Chapter 4

Excitons in $C_{60}$ studied by SHG and SFG

4.1 Fullerenes

Geometric figures have always been appealing to us. At present time, Escher’s geometric designs are world famous, because they go beyond the decorative content and stimulate reflection. A similar spirit can be found in the drawings of Leonardo da Vinci, who lived in the fifteenth century. An example of his work is a design of a truncated icosahedron cage, built up from 20 hexagons and 12 pentagons, having 60 vertices. This is a polyhedron which resembles a football (Fig. 4.1). Whether this has inspired the architect R. Buckminster Fuller, whose geodesic constructions are based on hexagons, is unknown. However, Kroto et al. [1] might have been inspired by Buckminster Fuller in solving the structure of a cluster consisting of 60 carbon atoms.

The vast variety of organic and biological molecules in nature is a result of the ability of carbon to form different covalent bonds. Until 1985 two forms of crystalline carbon were known: graphite and diamond. Graphite is a layered compound, where the sheets are made up from planar $sp^2$ hybridized carbon atoms. In diamond, the carbon atoms are tetrahedral $sp^3$ hybridized, and form a cubic crystal. The carbon experts realize that formerly there were six known crystalline forms of the element carbon, namely two kinds of graphite, two kinds of diamond, chaosit [2] and carbon(VI) [3, 4]. The latter two were discovered only recently, in 1968 and 1972. However, everybody was surprised when Kroto and co-workers suggested a new type of carbon in 1985, in which the atoms are arranged in closed shells [1]; the discovery of carbon molecules had taken place.

During experiments, aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space, Kroto and co-workers found clusters consisting of 60 carbon atoms. They suggested that such a cluster was a carbon molecule $C_{60}$, having the shape of a truncated icosahedron cage and icosahedral symmetry (Fig. 4.2). The deviation from the planar character observed in graphite is achieved by forming bonds with a hybridization intermediate between $sp^3$ and $sp^2$ [5, 6]. The researchers named the $C_{60}$ molecule: buckminsterfullerene, and the world gave it the nickname buckyball. In 1996 Curl, Kroto, and Smalley were awarded the Nobel Prize in chemistry for their discovery of fullerenes.

A thorough study of the fullerenes would not have been possible if Krätschmer and co-workers had not succeeded to produce macroscopic amounts of fullerenes in 1990, using the arc-discharge evaporation method [8]. The entire scientific community, enchanted by the beauty and the elegance of the highly symmetric $C_{60}$ molecule, eagerly started to study this new form of carbon, the fullerenes. At present time, seven years later, a lot is not yet understood [9, 10], despite much progress in development and insight, which will be briefly discussed below.

One of the first experiments performed was the determination of the molecular structure of $C_{60}$. Taylor et al., and Johnson et al. [11, 12] investigated $^{13}$C nuclear magnetic resonance (NMR) spectra of $C_{60}$ in solution. They found a single resonance line, indicating that all carbon atoms of the molecule are chemically equivalent, a property consistent with the proposed icosahedral symmetry ($I_h$). Infrared (IR)
Fig. 4.2. (a) Projection of a regular icosahedron. Vertices are centers of fivefold symmetry, triangular faces are centers of threefold symmetry, and edges are centers of twofold symmetry. The entire object has inversion symmetry. (b) Projection of a truncated icosahedron, created by flattening the vertices of a regular icosahedron. The symmetry elements remain the same as for the icosahedron. The C_{60} molecule is obtained by placing carbon atoms on the vertices. From Gensterblum [7].

measurements also confirmed the icosahedral symmetry of the C_{60} molecule: four IR active modes are to be expected and indeed were observed by Krätschmer et al. [8, 13].

The C_{60} molecule is the smallest and most stable fullerene. Fullerene is the name of an entire class of carbon molecules with the general formula C_{2n}, build up by 12 carbon pentagons and a varying number of hexagons. The smallest number of hexagons is 20, yielding a C_{60} molecule. The next stable fullerene has 25 hexagons forming a C_{70} molecule [14]. The shape of C_{70} is a kind of elongated C_{60} molecule (similar to a rugbyball, or an American football), due to the presence of an additional ring of 10 carbon atoms arranged along the equator.

The fullerene research got strongly stimulated by the discovery of superconductivity in the alkali-doped fullerenes, the so-called fullerides. K_3C_{60} has a transition temperature of T_c = 19 K [15]; for Rb_3C_{60}, T_c = 29 K [16], and for Cs_2RbC_{60}, T_c = 33 K [17]. Despite the large amount of research in the fullerides field, much is still hampering the understanding of the crystal structure, the electronic structure and related properties [9, 18, 19]. A typical example of such an open question is: why are K_1C_{60} and K_4C_{60} insulators, whereas K_3C_{60} is a metal? Lof et al. [20, 21, 22] explain this by claiming that the electron-doped C_{60} behaves as a Mott-Hubbard insulator. This would explain K_1C_{60} and K_4C_{60} being an insulator, but not that K_3C_{60} is a metal. Tjeng et al. resolved this by claiming that the bulk of K_3C_{60} is indeed an insulator, but its surface is metallic [23]. Since a K_3C_{60} surface would be charged and develop a huge electric field over the film thickness, the authors propose a K_{1.5}C_{60} surface. A K_{1.5}C_{60} surface on either side will be metallic and hence give no charging. Whether this issue is really solved remains to be seen, since O. Gunnarsson suggests that K_3C_{60} is not a Mott-Hubbard insulator, but well on the metallic side of it [19].
Fullerenes also form polymers. These polymers can be obtained by various procedures. In the case of C₆₀ one finds charge-transfer polymers [24, 25], pressure polymers [26], and photopolymers [27]. Ecklund and co-workers [27] were the first to report that C₆₀ can be photopolymerised under certain conditions. In a 2+2 cycloaddition, which is a photo-induced coupling between the π electrons of an excited triplet and those of a neighbouring ground-state molecule, the individual balls are united by a 4-membered ring to form a polymer. At 450 K it is possible to reverse the photopolymerization process and retain the pristine C₆₀ molecules.

Polymerization of C₆₀ is not the only possible chemical modification of the fullerene [28, 29, 30]. Currently about 5000 different species of fullerenes can be found in 'Chemical Abstracts' [31]. An example of fullerene chemistry is the attachment of amino groups [28]. For instance, amino groups are involved in TDAE-C₆₀, where TDAE is tetrakis(dimethyl amino)ethylene [32]. It is formed as a stoichiometric composition with a 1:1 ratio of TDAE to C₆₀. TDAE-C₆₀ exhibits ferromagnetism, and has a Curie temperature of Tᵥ = 16 K, which is the highest Tᵥ of any molecular organic ferromagnet [33, 34]. (Also in this field much is not yet well understood [35]).

