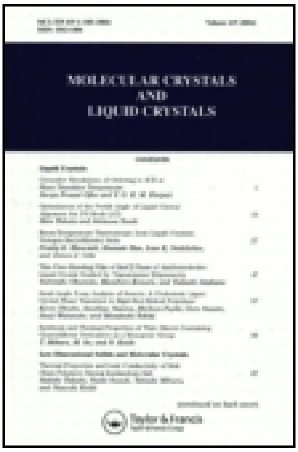

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A MICROSCOPIC MODEL FOR THE SECOND-HARMONIC GENERATION FROM C_{60}

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Abstract We discuss the microscopic origin of the Second-Harmonic Generation (SHG) resonance at $\hbar\omega$=1.81 eV, based on spectroscopic and thickness dependent SHG measurements on C_{60} thin films. We assign the three-level diagram responsible for the observed SHG resonance, and show it to be of magnetic-dipole-induced origin. Furthermore we explain the absence of almost any surface contributions, and the narrow line width of the involved HOMO-LUMO ($1^1A_g \rightarrow 1^1T_{1g}$) excitation at 1.81 eV.

INTRODUCTION

Fullerenes show large nonlinear optical susceptibilities due to the presence of the strongly delocalized π-electronic network. Although a second-order optical process within a centro-symmetric material - such as C_{60} - is forbidden within the electric-dipole (ED) approximation, a relative strong SHG response has been observed from C_{60} thin films.[1-4] This indicates the importance of nonlocal bulk contributions [including both electric-quadrupole (EQ) and magnetic-dipole (MD) processes], and/or ED allowed or field gradient induced surface contributions. Apart from being of fundamental interest, a proper understanding of the actual dominant mechanisms is of crucial importance for further application of the SHG technique, such as studies of the C_{60}-substrate interface-electronic structure. Furthermore we show the spectroscopic SHG to be applicable as a valuable tool in the interpretation of optical absorption spectra.

In previous publications we reported on a sharp SHG resonance at $\hbar\omega$=1.81 eV.[3,4] We used in-situ thickness scans and group theoretical arguments concerning the bulk tensor components to demonstrate the bulk character and MD-induced origin of the SH resonance. The relative huge SHG signal from the C_{60} is illustrated by the fact that the measured bulk susceptibility of C_{60} is an order of magnitude larger than $(c/\omega)\chi^{(2)}_{xxx}$ of non-centrosymmetric quartz. In this paper we briefly review our previous experiments, and present new temperature dependent data. The main issue will be a discussion of the underlying physical mechanisms.

THEORY

Up to the fist order gradients of the electric field $\underline{E}$, the induced second order generalized polarization $\underline{P}^{(2)}$ is given by:

$$\underline{P}^{(2)} = \underline{\chi}^{(D)}:\underline{E}\underline{E} + \underline{\chi}^{(Q)}:\underline{E}\nabla\underline{E} \ , \qquad (1)$$

where the third rank tensor $\underline{\chi}^{(D)}$ is the ED-susceptibility, and the fourth rank tensor $\underline{\chi}^{(Q)}$ is the nonlocal susceptibility. In the bulk of centro-symmetric media SHG is forbidden within the ED-approximation: $\underline{\chi}^{(D)}=0$. However, sheet-like SHG sources, denoted by $\underline{\chi}^{(D)}_{s}$, are in general present at the interfaces of the medium, where the inversion symmetry is broken.

The bulk SHG of isotropic media is described by three independent tensor components: $\chi_2 \equiv \chi^{(Q)}_{xxyy}$, $\chi_3 \equiv \chi^{(Q)}_{xyxy}$ and $\chi_4 \equiv \chi^{(Q)}_{xyyx}$. A fourth nonzero component is related to the former three: $\chi_1 \equiv \chi^{(Q)}_{xxxx} = \chi_2 + \chi_3 + \chi_4$. For convenience one usually writes the nonlocal bulk polarization in a vector notation:

$$\underline{P}^{(Q)} = \chi_2 \ \underline{E}(\underline{\nabla}\cdot\underline{E}) + \tfrac{1}{2}\chi_3 \ \underline{\nabla}(\underline{E}\cdot\underline{E}) + \chi_4 \ (\underline{E}\cdot\underline{\nabla})\underline{E} \ . \qquad (2)$$

Due to the zero divergence of $\underline{E}$, the χ_2 term never contributes. The χ_4 term disappears if only a single electromagnetic plane wave is present inside the medium. A well known fundamental difficulty in the application of SHG is the fact that χ_3 is experimentally completely inseparable from a certain combination of interface tensor components.[5] In a previous publication we explicitly showed how a full separation is possible, using the separation of the χ_4 contribution in a thin film geometry, and the relation between χ_3 and χ_4 from group theoretical arguments.

