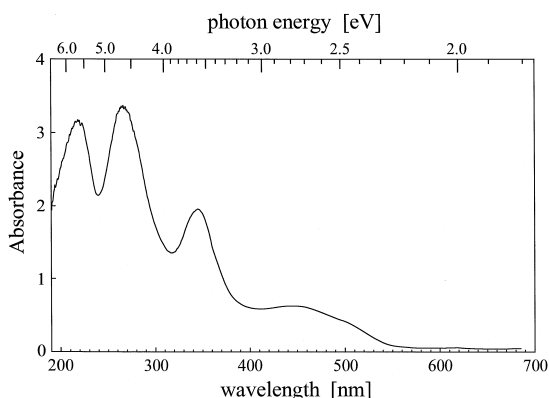

Fig. 1. Absorbance spectrum of a C_{60} sample in transmission geometry.

The SH signal is generated at the sample in a reflection geometry with a beam incident at an angle of 45°. The SH signal arising from the amorphous quartz substrate is below the detection limit. In the incident beam one of three commercial band-pass filters with transmission ranges 2700–850, 1000–700 and 750–400 nm clean the beam from SH intensity generated along the beam path. The reflected fundamental beam, which is collinear with the generated SH intensity is attenuated by 750–400 or 400–240 nm band pass filters, or a $CuSO_4$ solution before the SH photons pass into a double monochromator with a standard bialkali photomultiplier tube.

Repetitive spectral scans with alternating scan direction are performed by stepping the wavelength of the incident beam and scanning the monochromator at the doubled frequency. The filters in the beam path have to be exchanged to obtain the full scan range and the beam energy varies with wavelength therefore the spectrum had to be divided in 5 overlapping ranges (0.85–1.15, 1.0–1.3, 1.17–1.77, 1.74–2.16 and 1.95–2.30 eV). Simultaneously with the measurement of each spectral range a spectrum with a crystalline quartz plate (WP) in the beam path is recorded. The intensity maxima obtained in the WP scans are interpolated by a spline function and this function serves to normalize the spectrum. Finally, the complete spectrum is obtained by scaling the five sections with respect to each other in the overlapping regions.

The resulting spectra are averaged over several samples. Care was taken to avoid significant polymerization of the films. Polymerization of C_{60} proceeds continuously with the exposure to light at wavelengths in the absorption region of C_{60} (visible to UV) [9]. The scan intervals are therefore measured for each of the samples beginning with the lowest energy range and finishing with the highest energy range. The measured spot on a sample is frequently changed and a sample is discarded after a few hours of exposure to the laser pulses in the visible range. In addition, we avoid any exposure of a sample to light from the room illumination.

The SHG suppression measurements are made in a pump-and-probe scheme. With the tunable probe beam set on the peak of a selected SHG resonance a 30 ps pump beam at a 3.49 eV photon energy generates the electronic excitation of the sample. The

pump pulse is incident at an angle of $\sim 40°$ from the sample normal. Transients are recorded by varying the time delay of the probe pulse with respect to the pump pulse.

3. C_{60} SHG spectroscopy

The SHG spectrum of C_{60} (Fig. 2) shows three pronounced resonances and a weak one. In the following, the peak assignment will be discussed. The observed transitions and resonance conditions are illustrated in Fig. 3.