The large empty space present in every cage-fullerene is inviting to be filled. Up to now it has been demonstrated that several atoms, for example the group-3 metals (Sc, Y, La), and most lanthanides can be trapped inside the higher fullerenes such as C₈₂, and C₈₁ to form soluble and relatively stable endohedral metallofullerenes [36]. A characteristic feature of M@C₂₅⁻¹ metallofullerenes is the off-center position of the metal ion inside the fullerene cage [37, 38]. Combined with a charge transfer from the electron donor to the cage, this displacement leads to a dipole moment which is remarkably high for an encagement of trivalent metal ions (M³⁺). As an example, Fuchs and Rietschel found experimentally that La@C₈₂ has an effective dipole moment μ of 4.4 ± 0.4 D [39]. The ability to achieve a molecular alignment of the endohedral metallofullerenes in crystals or on clean surfaces may lead to future materials with novel solid-state properties [40].

The most fascinating members of the extensive family of fullerenes are possibly the nanotubes. The nanotubes can be envisioned as closed cylinders of hexagonal graphite that are capped by structures that contain pentagons [41]. Considerable interest was generated, when it was shown that the nanotubes could be prepared in large quantities [42, 43], and that they could be filled with other materials [44]. The carbon nanotubes, which can be considered as one-dimensional conductors, represent a new level of mesoscopic physics [45, 46]. Another product derived from carbon shells are the onions. Like nanoscale versions of Russian dolls, they are built from

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¹IUPAC has established the official nomenclature for all members of the fullerene-family. For instance, the IUPAC name of the C₆₀ molecule is [60]fullerene. The prescriptions, however, are not common knowledge, neither followed up. The notation M@Cₙ is also not allowed in the IUPAC language, but who could resist such a cute, dear, and short notation? Nobody!
concentric carbon shells [47, 48].

Prof. H.B.G. Casimir once said that it takes about 10-20 years before a new scientific discovery becomes applicable (and it can take 20 years longer before it is of industrial importance) [49]. In any case, it is certainly only a question of time before we will make use of the multifaceted applicability of the fullerenes. The first reports on their possible applications are appearing eleven years after their discovery: Single-Molecule Transistors [50], and Individual single-wall carbon nanotubes as quantum wires [51]. One of the problems in the field of nanodevices is that one-dimensional arrays of molecules are either semiconducting or insulating. The reason is that one-dimensional electron systems undergo a Peierls transition, a small rearrangement of the atoms or molecules, which results in the opening of an energy gap at the Fermi level [50]. However, the carbon nanotubes do not have the Peierls transition, and can therefore be one-dimensional conductors. Another application for the nanotubes might be as hydrogen-storage material for fuel-cell electric vehicles. Dillon and co-workers [52] showed that H$_2$ can condense to high density inside the narrow (single-walled) nanotubes.

An important development is the use of C$_{60}$ as a strong electron acceptor in the emerging field of 'plastic' electronics. A recent example is the photovoltaic cell, which is constructed out of blends of conducting polymers as donors, and C$_{60}$ molecules (or its derivatives) as acceptors. Such a photovoltaic cell gives rise to high-efficiency photovoltaic conversion. Yu and co-workers [53] used poly(2-methoxy-5-(2'-ethyl-hexyloxy)1,4-phenylene vinylene) (MEH-PPV) as a polymer-donor, whereas Veenstra and co-workers [54] used sexithiophene. Both devices have comparable energy conversion efficiency (2.9%).

### 4.2 Structural and electronic properties of C$_{60}$

Despite of the large amount of research done on C$_{60}$ and its derivatives, the electronic structure and the importance of solid-state band structure effects remain controversial. Solid C$_{60}$ seems to exhibit a dualistic behaviour. On the one hand it behaves as a molecular crystal in which the molecular properties (such as the vibrational states and electronic excitations) are only weakly perturbed by the crystal symmetry (compare [55], and [8]). On the other hand it behaves as a semiconductor, with a moderate (2.3 - 2.6 eV [20, 56]) band gap, which can be electron doped resulting in low energy impurity states and band widths of about 0.6 eV [57, 58]. Another difference in comparison to the behaviour of typical molecular crystals is that C$_{60}$ forms ionic compounds, which in some cases exhibit metallic and even superconducting [15] behaviour, clearly demonstrating the importance of one-electron band formation. The properties of these compounds are reminiscent of the charge-
transfer type of molecular solids such as the much studied TCNQ salts, except that the $C_{60}$ compounds usually show 3-dimensional behaviour rather than the 1- or 2-dimensional behaviour exhibited by the charge-transfer molecular solids. This, evidently, is due to the spherical structure of the $C_{60}$ molecule.

In this chapter we present evidence that in pure $C_{60}$ the excitons also exhibit this dualistic behaviour. The energies of the excitonic states are close to those of the gas phase molecule emphasizing the molecular characteristics, but charge fluctuations between different molecules, which lead to exciton propagation and crystal field splitting, result in mixing of different multiplets. Furthermore we will see, that the propagation of the exciton results in an excitonic band width, which is abnormally large for a molecular solid. All the above can be explained within a one- and two-particle band structure theory.

It is well established that the strong delocalization of the $p_\pi$-electron network (which is the case on a $C_{60}$ molecule) can result in strong nonlinear optical effects [59, 60, 61, 62]. Koopmans et al. [63, 64] have shown that the second-harmonic signal from $C_{60}$ is very strong due to a double resonance when the primary energy is tuned to the $^1T_{1g}$ excitonic state at 1.81 eV. This opens up the possibility to study the excitons inside the electronic band gap, in particular the exciton band width, the band splitting due to crystallographic phase transitions, and the mixing of multiplets due to the crystal symmetry.

To facilitate this study we have developed a theory for the exciton splittings and dispersions based on the molecular multiplet splittings and solid-state effects arising from a charge-transfer mechanism for the exciton propagation [20, 65]. The one-electron (-hole) hopping integrals required for this are obtained from a tight-binding fit to the local density approximation (LDA) band structure of $C_{60}$ as given by Satpathy et al. [66]. We show that reasonable agreement can be obtained with the experimental second-harmonic line shape with only one adjustable parameter, namely the $^1T_{1g}$ - $^1G_g$ molecular multiplet splitting. Before presenting the results, a short overview of the crystallographic and electronic structure of $C_{60}$ is given.

### 4.2.1 Crystallographic properties and structural phase transitions

The $C_{60}$ molecule has a shape that is very close to being spherical. However, it is not quite a sphere. It consists of pentagon and hexagon planes, such that all nuclei are on a sphere with a diameter of 7.1 Å. The length of a bond shared by two six-membered rings (6-6 bond) is shorter than a bond within a pentagon (5-6 bond). In Ref. [67] a list of carbon-carbon distances based on various experimental techniques and theoretical calculations is presented. For example, Hedberg et al. used gas-phase electron diffraction to determine that the length of the 6-6 bond is $1.401(1)$ Å and of the 5-6 bond $1.458(6)$ Å [68]. The 6-6 bond is often called a
double bond and the longer 5-6 bond a single bond, although they are both mainly aromatic in character [7]. Notwithstanding the different bond lengths, the structure retains the full symmetry of the icosahedral point group, meaning that all carbon atoms are still equivalent: each carbon atom is bonded by one double bond and two single bonds (Fig. 4.2(b)).