χ_3 and χ_4 are strongly related, since they only differ by a permutation of the last two indices. If the nonlocal interaction takes place at the fundamental frequency one finds $\chi_3/\chi_4=+1$ for an EQ process, and $\chi_3/\chi_4=-1$ for a MD process. This different behaviour is explained by respectively the symmetry and anti-symmetry of the EQ and the MD transition matrix elements under permutation of the last two indices.

EQ and MD interactions give rise to excitations of different symmetry. Taking into account the icosahedral point-group symmetry of C_{60}, group-theory shows that from the 1^1A_g ground state ^1H_g excitations are excited by EQ processes, and $^1T_{1g}$ excitations by MD processes. This information can be used either way: Knowing the origin of the excitation in the SHG process one can use the resulting ratio χ_3/χ_4 to obtain the full separation of interface and bulk contributions. On the other hand, having insight in the relative importance of interface and bulk contributions, χ_3/χ_4 obtained from the SHG experiment can be used to resolve the symmetry of the involved excitation. We stress that the features in the SHG spectrum are of true-origin character, and therefore much easier to analyze than the corresponding false-origin features in linear optical spectra.

EXPERIMENTAL RESULTS

C_{60} with a purity of better than 99.9% was evaporated from a Knudsen cell onto various substrates (fused quartz and hydrogen-terminated Si), at UHV pressures below 2×10^{-9} mbar. The experiments were carried out with a dye laser, pumped by the frequency doubled output of a Nd:YAG laser (repetition rate 10 Hz), thus producing 7 ns pulses with a pulse energy of approximately 5 mJ. More details of the sample-preparation and the optical set-up have been published elsewhere.[3,4]

Knowledge of the dispersion of the SHG response is of great importance for a proper understanding of the microscopic mechanisms. Figure 1 shows the dispersion of the phase resolved SHG response in the $\hbar\omega=1.6-2.0$ eV regime, for a very thin film (6 nm thickness) on top of a hydrogen-terminated and slightly stepped Si(111) substrate.[3] The phases in the figure are related to the phase of a non-dispersive SHG contribution from the Si substrate. The 90° phase gain of a very (infinitesimal) thin film with respect to a corresponding semi-infinite substrate contribution is properly taken into account.[4] The fits in the figure correspond to Eq. 3, but include a nondispersive background and a small phase offset, which can be shown to be due to the applied data analysis.

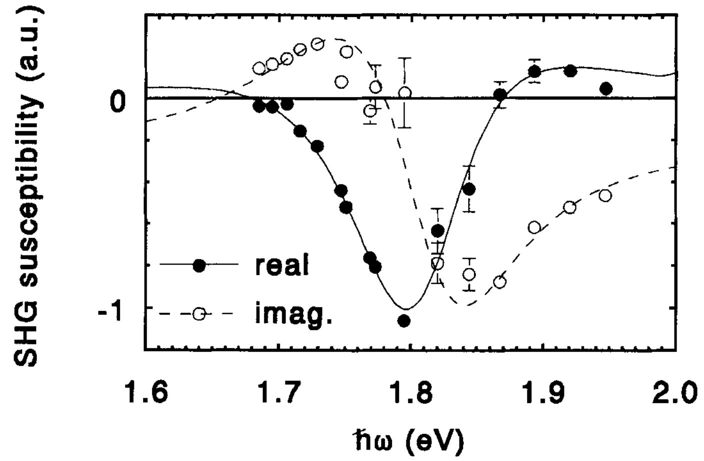

FIGURE 1 The phase resolved SHG susceptibility as function of the fundamental frequency, for a 6 nm thin C_{60} film. The measurement is done at room temperature, with a p-polarized input and output and a 45° angle of incidence.

The observed SHG resonance is strongly temperature (T) dependent. Figure 2 shows the (total intensity) SH response at room temperature (RT) and at T=430 K. Within this range only a negligible shift of the resonance frequency (< 0.01 eV) occurs. Despite the strong T-dependence of the resonant intensity, the nonresonant intensity is found to be T-independent. This suggests that the oscillator strength and the resonance frequency in this T-range are to a good approximation T-independent. This is confirmed by the drawn curves, representing doubly resonant Lorenzian fits (Eq. 3) in which only the line width (Γ_1) was taken to be T-dependent. Γ_1 is found to be proportional to T in this T-interval.

Preliminary experiments down to T=100 K show a further decrease of Γ_1, but also a gradual blue-shift (~0.02 eV) of the resonance frequency, while scanning through the phase transition at 256 K.