Within the measured range, two major ED transitions are known to occur. They correspond to transitions between the HOMO and the LUMO + 1 (2.8
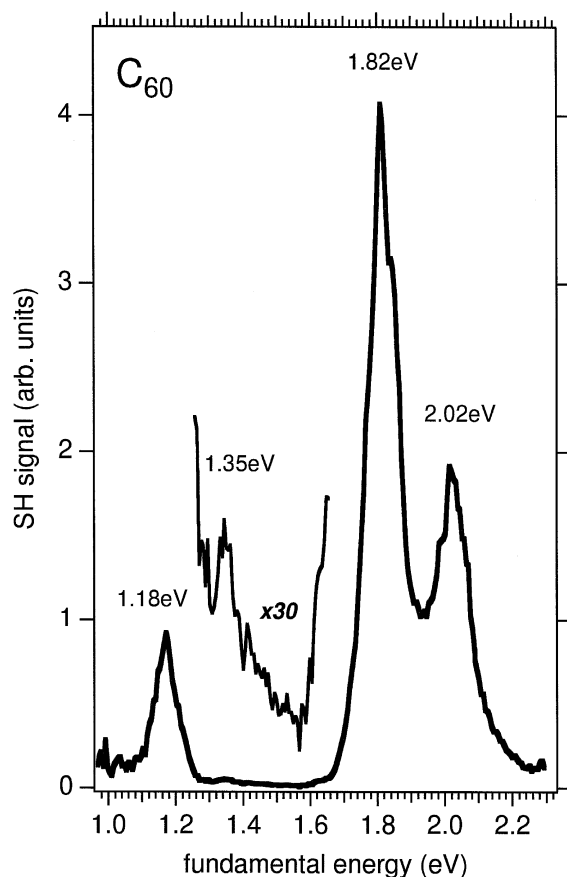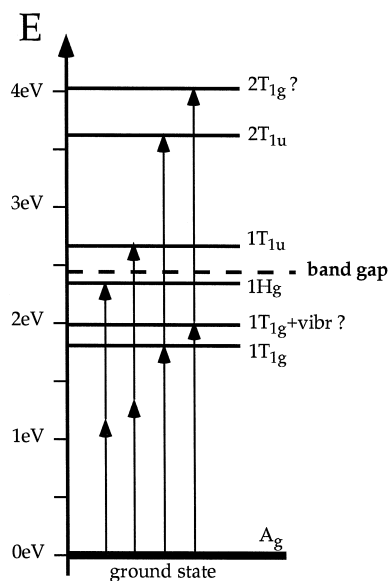

Fig. 3. Assignment of the four resonances in the C_{60} spectrum (Fig. 2) to excitonic transitions in C_{60}. The resonance conditions are indicated by the arrows. For assignments with question marks, please refer to the discussion in the text.

Fig. 2. C_{60} thin-film SHG spectrum. The incident beam is s-polarized. The energy values indicate the peak positions (see also Table 1).

eV) and between the HOMO − 1 and the LUMO (3.6 eV). In the SHG spectrum (Fig. 2) they appear at the fundamental energies 1.35 and 1.82 eV, respectively. The allowed transition at 1.35 eV is weak even compared to the observed forbidden transitions (see below). This may result from the fact that its transition dipole moment is small and from the symmetry rules of SHG which mean that only an interface contribution can be observed.

For the dipole forbidden electronic transitions between the HOMO and LUMO states, four transitions can be derived. They are between the A_g ground state and excitonic states of T_{1g}, T_{2g}, G_g and H_g symmetry. Whereas the first three states are almost degenerate and were calculated to lie within an interval of 0.1 eV, the last one is higher by ~ 0.5 eV [10,11]. The lowest singlet excitonic state in the solid has been shown to have a majority T_{1g} symmetry [12,13]. In the solid it has been assigned to observed resonances at 1.80 [14] and 1.846 eV [15]. It is reached from the ground state by a magnetic dipole (MD) transition and is another transition which can be assigned to the SHG peak at 1.82 eV. In accordance with its substantial intensity this peak is dou-

bly resonant as reported already by Koopmans et al. [14]. The peak at 1.18 eV lies at a one-photon energy, which is below the lowest excitonic state in C_{60} (1.55 eV [16]). It must thus be resonant at the two-photon energy, namely at 2.36 eV, which is 0.54 eV above the T_{1g} state and may thus be assigned to the electric quadrupole (EQ) transition to the H_g state [3]. We remark that a peak observed in electroabsorption spectroscopy at 2.35 eV was assigned to a charge transfer (CT) exciton [17,18], which can contribute in SHG spectroscopy. It may, in fact, be that both states are identical as the H_g state already lies close to the band gap and possesses a much larger CT character than the lower excitons [10].