The solid phases of the fullerenes are called fullerites. At room temperature the crystal structure of C\textsubscript{60} fullerite is face-centered cubic (fcc) with four molecules per unit cell and a lattice constant of 14.17 ± 0.01 Å [69]. This means that the nearest-neighbour distance between two C\textsubscript{60} molecules is 10.0 Å. The space group is Fm\textsuperscript{3}m with the point group m\textsuperscript{3}m, which involves fourfold axes. Since the icosahedral point group of a C\textsubscript{60} molecule lacks a fourfold axis, a question arises about the orientation of the molecules in the crystal lattice. This shows that C\textsubscript{60} is indeed not spherical.

The orientation of the molecule with the highest possible symmetry with respect to a cube, the so-called standard orientation, is shown in Fig. 4.3: the C\textsubscript{60} molecule has the required threefold axes along the <111> directions, but has a twofold rather than a fourfold axes along the <100> directions. Rotation of the molecule by 90\degree\textsuperscript{o} about any [100] axis (or by a 44.48\degree rotation about any [111] axis [7]) produces its merohedral image, and an equal superposition of these two images restores the required fourfold symmetry. Thus, the experimentally observed Fm\textsuperscript{3}m symmetry can be obtained by assuming disorder between both merohedrally related configurations [70]. A completely random orientation of the C\textsubscript{60} molecules [71], so that a time-averaged molecule is a spherical shell, will also give a Fm\textsuperscript{3}m symmetry.

To distinguish between these two models dynamical measurements such as NMR are needed. These NMR measurements [72, 73] are consistent with random diffusive disorder (spherical shell model), rather than twofold merohedral disorder. They show a orientational correlation time \( \tau \approx 10 \) psec, which are only three times longer than the one calculated for free rotation while it is shorter than the value measured for C\textsubscript{60} in solution (15.5 psec).

Upon cooling below \( T_c \approx 260 \) K the high-temperature fcc lattice symmetry of C\textsubscript{60} fullerite is lowered to simple cubic [69]. Heiney \textit{et al.} deduce from their x-ray powder-diffraction data that, after the transition to simple cubic, the crystal structure still consists of four molecules per unit cell. However, the four molecules, which are equivalent in the fcc structure, become inequivalent in the simple cubic. The structural phase transition occurs via orientational ordering of the molecules with centers still at their fcc lattice sites. The space group of the ordered structure is Pa\textsuperscript{3} [69, 74], and is obtained as follows. Let us start from an fcc crystal in which all molecules have one of the two standard orientations (see Fig. 4.3). Next, the molecules centered at \((0,0,0)\), \((\frac{1}{2},\frac{1}{2},0)\), \((\frac{1}{2},0,\frac{1}{2})\), and \((0,\frac{1}{2},\frac{1}{2})\) are rotated over the same angle \( \Gamma = \Gamma_1 \), but about \textit{different} \( <111> \) axes: [111], [1,1,1], [1,1,1], and [1,1,1], respectively. The rotation angle \( \Gamma_1 \) is not fixed by symmetry, and is experimentally determined to be in the range 22-26\degree [74, 75].
The two standard orientations of $C_{60}$ molecules in which the twofold and threefold molecular axes are aligned with $<100>$ and $<111>$ cubic directions, respectively. The standard orientation (b) transforms into (a) by a rotation of $90^\circ$ about any of the [100] axes, or by a $44.48^\circ$ rotation about any [111] axis. From Gensterblum [7].

The orientational order in the low-temperature phase cannot be explained in terms of van der Waals bonding alone, but requires a model which also includes electrostatic repulsion. David et al. [76, 77] noted that in the $P_\alpha\bar{3}$ structure the short electron-rich inter-pentagon 'double' bonds face the electron-poor pentagons of neighbouring $C_{60}$ molecules (orientation 1). This is illustrated in Fig. 4.4(a). The rotation angle $\Gamma = \Gamma_1$ around the [111] axes ensures that all twelve nearest-neighbour interactions are optimized$^2$. Subsequent studies reveals that a different rotation angle $\Gamma = \Gamma_1 + 60^\circ$ is also possible in the low-temperature phase [77]. In this case a hexagon on one molecule faces a 'double' bond on a neighbouring molecule giving rise to a second equilibrium distribution (see orientation 2 in Fig. 4.4(b)).

The temperature dependence of the cubic lattice constant of $C_{60}$, determined from high-resolution powder neutron diffraction, exhibits a first-order phase transition at 260 K and a second-order transition at 90 K [77]. David and co-workers found that, below the 90 K transition, the probability that any given molecule has orientation 1 (a 'double' bond facing a pentagon) is independent of the temperature and equal to 0.835. However, the probability for orientation 1 is decreasing for increasing $T$ above 90 K, until it reaches a value of about 0.61 at $T = 260$ K.

Summarizing, at $T > 260$ K all $C_{60}$ molecules are rotating freely in all directions. After the orientational-ordering phase transition temperature at 260 K, the $C_{60}$ molecules can alternate between two equilibrium positions corresponding to the orientation 1 and 2, respectively, until at 90 K they get 'frozen in', with a 5:1 probability for the orientation where the double bond faces a pentagon rather than a hexagon.

$^2$Note that David et al. [76, 77] use another definition for the angle than Heiney et al. [69, 78] and Copley et al. [79].
4.2. Structural and electronic properties of $C_{60}$

Fig. 4.4. Views from a $C_{60}$ molecule to one of its nearest neighbours. At (a) both molecules have the $\Gamma = \Gamma_1$ orientation, so that a pentagon on the origin molecule faces a 6:6 short bond on its neighbour. At (b) the origin molecule has the $\Gamma = \Gamma_1 + 60^\circ$ orientation, and one of its hexagons faces the neighbour's short bond. After Copley et al. [79].

4.2.2 Electronic structure and excitation spectrum.

Fullerenes differ from the two other allotropic forms of carbon, graphite and diamond, in the way the hybridization of the atomic s- and p-levels occurs. Carbon has $1s^22s^22p^2$ electronic configuration. Considering only the 2s and 2p levels, the $sp^3$ hybridization in diamond gives rise to a bond angle of $109.5^\circ$ and four identical $\sigma$-type bonds. In graphite, the $sp^2$ hybridization produces three strong equivalent planar $\sigma$-type bonds with a bond angle of $120^\circ$. The out-of-plane p-orbitals result in $\pi$-bonds and weak interplanar bonding. In $C_{60}$, the curvature of the surface at a carbon atom position is achieved by forming bonds with intermediate hybridization: the three $\sigma$-orbitals have $sp^{2.278}$ hybridization and the $\pi$-orbital has $s^{0.06}p$ hybridization [80].

In spectrum calculations the influence of the curvature on the hybridization is often neglected, and the $\sigma$-bonds are considered to be 2s orbitals hybridized with the two in-plane $2p_x$ and $2p_y$ orbitals. The remaining $2p_z$ orbitals are mixed to form molecular $\pi$-orbitals. Due to the strong $\sigma$-overlap between neighbouring carbon atoms, the $\sigma$-states are pushed away from the Fermi level [81]. As a result, the low-energy excitations (up to several eV) involve predominantly the $\pi$-states, and for their description one can thus restrict the analysis to the 60 $\pi$ electrons of the $C_{60}$ molecule [82].