Finally, to resolve all distinguishable surface and bulk tensor components, we carried out in-situ thickness scans during the evaporation process. In ref. 4 we discussed such scans for C_{60} films measured at ħω=1.81 eV, showing the dominance of the bulk processes, but also proving the existence of finite surface contributions.

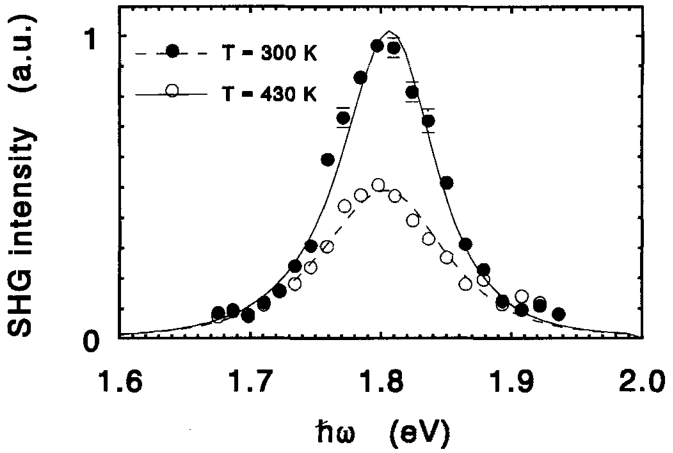

FIGURE 2 The SHG resonance at RT and T=430 K, showing the SHG intensity obtained from a film of 350 nm thickness.

DISCUSSION

In the interpretation of the frequency dependent measurements we assume a dominant bulk response. Let us first inspect the dispersion curve of Figure 1. It shows that the real part of the SHG response is peaked right at the resonance. This indicates the presence of a double resonance of the form:

$$\chi^{(Q)} \propto \frac{1}{(2\omega-\omega_2+i\Gamma_2)(\omega-\omega_1+i\Gamma_1)}, \qquad (3)$$

where both the fundamental (ω) and the SH frequency (2ω) are at - or close to - an electronic excitation, described by excitation frequencies ω_1 and ω_2, and HWHM line widths Γ_1 and Γ_2, respectively.

Based on this doubly resonant character, we conclude on the following model for the dominant three-level diagram. Note that 2ω in our resonant experiments is close to the strong $h_g \rightarrow t_{1u}$ absorption band (of ${}^1T_{1u}$ symmetry) in the linear optical spectrum of solid C_{60}.[6] We expect the same excitation to take part in the SHG diagram, and therefore: $\hbar\omega_2 = 3.56$ eV and $\hbar\Gamma_2 = 0.23$ eV (from ref. 6). A fit of the data of Figure 1 then gives: $\hbar\omega_1 = 1.81$ eV and $\hbar\Gamma_1 = 0.06$ eV. We assign this to the ED-forbidden $h_u \rightarrow t_{1u}$ (HOMO→LUMO) excitations, which from optical absorption spectra are known to be situated around 1.8-2.3 eV in solid C_{60}. The MO-scheme of the corresponding three-level diagram is indicated in Figure 3.

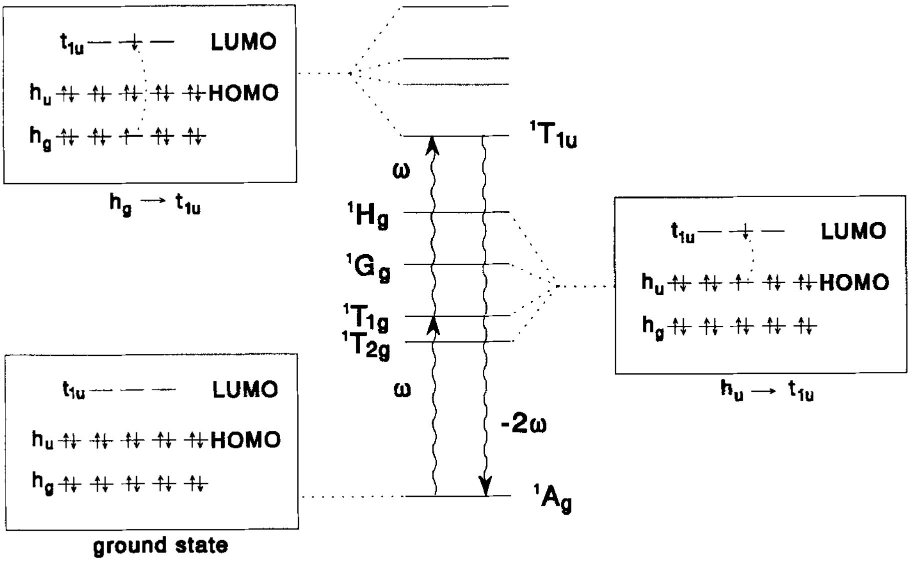

FIGURE 3 Part of the singlet excitation spectrum of C_{60} (not on scale), showing the three-level diagram responsible for the 1.81 eV SHG resonance.