The resonance at 2.02 eV lies in the range of the above-mentioned excitonic states. However, it is too high in energy (0.2 eV above T_{1g}) to be assigned to the T_{2g}, or the G_g state derived from the HOMO–LUMO transitions. There are three possible origins of the peak: (a) It can be a transition to a T_{2u} state (obtained for an electron in the LUMO and a hole in the HOMO − 1), which was found in a calculation to be only 0.15 eV above the G_g state and confirmed at 2.07 eV by experiment for matrix isolated molecules [19]. (b) It can be a vibronic transition based on the T_{1g} electronic state by coupling to a vibration near 1600 cm^{-1}. Finally, (c) it can be due to a transition at the doubled energy at 4.04 eV. Concerning case (a), the electronic T_{2u} transition is of high multipole-order and should be much weaker than MD or EQ transitions. Concerning case (b) several vibrational modes are located near 1600 cm^{-1}. If the intensity distribution was similar to the case of molecular spectroscopy we may in fact expect an intensity maximum between 1400 and 2000 cm^{-1} [19]. The slow decrease of the 1.82 eV peak on its high-energy side also suggests a vibrational origin. However, we cannot expect that the coupling to vibrations alone can be sufficiently intense to compensate for the loss of the double resonance condition due to the displacement from the 3.6 eV transition. Even in the case of Herzberg–Teller active vibrations, which lead to a well-pronounced peak in low-temperature absorption spectra near 2.0 eV [20,21], the transition would not remain strong as it would gain intensity only at the surface but not in the bulk. We would have a situation comparable to the one of the ED transition at 1.35 eV. We thus

have to suppose a transition which is resonant near 4.04 eV in order to explain the substantial intensity in the 2.02 eV peak as well as the absence of a peak at 1.01 eV, which would be expected for a strong transition at 2.02 eV. Making a choice for the assignment with the possibly highest intensity we propose a double resonance with a transition at 4.04 eV and the vibrational structure of the T_{1g} state peaking at 2.02 eV. The transition at 4.04 eV might correspond to a broadened ED transition calculated to appear ~ 0.3 eV above the 3.6 eV resonance [11]. However, as the absorption spectra show a minimum at 4.0 eV, it is more probable that the peak is due to a transition between the HOMO − 1 and LUMO + 1 states some 0.6 eV above the 3.6 eV ED transition [11], which provides states of T_{1g} and H_g symmetry reached from the ground state by MD and EQ transitions, respectively. Calculations of the nonlinear susceptibility discussed below indicate that there is no 2.02 eV transition of strong EQ character, which suggests an ED or MD transition at 4.04 eV.

The full peak width at half maximum of the resonances range from 0.06 to 0.12 eV (see Table 1). It is evident from the discussion in Section 2 that these widths contain only negligible contributions from the instrumental resolution. The resonances are much sharper than the structures in absorption spectroscopy of the C_{60} solid [22–24], as can also be seen by comparison with Fig. 1. Below room temperature still smaller linewidths have been observed by SHG spectroscopy [25]. A small peak width can be expected for the lowest excitons from their bandwidth, as has been shown by Eder et al. [26]. On the other hand, linewidths of ED transitions in solid C_{60} are larger than 0.2 eV. One reason is the efficient

Table 1
Resonance positions, widths and relative peak heights for the four observed transitions in Fig. 2

Observed SHG peaks of C_{60}		
peak energy (eV)	FWHM (eV)	relative peak height
1.18	0.08	0.2
1.35	0.06	0.005
1.82	0.11	1.0
2.02	0.12	0.3–0.5

The proposed assignment is represented in Fig. 3.

decay of the molecular state to free carrier states. It is surprising that the linewidth of the peak at 1.35 eV, which corresponds to the ED transition to the $1T_{1u}$ state at 2.7 eV, is the sharpest line in the spectrum. The decay must therefore still be comparatively slow for the $1T_{1u}$ state. Other contributions to line broadening (e.g., due to vibrations) contribute less to SHG spectra than to absorption spectra. In a similar line of arguments, the narrow linewidth of the 2.02 eV peak supports an assignment to a double resonance rather than a single resonance at 4.04 eV.

We shortly remark that no SHG peak is found at the spin-forbidden excitation of the lowest triplet exciton at 1.55 eV [16].

Comparison with the literature shows that the peak at 1.82 eV confirms the position and width of the resonance first found by Koopmans et al. [14]. A significant SH signal is also found for a fundamental energy of 1.165 eV, which was the energy of the study at fixed wavelength by Wilk et al. [3]. Our measurement demonstrates that this study was in fact done close to the maximum of the resonance. The observation of a resonance at 2.02 eV in a sum-frequency generation (SFG) measurement was only recently reported [27]. In that work, the resonance could, however, not be observed in SHG and it was argued that a resonance at the doubled energy was missing. The reason for the discrepancy with this work is not yet clear. The observed resonance, which appears much weaker than the T_{1g} excitonic transition at 1.8 eV, was assigned to an ED transition due to Herzberg–Teller coupling of the t_{1u} vibrational mode with the T_{1g} excitonic transition.