The simplest theory is obtained by making a spherical approximation for the $C_{60}$ molecule. This leads to the model of free electrons confined to a spherical shell [83], with particles of mass $m^*$ and angular momentum $l$. For a sphere of radius $R$, the
kinetic energy is given by [81]:

\[ E_l = \frac{\hbar^2 l(l+1)}{2m^* R^2} \]  (4.1)

Including spin degeneracy the number of states with energy \( E \leq E_l \) is \( 2(l+1)^2 \) [84]. Considering the 60 \( \pi \) electrons of one \( C_{60} \) molecule, the states up to \( l = 4 \) would be filled by 50 electrons, and the remaining 10 electrons would be distributed within the 22-fold degenerate \( l = 5 \) shell. This immediately reveals one of the drawbacks of the sphere model: it does not reproduce the closed shell configuration. Nevertheless, in his Ph.D. thesis Koopmans shows that the correspondence of the free-electron sphere model for \( l \leq 3 \) with the more refined LCAO (Linear Combination of Atomic Orbitals) calculations is excellent. For the highest level involved (\( l = 5 \)) one can take into account the level splitting associated with the icosahedral point symmetry of the potential due to the position of the carbon atoms. The \( l = 5 \) orbitals are then decomposed into \( t_{2u}^{(5)} + t_{2g}^{(5)} + h_{u}^{(5)} \), where \( t_{2u}^{(5)}, t_{2g}^{(5)} \), and \( h_{u}^{(5)} \) are (odd) irreducible representations of \( I_h \), with dimensions 3, 3, and 5, respectively (Table 1 of [82]). Filling the five degenerate \( h_{u}^{(5)} \) orbitals now leads to a closed (sub)shell. Calculations based on the LDA method [57, 66], which are more sophisticated than the free-electron sphere model or the LCAO approach, have also been applied to \( C_{60} \), and reproduce an electronic structure in good agreement with experiment.

In Fig. 4.5, we show the part of the molecular-orbital (MO) scheme for \( C_{60} \), which is related to the low-energy optical excitations. The \( h_{u}^{(5)} \) orbital is the highest-occupied molecular orbital (HOMO) whereas the \( t_{2u}^{(5)} \) is the lowest-unoccupied molecular orbital (LUMO). They both have \textit{ungerade} character, implying that the lowest excitation, \( h_{u}^{(5)} \rightarrow t_{2u}^{(5)} \) transition, is electric-dipole forbidden. Therefore, the HOMO-LUMO transitions that appear in optical absorption measurements are only weakly allowed due to a Herzberg-Teller and/or a Jahn-Teller vibronic effect [85]. Techniques such as electron-energy-loss spectroscopy (EELS), two-photon absorption (TPA), and second-harmonic generation (SHG) are more suitable in observing these low-lying electric-dipole forbidden transitions, because of their different selection rules.

These considerations are valid for a single \( C_{60} \) molecule. In an \textit{isolated} \( C_{60} \) molecule, the lowest singlet states are found at an excitation energy of \( \approx 1.91 \) eV [86, 87]. The lowest singlet states in \textit{solid} \( C_{60} \) are between 1.81 eV [63] and 1.85 eV [88], as observed with SHG and TPA. This means that the "solid-state red-shift" is about 60 to 100 meV. It represents the combined effect of band formation and crystal-field-like splitting of the particle-hole multiplet of a \( C_{60} \) molecule in an fcc lattice.

In \textit{solid} \( C_{60} \) the gap between HOMO and LUMO derived bands, as determined from PES (Photo Electron Spectroscopy) and IPES (Inverse Photo Electron Spectroscopy) experiments, is about 2.3 eV [20]. This is a strong indication that all
low-energy excitations, (ℏω < 2.3 eV) as found in optical experiments, are Frenkel excitons. EELS experiments on solid C₆₀ [89] exhibit states with an excitation energy of ≈ 1.5 eV, i.e., even lower than the optically observed singlet excitons. This suggests that these states can be interpreted as triplet excitons.

If we take a closer look at the lowest particle-hole excitations of an isolated molecule, we see that, by exciting an electron from one of the fivefold degenerate HOMO into one of the threefold degenerate LUMO, one obtains 3x5 = 15 degenerate lowest-energy configurations. This degeneracy is lifted by the Coulomb interaction between the electron and the hole, which gives rise to a multiplet splitting of electron-hole states. Using group theory we can identify this multiplet splitting as:

\[ t_{1u} \otimes h_u = T_{1g} + T_{2g} + G_g + H_g \]  

where \( T_{1g}, T_{2g}, G_g, \) and \( H_g \) label the (even) irreducible representations of \( I_h \) with dimensions 3, 3, 4, and 5, respectively. Quantum chemical calculations estimate the splitting in energy of the different electron-hole states to be about 0.35 eV [90].

In this chapter various optical transitions will be discussed. In order to keep the discussion below as clear as possible, we start by presenting a summary of all optical transitions mentioned in this chapter in Table 4.1.

On the left hand side of Fig. 4.6 are shown the final states, i.e., electron-hole excitations on a single buckyball, important for our SHG experiments. Also shown is the multiplet with an energy above the electrical conductivity gap. This multiplet is due to the electric-dipole allowed \( h_{y}^{(4)} \rightarrow t_{1u}^{(5)} \) excitation, containing, among others, a threefold degenerate \( 2T_{1u} \) singlet state. Below the conductivity gap we see the \( ^3T_{1g}, ^1G_g, ^1T_{2g}, \) and \( ^1H_g \) states. Their energy sequence, illustrated (schematically) in Fig. 4.6, is according to the latest semi-empirical calculations of Negri et al. [91]. Several research groups have found that the three lowest singlet excitonic states
Table 4.1. A summary of the various optical transitions discussed in this chapter. The superscript in the transition column represents the quantum number \( l \) (see also Fig. 4.7). Their energy is listed in the last column. MD stands for magnetic dipole, EQ for electric quadrupole, and ED for electric dipole.

<table>
<thead>
<tr>
<th>transition</th>
<th>final state</th>
<th>excitation process</th>
<th>( \hbar \omega ) (eV)</th>
</tr>
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<tbody>
<tr>
<td>( h_{\nu}^{(5)} \to t_{1u}^{(5)} )</td>
<td>( 1^T_{1g} )</td>
<td>MD</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>( 1^G_g )</td>
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</tr>
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<td></td>
<td>( 1^T_{2g} )</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>( 1^H_g )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1^T_{1g} + \nu_{ph}(t_{1u}) )</td>
<td>EQ</td>
<td>2.2-2.3</td>
</tr>
<tr>
<td>( h_{\nu}^{(5)} \to t_{1g}^{(6)} )</td>
<td>( 1^T_{1u} )</td>
<td>ED</td>
<td>2.02</td>
</tr>
<tr>
<td>( h_{\nu}^{(4)} \to t_{1u}^{(5)} )</td>
<td>( 2^1T_{1u} )</td>
<td>ED</td>
<td>2.75</td>
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<tr>
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<td>( 3^1T_{1u} )</td>
<td>ED</td>
<td>3.71</td>
</tr>
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</table>

are very close in energy, and the question, which is really the lowest one, is not completely solved yet [90, 92]. Theoreticians are divided between assigning the \( 1^T_{1g} \) [93] and the \( 1^T_{2g} \) [92] as the lowest exciton. However experiments seem to indicate the \( 1^T_{1g} \) as the lowest state [94, 95], and also if calculations are combined with spectroscopic measurements, the \( 1^T_{1g} \) state is the winner [91].

