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EXCITON PROPAGATION STUDIED BY TEMPERATURE DEPENDENT OPTICAL SECOND-HARMONIC GENERATION FROM C₆₀ FILMS

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Abstract

We studied the dynamics of the electric dipole (ED) forbidden ${}^1T_{1g}$ excitonic state of C₆₀ at $\hbar\omega=1.8$ eV using temperature dependent Second-Harmonic Generation (SHG). We found a strong temperature dependence of the SH intensity and a splitting of the resonance structure below the first order rotational ordering phase transition at 260 K. We interpret this splitting as Factor Group or Davydov splitting. The magnitude of the splitting (40 meV) and the large exciton band width (100 meV) will be explained with a charge transfer mediated propagation mechanism.

1. Introduction

In recent years considerable interest has been generated in the study of the physical properties of C₆₀ solids. These materials seem to exhibit a dualistic behaviour, on the one hand they behave like weakly van der Waals bound molecular solids, while on the other hand they behave like semiconductors with a moderate (2.3 eV [1]) band gap. The properties of the fullerene compounds show some resemblance to the charge transfer type of molecular solids like the much studied TCNQ salts. In this paper we present evidence that the low lying excitonic states of solid C₆₀ exhibit such dualistic behaviour. There is experimental evidence that the energies of the excitonic states are very close to the corresponding excited states in the gas phase, emphasizing the preservation of the molecular character in the solid. But the propagation of the excitons results in abnormally large excitonic bandwidths for ED forbidden transitions in molecular solids.

Koopmans *et al.* [2,3] has shown that the ED forbidden ${}^1T_{1g}$ excitonic state at 1.81 eV is readily accessible by magnetic dipole selection rules and can be probed in a doubly resonant SHG experiment. With this technique we probe the dynamical properties of the ${}^1T_{1g}$ excitonic state in solid C₆₀ by studying the temperature dependence of its dispersional width and the observed splitting of the excitonic band below the rotational ordering phase transition [7].

2. Experimental

C₆₀ with a purity better than 99.99% was evaporated from a Knudsen cell onto a substrate (fused quartz or MgO) at UHV pressures below $4 \cdot 10^9$ mbar. For the SHG

experiments a Nd:YAG laser was used to pump a dye laser, producing 7 ns pulses with an energy of approximately 6 mJ/pulse and a repetition rate of 10 Hz. We used frequencies in the range $\hbar\omega = 1.7\text{...}2.0$ eV. SH intensities were calibrated using the SH signal of a reference Quartz crystal. All SHG experiments were performed using a fixed angle of incidence (45° to the surface normal) and a mixed (i.e. s + p) input polarization. The p-polarized component of the specular reflected SH was detected. The temperature dependent SHG experiments were performed by using a He-flow cryostat (4 - 500 K). More experimental details can be found in [12].

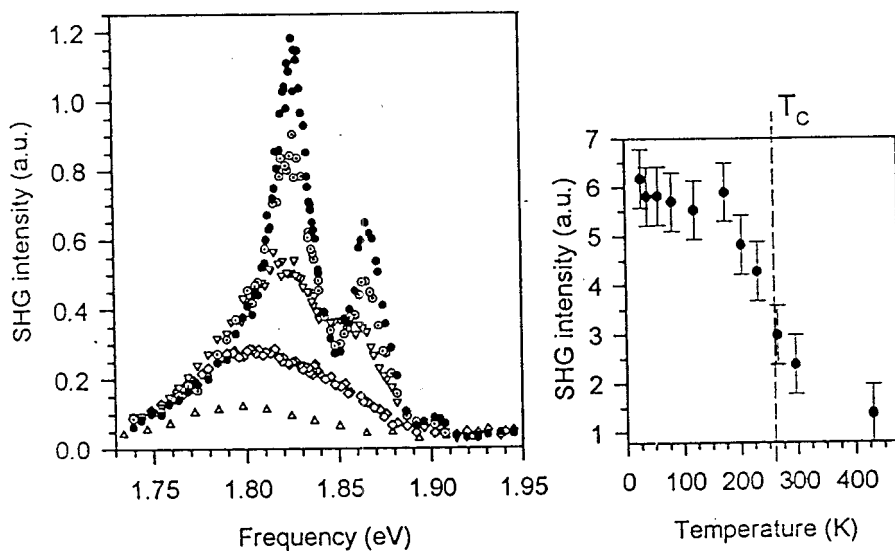


Fig.1. The temperature dependent SHG of C_{60} thin film using m-p polarization combination. $\Delta = 430$ K, $\diamond = 265$ K, $\nabla = 203$ K, $\circ = 120$ K, $\bullet = 27$ K.