Qin et al. [1] determined theoretically the dispersion of the quadrupole response for single C_{60} molecules. They find resonances at 1.09 and 1.86 eV. The first one is only ~ 0.1 eV lower than the lowest peak we observe. The second one is in good agreement with our measurement. The calculated peak is of asymmetric shape but no separate feature appears near 2 eV. This indicates that the peak observed at 2.02 eV is not due to an EQ transition. Between the two calculated peaks a sharp minimum appears which seems to be due to a change of amplitude sign. The experiment shows a similarly sharp minimum at 1.57 eV. The overall agreement with the calculation is good although one may suspect that the peak calculated for 1.86 eV has a

different physical origin than that suggested by the assignment of the observed 1.82 eV resonance. Shuai and Brédas [2] calculated EQ and MD hyperpolarizabilities. While the MD hyperpolarisability tensor element which they plotted shows essentially an increase with energy, the quadrupole tensor element exhibits maxima at 0.6, 1.8 and 2.4 eV. The maximum at 1.8 eV agrees with experiment.

4. C_{60} SHG suppression

The response of resonant SH signals to the excitation of the sample with UV pulses is shown in Fig. 4. The signal on the 1.18 eV resonance (Fig. 4 top) decreases rapidly and remains at a substantially reduced level for much longer than 1 ns, as described in an earlier publication [7]. In contrast, the resonances at 1.82 and 2.02 eV show no comparable change of signal for the same excitation intensity (Fig. 4 middle and bottom panel). The pump response of the 1.35 eV peak cannot be measured due to the small signal.
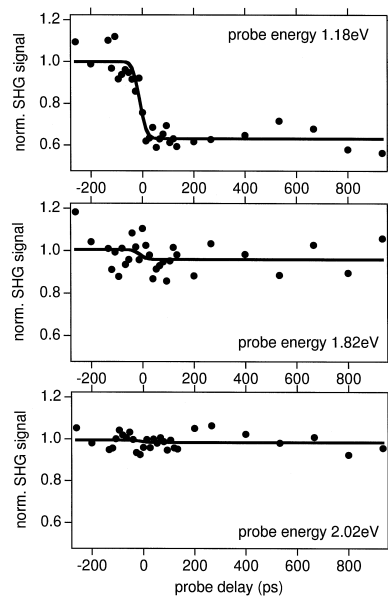

Fig. 4. Pump-and-probe transients normalized to the signal without pump beam. The points are the data and the lines represent the best fit of a step function convoluted with the time resolution of the measurement. 3.49 eV pulses generate the excitation at $t = 0$. The pump density is the same in all three measurements (~ 5 $\mu J/cm^2$). The probe beam which generates the SH signal is on the resonances indicated by their peak energy.

We demonstrated earlier that the SHG suppression is due to the presence of excitons at low concentration ($< 1\%$) [7]. Transients measured for C_{60} films separated from a Au surface by a thin spacer layer of varied thickness are in good agreement with the assumption that the signal suppression is due to the singlet T_{1g} exciton [28]. For the pump intensities used in the experiments, the ground state is not remarkably depleted which excludes a reason for the SH signal change corresponding to the mechanism in transient absorption spectroscopy. From Fig. 4, we see that the SH intensity at 2.02 eV is not affected by the low exciton concentration. The effect on the 1.82 eV peak is possibly small but not statistically significant. We thus find that the strong SHG suppression does not work equally well for all resonances but appears to be specific to the 1.18 eV peak.

A likely mechanism for SHG suppression is a loss of phase coherence between the radiating states located on different molecules. This mechanism was suggested by Janner et al. to explain the decrease of SH signal from the C_{60} T_{1g} exciton with increasing temperature [25]. The specific behavior of the 1.18 eV resonance could then be due to an increased sensitivity to dephasing for an excitonic transition at the doubled frequency compared to a transition at the fundamental frequency. Based on the formalism by Villaeys et al. [29], we find that a strong difference between fundamental and SH dephasing exists only if the dephasing time is long compared to the pulse duration. The sharp decrease of the signal at $t = 0$ in the transient in Fig. 4 (top) demonstrates, however, that this is not the case here.