Our SHG data clearly show that the resonance at about 1.81 eV is of \( 1^T_{1g} \) origin [63, 96] and, as will be discussed below, that the data can be properly explained by assuming that the \( 1^T_{1g} \) and \( 1^G_g \) are (nearly) degenerate. This corresponds well with the latest assignments of the \( 1^T_{1g} \) and \( 1^G_g \) transitions by Negri et al., based on recent fluorescence spectra of \( C_{60} \) [91, 97]. The \( 1^T_{2g} \) state is situated at a slightly higher energy than the \( 1^T_{1g} \) and \( 1^G_g \) states. Everybody agrees that the \( 1^H_g \) state is the highest of the multiplet, well separated from the other three. The \( 1^H_g \) state is situated at about 2.2 - 2.3 eV [81, 90, 98] with respect to the \( 1^A_g \) state.

Shirley and co-workers calculated the exciton levels in solid \( C_{60} \) using a model Hamiltonian, and found, some well-defined charge-transfer excitonic states at energies immediately above the Frenkel exciton levels. These are consequently energetically close to the electron-hole continuum [92]. They deduced that the \( 1^T_{2g}, 1^T_{1g}, \) and \( 1^G_g \) singlet excitons have nearly complete Frenkel character, whereas the \( 1^H_g \) exciton acquires considerable charge-transfer character. They defined the amount of Frenkel character as the likelihood that the electron and hole are on the same molecule, and the amount of charge-transfer character as the likelihood that the electron and hole are on adjacent molecules. These charge-transfer excitons are at an energy \( U - V \) (the difference between the on-site Coulomb interaction \( U \), and
Fig. 4.6. Part of the singlet excitation spectrum of $C_{60}$ with, on the left hand side, the intramolecular (on the $C_{60}$ molecule) excitations and, on the right hand side, the solid-state interband excitations. The multiplets of the optically forbidden HOMO $\rightarrow$ LUMO excitations have an energy lower than the conductivity gap of 2.3 eV, and are therefore Frenkel excitons. The (broad) arrows at the left show the three-level diagram responsible for the 1.8 eV SHG resonance. The Frenkel excitons can propagate via the nearest-neighbour charge-transfer (CT) states, which are $U - V$ higher in energy (see Eq. (4.3)).

the nearest-neighbour Coulomb repulsion $V$, [99, 100]) with respect to the exciton ground-state energy.

When an electron and hole are not bound together, but far apart moving independently (which costs a minimum energy of 2.3 eV), we are dealing with the interband transitions in solid $C_{60}$. Such transitions are shown on the right hand side of Fig. 4.6. Note that in a solid, unlike for a molecule, the $^1T_{1g}$, $^1G_g$, $^1T_{2g}$, and $^1H_g$ symmetries are not completely realized, because the site symmetry of a $C_{60}$ molecule in a solid is not $I_h$ but $m\bar{3}m$ at most. However, the relatively small size of the solid-state effects ($\approx 60\text{-}100\text{ meV}$) as compared to the estimated multiplet splitting ($\approx 0.35\text{ eV}$) suggests that one may find exciton bands with a reasonably well-defined "multiplet parentage". Moreover the weak coupling between neighbouring $C_{60}$ molecules, implies that transitions that take place within a single molecule are highly dominant. Hence, the symmetry of the "parent multiplet" will largely decide the "observability" of the respective exciton band. The $^1T_{1g}$ state can be reached by a magnetic-dipole transition from the $^1A_g$ ground state, while the $^1H_g$
state can be reached by an electric-quadrupole transition. Excitations corresponding to the remaining two representations \(^1T_{2g}\) and \(^1G_g\), would require even higher multipoles, meaning that bands which originate from these multiplets will not be observed experimentally.

A larger part of the MO scheme for \(C_{60}\) is shown in Fig. 4.7. This illustration will be especially useful for section 4.4, in which the sum-frequency generation (SFG) measurements will be presented and discussed in relation to the three lowest electric-dipole-allowed transitions (indicated by the arrows in Fig. 4.7 and summarized in Table 4.1). The lowest electric-dipole-allowed transition is the \(h_{1u}^{(5)} \rightarrow t_{1g}^{(6)}\) one, resulting in the \(^1T_{1u}\) final state (hereafter referred to as \(^1T_{1u}\)) at about 2.75 eV [102]. The experiment of Wilk et al. [98], discussed in section 4.4, also involved this transition. The second lowest electric-dipole-allowed transition is the \(h_{y}^{(4)} \rightarrow t_{1u}^{(5)}\) transition. In this case, one of the final states is the \(^2T_{1u}\) state. In our SHG experiment, the magnetic-dipole transition at 1.8 eV was probed resonantly, whereas the \(2\hbar\omega\) resonance involved was the \(^2T_{1u}\) state (at about 3.6-3.7 eV) [63]. The \(h_{1u}^{(5)} \rightarrow h_{y}^{(6)}\) transition is the third lowest electric-dipole transition [93, 101]. The final state involved in this transition is the \(^3T_{1u}\) state at about 4.7 eV [102]. In a SHG experiment, in which the fundamental frequency \(\omega\) is probing the electric-quadrupole-induced excitation resonantly (at about 2.3 eV [98]), the \(2\hbar\omega\) can be on resonance with the \(^3T_{1u}\) state.
4.3 Temperature-dependent SHG of the $^{1}T_{1g}$ exciton

4.3.1 Sample preparation and experimental results

$C_{60}$ with a purity better than 99.99% was evaporated from a Knudsen cell onto a substrate at UHV pressures below $4 \times 10^{-9}$ mbar. As substrates we used fused quartz or at low temperature MgO, a good thermal conductor.

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. The fundamental frequency was scanned in the range $\hbar \omega = 1.7 - 2.0$ eV. The second-harmonic intensities were calibrated by using a reference quartz crystal in a transmission geometry, carefully tuned to a Maker fringe optimum by fine-tuning the frequency. All SHG experiments are performed at a fixed angle of incidence (45° to the surface normal) and the specular reflected second-harmonic signal was detected.

The SHG of thin $C_{60}$ films exhibit complicated thickness- (and through the dispersion also frequency-) dependent interference phenomena. We already showed before [64] that for a $m_{\text{in}} \rightarrow p_{\text{out}}$ polarization ($m \rightarrow p$) combination (where $m$ stands for mixed meaning 50% $p$ and 50% $s$ polarized light) the second-harmonic interference pattern exhibits a broad minimum for $C_{60}$ film thicknesses of around 250 nm (see also Fig. 4.18). Therefore, we chose a $m \rightarrow p$ polarization combination and a thickness of 250 nm for the measurements presented in here, so that dispersive interference effects can be neglected\(^3\).