Fig.2. The temperature dependence of the total SH intensity, which is strongly enhanced just below the phase transition at $T_C = 260$ K

3. Results

The SH intensity measured as a function of the fundamental frequency ($\hbar\omega$) is shown in Fig.1 for different temperatures. The resonance (at about 1.8 eV) clearly shows a blue shift at low temperatures. Below the rotational phase transition temperature the resonance structure splits up into two peaks. At low temperatures this splitting amounts to 40 meV. The total dispersional bandwidth of about 100 meV (at the base) is large for a molecular crystal where an ED forbidden transition is involved.

The temperature dependence of the total SH intensity is shown in Fig.2. Notice the strong SH intensity enhancement just below the phase transition temperature.

4. Discussion

Neutron diffraction experiments have shown that going through the rotational ordering phase transition the number of buckyballs per primitive unit cell changes from one (in a FCC lattice) to four (in a SC lattice) [7]. In the isolated C₆₀ molecule the molecular wave functions form the basis of the irreducible representations of the molecular point group (I_h). In the solid in a simple cubic lattice we can construct crystal wavefunctions, which are linear combinations of the molecular wavefunctions in a unit cell in such a way that they form the basis for the irreducible representations of the Factor Group (T_h). In the interpretation of recent two photon experiments Muccine *et al.* have discussed the splitting of the three fold degenerate ¹T_{1g} exciton band in T_h [8]. They show that the ¹T_{1g} exciton band correlated with 12 bands of ¹A_g, ¹E_g and 3 ¹T_g symmetry. Only the 3 ¹T_g bands will be accessible by magnetic dipole selection rules. In consequence we interpret the splitting at low temperature as a crystal field induced Factor Group or Davydov splitting between two of the ¹T_{1g} excitonic states. The measured dispersional bandwidth of 100 meV and the large Davydov splitting seems to be remarkable for an optical transition with an almost zero ED transition oscillator strength. With the usual for molecular crystals used exciton propagation mechanism (a transition dipole - transition dipole or multipole mechanism) one would expect an only very small dispersional width of the excitonic states and a Davydov splitting of a few meV. Lof *et al.* [1] suggested for this case a charge transfer mediated propagation mechanism, which also was used for the lowest singlet state of Naphthalene [4], and the charge transfer TCNQ salts [5]. The net effective exciton hopping integral is given by

$$T^{\text{exciton}} = \frac{Zt_{e(h)}}{U - V} \quad (1)$$

where $t_{e(h)}$ are the single electron (hole) nearest-neighbour hopping integrals, Z is a geometrical constant and the energy $U - V$ is the difference between the onsite Coulomb interaction and the nearest-neighbour Coulomb repulsion [6].

The strong temperature dependent SH intensity can be explained in terms of dynamic rotational disorder. The rotational disorder above the phase transition will lead to a depression of the SH response by dephasing processes (T₂) within the timescale determined by the excitation transition matrix elements. Photoluminescency experiments show also a strong temperature dependence of the intensity. These changes occur at some lower temperature compared with the phase transition and the interpretation is still controversial [9,10,11].

5. Conclusions

We have studied the dynamics of the by magnetic dipole selection rules accessible ¹T_{1g}

excitonic state at $\hbar\omega = 1.81$ eV by doubly resonant temperature dependent SHG experiments. We found a very strong temperature dependence of this resonance. Its SH intensity increases dramatically with decreasing temperature. We explained this by a rotational disorder induced T_2 dephasing mechanism. Below the rotational ordering phase transition the SH resonance structure splits up into two bands. We attribute this splitting to the Factor Group or Davydov splitting which finds its origin in the presence of four molecules per unit cell in the low temperature phase. The observed unexpected large Davydov splitting of 40 meV, combined with the unusual dispersional bandwidth of 100 meV, are explained with a charge transfer mediated mechanism for the propagation of the exciton.

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