Since the multiplet splitting of the relevant electronic excitations (~ 0.5 eV) is much larger than $\hbar\Gamma_1 = 0.06$ eV, a proper discussion of the SHG spectrum should include these multiplet effects. The HOMO→LUMO singlet excitations split up in four levels of $^1T_{1g}$, $^1T_{2g}$, ^1G_g and ^1H_g symmetry, respectively. From the ground state, the $^1T_{1g}$ level can be reached via a MD process, and the ^1H_g level via an EQ process. Since quantum-chemical calculations[7] in combination with optical absorption measurements[8] strongly suggest the $^1T_{1g}$ level to be situated around 1.8 eV, and the ^1H_g level at least above 2 eV, it can only be the $^1T_{1g}$ level which is involved in our 1.81 eV SHG resonance. This means that the SHG is of MD-induced character. Such a MD mechanism is very efficient for large spherical molecules, especially if an electronic transition is involved between two states characterized by the same angular momentum quantum number (l). In this sense, the large radius of the C_{60} molecule, and the fact that the HOMO and LUMO are both of l = 5 character, explains the large bulk SHG susceptibility of C_{60}.

The MD character is confirmed by the thickness scans of ref. 4. Neglecting the interface contributions to the SHG, a ratio χ_3/χ_4 is found very close to -1, as expected for a MD processes. From the presented analysis, we therefore uniquely identified the 1.81 eV excitation as the true-origin $^1T_{1g}$ excitation. This identification can be used as a useful premise in the interpretation of the complex optical absorption spectra.

Once having found the exact origin of the SHG, the ratio χ_3/χ_4 is set exactly to -1 and is used as the additional constraint necessary for a full separation of all interface and bulk tensor components. In ref. 4 we thus find an upper limit to all the interface tensor components of only a few percent of the bulk tensor components. This might seem surprising. Although for a molecular crystal - like C_{60} - the pure ED-allowed surface contribution is expected to be small, the field gradient induced contribution is known to be proportional to the bulk susceptibility, so that a strong bulk SHG would also imply a strong surface contribution. However, it has been shown that the effective surface susceptibility scales with χ_1 and χ_2, not with χ_3 and χ_4.[9] Since χ_1 and χ_2 are zero by symmetry for MD processes, the MD character of the SHG is a natural way to explain the extreme dominance of bulk SHG over surface SHG.

A final point which still has to be explained is the large difference of the line widths Γ_1 and Γ_2. We suggest the following mechanism to account for this difference. Of importance is the localized (intra molecular) character of the optical excitations, and the strongly correlated nature of C_{60}. All excitations below the conductivity gap of C_{60} (2.3 eV) are necessarily of true excitonic character.[10] This means that the 1.8 eV excitation cannot delocalize into a separate electron and hole, and is characterized by a long life time and small Γ_1. On the other hand, the 3.6 eV excitation is well above the conductivity gap, and can decay, therefore, into the delocalized e-h pair continuum, which explains the life time broadening of Γ_2. Note that $h\Gamma_2$ is of the order of the inter-molecular hopping integral, or band width (0.4 eV).

The strong temperature dependence of Γ_1 indicates the importance of homogeneous line broadening. Taking into account the ~1 ns life-time of the lowest singlet excitations[11], the line width of several hundredths of an eV has to be explained by pure dephasing processes. The almost linear T-dependence of

Γ_1 may be explained by Bose-Einstein statistics in the limit of T far above the characteristic (inter-molecular) phonon frequency. The blue-shift across the phase transition is in agreement with a shortening of the double bonds and a lengthening of the single bonds (both by ~0.003 Å), thus widening the HOMO-LUMO gap.[12]

In conclusion, we resolved most of the basic questions regarding the origin of the strong SHG response of C_{60} in the 1.5-2.0 eV range. Based on the models discussed here, we can make predictions about the SHG response in frequency regimes, not covered by our experiments. SHG resonances are expected both for ω and 2ω corresponding to the $1^1A_g \rightarrow 1^1H_g$ (HOMO→LUMO) excitation in the 2.0-2.5 eV range. Both are of EQ character. Unlike the MD resonance, their surface and bulk contributions are predicted to be of roughly equal magnitude, due to the field gradient mechanism at the surface.

The SHG methods and the microscopic interpretation described throughout this paper will be very useful in a detailed study of changes in the resonance frequencies and multiplet structure of the HOMO-LUMO excitations. Such changes, as induced by doping or surface effects, may give valuable information about - for instance - screening effects in doped and undoped fullerenes.

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