The temperature-dependent SHG experiments were performed using a He-flow cryostat (4 - 500 K). The temperature was measured with a thermocouple glued to the substrate. Possible effects of heating during the laser pulse were examined by varying the laser power. We found that below 100 K the temperature during the laser pulse was about 20-30 K higher than the one measured with the thermocouple. At higher temperatures, in particular around the rotational-ordering phase-transition temperature (260 K), no heating by the laser pulse was detected.

In Fig. 4.8 the second-harmonic intensity measured at various temperatures is shown as a function of the fundamental photon frequency ($\hbar \omega$). Around room temperature we observe the resonance at about 1.8 eV already previously reported [63, 64]. Note for decreasing temperature the strong enhancement of the second-harmonic intensity, the overall blue shift and the temperature dependence in the line shape of the resonance. Fig. 4.9(a) and Fig. 4.9(b) show the temperature dependence of the zeroth and first moment of the spectrum corresponding to the integrated intensity and to the mean frequency, respectively. In both cases we see a strong

\(^3\)At least for the energy range in which the $m \rightarrow p$ second-harmonic signal is constant, i.e., for 1.7-1.9 eV.
Chapter 4. Excitons in $C_{60}$ studied by SHG and SFG

Fig. 4.8. The temperature-dependent SHG of $C_{60}$ films using a $m \to p$ polarization combination. The (low) temperatures are not corrected for the heat induced by the laser.

Figures 4.8 and 4.9 show the temperature dependence at the phase-transition temperature of 260 K. It is also just below this temperature that we observe a splitting of the resonance into two peaks with an intensity ratio of about 3:1. The splitting is about 40 meV. The total width of the signal at the base of the line is approximately 100 meV, which is very large for an exciton band width of a molecular crystal, as discussed below.

4.3.2 Data interpretation and exciton propagation

Looking at the data in Fig. 4.8 and Fig. 4.9, there are three main features to be explained: (i) the splitting of the signal below the phase transition; (ii) the line width larger than expected for an electric-dipole forbidden transition in a molecular...
4.3. Temperature-dependent SHG of the $^{1}T_{1g}$ exciton

Fig. 4.9. The temperature dependence of (a) the zeroth moment of the SHG spectrum corresponding to the total intensity, and of (b) the first moment corresponding to the mean frequency ('averaged peak position'). Notice that the strongest temperature dependence is at the phase-transition temperature of 260 K ($T_c$).

crystal, and (iii) the overall strong temperature dependence of the second-harmonic intensity and line shape.

(i) The splitting

We can consider four possible mechanisms for the splitting, namely a Jahn-Teller effect, a Davydov splitting, a Herzberg-Teller coupling mechanism, and a mixing of the electronic molecular states. A Jahn-Teller splitting can probably be discarded, since it is expected to be at most 12 meV for the singlet states as determined by Wang et al. [103]. Before discussing the other three possibilities we briefly review the basic ideas involving the propagation of excitations and their observation by SHG.

Let us consider first the various possible excitations. Fig. 4.5 is a schematic picture of the double resonant SHG process observed in this energy range [64]. The three level diagram consists of a magnetic-dipole transition from the molecular ground state to the $^{1}T_{1g}$ electron-hole excited state (involving a $h_{1u}^{(5)} \rightarrow t_{1u}^{(5)}$ single-electron
transition), followed by an electric-dipole transition to the $2^1T_{1u}$ electron-hole state at about 3.6 eV ($h_g^{(4)} \rightarrow h_u^{(5)}$), and finally an electric-dipole transition back to the ground state ($t_{1u}^{(5)} \rightarrow h_g^{(4)}$). Linear-optical experiments exhibit a strong electric-dipole allowed transition at 3.56 eV with a half width at half maximum of 0.23 eV. Since this width is much larger than the one observed in our experiment (0.06 eV at room temperature) we concluded that the sharp features in the SHG spectrum must be related to the intermediate $^1T_{1g}$ exciton state [96, 81]. This difference in width can easily be understood by comparing the intramolecular excitations, where the electron and the hole are bound, with the intermolecular electron-hole excitations (interband transitions). The last determines the conductivity gap involving dissociated electron-hole states. As measured by photoconductivity [104], or by combined photoelectron and inverse-photoelectron spectroscopy [20] this gap is 2.3 eV. In Fig. 4.6 we show the energy level scheme of the intramolecular excitonic excitations (on the left-hand side) and the solid-state intermolecular band gap excitations (on the right-hand side). The molecular $2^1T_{1u}$ state at 3.6 eV is well inside the intermolecular electron-hole continuum and will decay into this with a hopping integral comparable to the one-electron (-hole) band width. The $^1T_{1g}$, however, is an electron-hole bound state, inside the band gap, and can therefore have a long lifetime. The extra energy required to dissociate the electron-hole pair of the exciton (i.e., the exciton binding energy) is directly related to the on-site Coulomb interaction measured to be about 1.3 - 1.6 eV by Lof et al. [20]. Since the $^1T_{1g}$ exciton is bound and the transition to the ground state is electric-dipole forbidden, we expect it to be very long lived and we would expect a very small exciton dispersion by conventional optical dipole - optical dipole intermolecular propagation. The still quite large total width of more than 100 meV is therefore difficult to understand in the limit of a molecular solid. It is, however, well known that band structure effects in $C_{60}$ are not negligible. Lof et al. [20] already suggested a propagation mechanism which could lead to a substantial exciton dispersion involving virtual charge-transfer states. A similar mechanism was previously suggested by Choi et al. [105] to explain the dispersionsal width of optically forbidden excitons in molecular crystals. It is also very similar to the so called superexchange mechanism used to describe Frenkel d-d excitons in 3d transition metal compounds [106, 107].

We will now have a closer look to this excitonic propagation mechanism. In Fig. 4.10(a) this mechanism is shown pictorially: an electron-hole pair on site $i$ can propagate to a neighbouring site $j$ via a virtual excited intermediate state. This intermediate nearest-neighbour (charge-transfer) state, in which the electron is on site $i$ and the hole on a nearest-neighbour site $j$ (or vice versa), is at an energy $U - V$ (the difference between the on-site Coulomb interaction and the nearest-neighbour Coulomb repulsion [99, 100]) higher than the exciton ground state energy. The net
effective exciton hopping integral following from perturbation theory is given by:

$$T^\text{exciton} = \frac{2t_e t_h}{U - V},$$  \hspace{1cm} (4.3)

where $t_{e(h)}$ are the average single electron (hole) nearest-neighbour hopping integrals. It should be noticed that the same electron- and hole-hopping integrals appear in expressions for the red shift of an exciton energy in the solid relative to the corresponding one in the gas phase (see also Fig. 4.10(b)). Indeed, the red shift to first-order in perturbation theory is then given by:

$$\Delta E = K \left( \frac{t_e^2 + t_h^2}{U - V} \right),$$  \hspace{1cm} (4.4)

where $K$ is a geometrical factor related to the symmetry of orbitals and the nearest-neighbour coordination number. As an example, one has $K = 12$ \cite{108} for a totally symmetrical one-electron and one-hole orbital in a fcc lattice. To estimate the red shift of the $^1T_{1g}$ state we look at the isolated $C_{60}$ molecule for which Gasyna et al. \cite{87} found the $^1T_{1g}$ state at about 1.91 eV. The same value has been assigned to the $^1T_{1g}$ state by Negri et al. \cite{90} using the absorption spectra of $C_{60}$ in n-hexane solution of Leach et al. \cite{86}. Koopmans et al. found the $^1T_{1g}$ in solid $C_{60}$ resonant at 1.81 eV. This means that in the solid state this exciton is red shifted by 100 meV, which is in the same order as the exciton band width. This supports
the above mentioned exciton hopping mechanism. Detailed calculations of the one-electron (-hole) hopping integrals show that only nearest-neighbour hopping has to be considered [65]. Therefore, this exciton hopping mechanism does not destroy the molecular Frenkel character of the exciton.