The result thus shows that there is a specifically efficient coupling between the H_g state and the lowest singlet or triplet excitons generated by the pump pulse. One may speculate that this efficient interaction is due to the CT character of the H_g state and the fact that the diffusion of the lowest excitons proceeds via a virtual CT state [25].

5. C_{70} SHG spectroscopy

The SHG spectrum of C_{70} (Fig. 5) is obtained in the same way as described for C_{60}. A weak resonance is observed at 1.26 eV and a steep signal rise
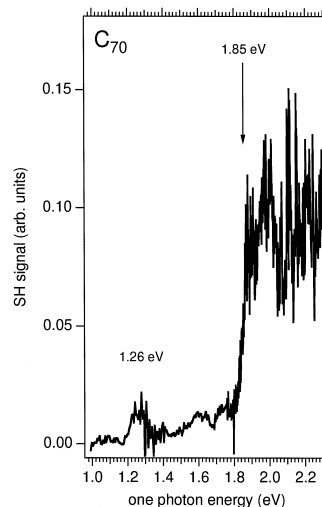

Fig. 5. C_{70} thin-film SHG spectrum. The incident beam is p-polarized.

at 1.85 eV indicates a broad resonance in which no structure is resolved.

To our knowledge no SH intensity was yet observed for C_{70}. This may be understood from the fact that: (a) the broad structure at $E > 1.83$ eV is still very weak; and (b) the peak observed at $E = 1.26$ eV does not extend to the fundamental frequency of Nd:YAG lasers (1.165 eV). The rise at 1.85 eV coincides roughly with the onset of absorption at the energy of the singlet exciton. The lowest singlet (S_1) and triplet (T_1) excitons were assigned for isolated molecules in an Ne matrix to 1.93 and 1.56 eV, respectively [30]. The singlet corresponds well to the onset of SHG intensity, if we assume that there is a shift between matrix isolated C_{70} and the solid, of ~ 0.1 eV, similar to C_{60}. The proximity of the next higher singlet exciton (S_2), which is located 0.2 eV above S_1 and higher excitonic states may lead to the broad structure above 1.85 eV. The peak at 1.26 eV, however, is too low in energy to allow an assignment to the triplet exciton. Thus, as in the case of C_{60}, the spin forbidden transition is not observed. The peak coincides rather with a broad feature in absorption spectra near 2.66 eV in solution which represents, according to a tight-binding calculation [31], two strong dipole allowed molecular transitions $a2''(\text{HOMO}) \rightarrow a1'(\text{LUMO} + 2)$ and $e1''(\text{HOMO5}) \rightarrow e1''(\text{LUMO} + 1)$. In the solid a similar feature appears at 2.41 eV [32]. Theoretical calculations of

C_{70} SHG spectra were made by Shuai and Brédas [2]. The EQ contribution calculated for C_{70} has non-vanishing values in a sharp peak at 1.2 eV and in a broad structure between 2.0 and 2.4 eV, which is in good agreement with the experimental C_{70} spectrum.

The lower symmetry of the C_{70} molecule, with respect to C_{60}, makes the low-energy part of the absorption spectrum of the solid richer in ED allowed transitions. In contrast, the SHG spectrum shows only two features with low intensity. Numerous dipole allowed transitions are absent. This and the agreement with calculated spectra suggest that as in the case of C_{60}, the forbidden transitions may be observed most easily. A dipole-forbidden transition was in fact predicted at 2.49 eV by Kajzar et al. [33]. It would be in even better agreement with the 1.26 eV peak than the dipole allowed transitions discussed above.

6. Conclusions

We presented optical second-harmonic generation (SHG) spectra of C_{60} and C_{70} between 1.0 and 2.3 eV fundamental photon energy. Linewidths of typically 0.1 eV are observed. Transitions of lower multipole orders can be readily observed for C_{60}. For C_{70}, the signals are much weaker and many ED allowed transitions are missing. For both fullerenes the lowest singlet excitons are observed while intensity due to the triplet excitons is not found. The pump beam induced suppression of the SH signal on C_{60} resonances is only efficient for the peak at the lowest fundamental photon energy. This suggests that the suppression is due to a coupling between the lowest H_g and T_{1g} excitonic states.

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