In the low-temperature phase there are four differently orientated molecules per unit cell so that the exciton band at the $\Gamma$ point can split up into two or more bands. This splitting, called the Davydov splitting, which represents the second possible explanation, is of the order of the exciton band width and is prominently due to the dependence of the exciton transfer integral on the relative orientation of neighbouring molecules.

Two-photon excitation data of $C_{60}$ single crystal measured at 4 K by Muccini et al. [88] show a band at 1.846 eV which is assigned to the same lowest forbidden Frenkel exciton of $^1T_{1g}$ symmetry as discussed in this chapter. They also find a second band at higher energy (1.873 eV). They discuss the splitting between these two bands as a possible Davydov splitting. They give an alternative assignment of the second band as being due to a second forbidden electronic state. Indeed semi-empirical quantum-chemical calculations [90] have shown that there are several closely spaced forbidden states which lie in a narrow energy range [88]. The two-photon spectrum of Muccini et al. strongly resembles the low temperature second-harmonic resonance in Fig. 4.8. However, their two-photon absorption, being a third-order nonlinear optical experiment, involves other selection rules than our SHG experiment.

In order to get a more detailed understanding of our experimental results, we carried out the full exciton calculation starting from the basic ideas described by Eq. (4.3) and Eq. (4.4). The details have been published elsewhere [65]. Here we restrict ourselves to briefly describe the ingredients of the calculations and the results. In the full calculation the orbital degeneracy of the $t_{1u}^{(5)}$ (threefold) and $h_{1u}^{(5)}$ (fivefold) must be taken into account, so that there are several electron- and hole-hopping integrals depending on the orbital quantum numbers. Satpathy et al. [66] have described how those integrals can be obtained from one-particle band structure calculation using a tight-binding fit. The electron- and hole-hopping integrals are a function of the relative orientation of the $C_{60}$ molecules. These integrals are completely determined from a single fit to the band structure for a particular given structure. Also we must take into account the multiplet structure of the molecular excitations due to the intramolecular Coulomb interaction as described by Negri et al.. These multiplet splittings are not very well known but can be obtained from optical or electron-energy-loss data of the gas phase or in solution. The effective exciton-transfer integrals are then a sum of products of electron- and hole-transfer integrals divided by $U - V$. The degree to which each of the electron- and hole-hopping integrals contribute to the dispersion of a particular exciton is determined
by the weight of the electron-hole product function in the particular excitonic state under consideration. In addition to the broadening of the molecular multiplets into bands, there is also a mixing of the various molecular exciton states because of the lowering of symmetry in the crystal.

The only remaining parameters are $U - V$ and the molecular multiplet splitting. Concerning $U - V$, a rough estimate can be derived from the Auger data of Brühwiler et al. [99]: $U \approx 1.1$ eV (0.2 eV is subtracted because of the higher exciton energy of a singlet), and $V \approx 0.7$ eV. This leaves us with $U - V \approx 0.35 \pm 0.2$ eV. An independent estimate for $U - V$ can also be obtained from the experimental red shift as given in Eq. (4.4). Taking $U - V = 0.35$ eV we get a calculated red shift comparable to the experimental observed one. Concerning the multiplet splitting we will see below that all we need for the present model is a small $^1T_{1g} - ^1G_g$ splitting.

These exciton dispersion calculations, show that the four $^1T_{1g}$ band at the $\Gamma$ point splits up in three $^1T_g$ bands, one $^1A_g$ and one $^1E_g$ band [65]. This can be expected from group theoretical arguments because of the transition from the space group $Fm\bar{3}m$ of the high temperature phase to the space group $P\bar{a}3$ of the low temperature phase [109, 110]. The Davydov splitting is found to be about 30 meV [65], which is close to the experimental splitting (40 meV) of the two peaks. The calculation, however, predicts that more than 90% of the weight would be in the lowest $^1T_g$ band (Fig. 4.11 (a)). This is inconsistent with our data! Therefore, the Davydov splitting can also be discarded.

The next possible mechanism, which could explain the splitted structure in our SHG data is a Herzberg-Teller coupling mechanism. Electric-dipole forbidden transitions (like $^1A_g \rightarrow ^3T_{1g}$) can become partially allowed due to a Herzberg-Teller vibronic coupling. This means that the participation of specific molecular vibrations could lead to weakly allowed transitions, which are then shifted in frequency from the purely electronic 0-0 transition (the true origin) [90]. Guss et al. interpreted their fluorescence spectrum of solid C$_{60}$ at low temperature in terms of the Herzberg-Teller coupling [111]. They observed several pairs of emission lines spectrally separated by about 33 meV [111]. Each doublet in the spectrum was explained in terms of two distinct molecular vibrations, i.e., a pair of emission lines corresponds to 1437 cm$^{-1}$ $t_{1u}$- and 1646 cm$^{-1}$ $h_u$-related false origins, as was already mentioned by Negri et al. [90].

Schlaich et al. tried also to interpret their one-photon and two-photon excitation spectra, where each peak exhibits also a $\approx 30$ meV splitted doublet structure, in terms of Herzberg-Teller coupling. In Ref. [94] they assigned the most dominant transition pair (2.015 and 2.045 eV) as either two distinct vibrations ($t_{1u}$ and $h_u$) in the Herzberg-Teller coupling scheme of the lowest $^1A_g - ^1T_{1g}$ transition or as only one vibration ($t_{1u}$). In this second case the line-splitting was claimed to be a consequence of the two possible alignments of neighbouring C$_{60}$ molecules below
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\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4_11}
\caption{Comparison of the SHG data (open circles) taken at the lowest temperature (27 K) with the theoretical calculations (dashed line) for an isolated $^1T_{1g}$ state (a), and for degenerate $^1T_{1g}$ and $^1G_g$ states (b). The vertical bars indicate the positions of the exciton bands at the $\Gamma$ point.}
\end{figure}

\approx 90$ K. In a later paper [112] the same data were explained only in terms of the second case (thus no relation between the 30 meV splitting and a Herzberg-Teller coupling).

A Herzberg-Teller mechanism could affect our SHG data in two ways. One possible way is that both peaks in Fig. 4.8 are false origins\footnote{This means that in both cases the $^1T_{1g}$ state is not probed directly (the true origin), but the $^1T_{1g}$ state, coupled with one or several phonons (false origin).}. Following the interpretation of Guss et al. [111] the double peak structure is then determined by two distinct molecular vibrations. Based on very detailed data analysis from Koopmans \textit{et al.} [64, 63, 96, 81], we are of the opinion that the 1.8 eV resonance is the true origin of the $^1T_{1g}$ state. This leaves the second possibility: namely, only the second peak (at 1.866 eV) is due to a Herzberg-Teller coupling. In order to couple the $^1T_{1g}$ state to an optically allowed transition a $t_{1u}$ or an $a_u$ phonon is needed. Theory and
experiment [8, 90] show, however, that the lowest possible phonon is the $t_{1u}$ mode at about 530 cm$^{-1}$ (66 meV). This phonon is still too high in energy to be able to account for the second peak. Thus, we can exclude a Herzberg-Teller coupling mechanism as possible source for our splitting.

Another explanation for the second-harmonic splitting appears to be possible when all molecular multiplet states and their mixing are included. As already mentioned, the quantum-chemical calculations of Negri et al. [90] show that the $^1T_{2g}$ and $^1G_g$ states (in terms of states of isolated $C_{60}$ molecules with icosahedral symmetry) are nearly degenerated with the $^1T_{1g}$. In the crystal, however, the point group symmetry is lower. This gives rise to a mixing of the icosahedral electronic eigenstates (compare with Table VIII of [110]). When this mixing of the $^1T_{1g}$ and $^1G_g$ states is taken into account in the exciton dispersion calculations [65], a second somewhat smaller peak arises at higher energy. Accordingly, the main peak at 1.826 eV is (in terms of molecular states) a mixed state of $^3T_{1g}$ with some $^1G_g$ character, and the second peak at 1.866 eV is a $^1G_g$ state with some $^1T_{1g}$ character. Since we probe in our SHG experiment only the $^1T_{1g}$ component, this would explain the difference in intensity. Fig. 4.11 shows the calculated spectrum with (Fig. 4.11(b)) and without (Fig. 4.11(a)) mixing in of the $^1G_g$ state. The ”mixed” curve agrees well with the experimental data (at the lowest temperature).

Although the $^1T_{2g}$ state is also very close to the $^1T_{1g}$, the calculations show that these two states do not mix, because the neighbouring molecules do not have the required orientation to allow a mixing of the corresponding electronic orbitals. Note that for the $^1T_{1g}$ and $^1G_g$ mixing the same exciton-transfer integrals are involved as in the case of a Davydov splitting. Because of these exciton-hopping integrals, described by Eq. (4.3), such a large Davydov splitting (compared to common molecular crystals where an electric-dipole forbidden transition is considered) and a $^1T_{1g}$ and $^1G_g$ mixing become possible. The same exciton-dispersion calculations [65] based on degenerate $^1T_{1g}$ and $^1G_g$ multiplets is consistent with the two-photon emission data of Muccini et al. [88].

(ii) Line width

Assuming that the exciton band width is primarily due to a dispersive width as discussed above, we look again at the temperature dependence of the line shape. First of all, we might have expected to see only the zero quasi momentum ($k = 0$) exciton because of the long optical wavelength. At high temperatures, however, the

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5In our SHG experiment we can probe apart from magnetic-dipole-allowed transitions (like the $^1T_{1g}$ state) also electric-quadrupole-allowed transitions. The $^1H_g$ (see Fig. 4.6 and Table 4.1) is electric-quadrupole allowed. However, the calculations of Negri, Orlandi, and Zerbetto [90] and our calculations [65] show that the $^1H_g$ state is about 300 meV above the $^1T_{1g}$, far out of our detectable range.
molecules are rapidly rotating resulting in a dynamic orientational disorder which will break the translational lattice symmetry and the $\Delta \mathbf{k} = 0$ selection rule at long wavelengths\textsuperscript{6}. In the extreme case of no translational symmetry we would expect to see just the total exciton density of states, as we believe is indeed the case at high temperatures.

Upon lowering the temperature below the phase transition at 260 K the rotations are strongly reduced, leading to a decrease of the dynamic disorder and therefore to an enhancement of the $\Delta \mathbf{k} = 0$ selection rule. Since $\mathbf{k}$ then becomes a good quantum number we expect to see only the exciton states with $\mathbf{k}$ vectors close to $\Gamma$, the center of the Brillouin Zone.

The blue shift of the first moment of the SHG spectrum (Fig. 4.9(b)) for decreasing temperature most probably has its origin in the orientational ordering, which takes place at the phase-transition temperature (260 K). In the low-temperature phase ($T < 260$ K) the C\textsubscript{60} molecules can only jump between two equilibrium positions and at $T < 100$ K they are practically frozen in, whereas in the high-temperature phase ($T > 260$ K) the C\textsubscript{60} molecules rotate freely in all directions [69, 77]. Calculations of the electron- (hole-) transfer integrals for both phases show that the hopping integrals for the high temperature phase are larger than those for the low temperature phase. This means that in the low temperature phase, where a double carbon-carbon bond faces a pentagon or an hexagon, the exciton propagation is less favourable, resulting in a narrowing of the band. Since we are probing the $^1\text{T}_{1g}$ state, which lies at the bottom of the band, a narrowing of the band gives rise to a blue shift of the $^1\text{T}_{1g}$ state. The difference in magnitude of the low- and high-temperature hopping integrals has its impact on still another process. Eq. (4.4) gives the relation between the electron- (hole-) hopping integrals and the red shift of a state in the solid compared to the gas phase. Thus, we expect that the red shift of the $^1\text{T}_{1g}$ state is less at low temperature (where the hopping integrals are smaller than those for the high-temperature phase) than at high temperature. This also results in a blue shift. Calculations, however, show that the first process is the dominant one in our observed blue shift.

(iii) Intensity

What about the strong temperature dependence of the second-harmonic intensity? Also this can be explained in terms of the dynamic rotational disorder. SHG depends strongly on the retention of coherence in the $^1\text{T}_{1g}$ intermediate exciton state in a time scale determined by the excitation transition matrix elements. The inten-

\textsuperscript{6}Of course, if the rotational timescale could even get in the vicinity of the electron or hole hopping timescale, one would be back to an effective uniform system, but now with averaged electron and hole hopping integrals. This is a highly unreasonable system, since the one-electron and one-hole hopping integrals are of the order of eV, and the rotational energy is of the order of $\mu$eV.
sity of the SHG goes like $(N_{coh})^2$ where $N_{coh}$ is the number of molecules coherently (in phase) contributing to the signal. Rotational motion during excitation results in dephasing of true oscillators so that $N_{coh}$ is expected to decrease strongly with temperature. This is a so called $T_2^*$-like (i.e., pure dephasing time) relaxation process. One expects, therefore, a strong dephasing if the rotation time of a $C_{60}$ molecule is of the same order as the time between the first and second transition. We estimate the time of revolution for a freely rotating $C_{60}$ molecule at temperature $T$ as:

$$\tau_{\text{rot}} = 2\pi \sqrt{I / 2k_BT},$$

where $I = 1 \cdot 10^{-43}$ kgm$^2$ is the moment of inertia of the molecule. Since the rotation axes and angular velocity of neighbouring $C_{60}$ molecules are uncorrelated, the rotational motion during the lifetime of the intermediate state leads to a stochastic dephasing of the wave function on the individual molecules. An estimate for the time between the magnetic-dipole transition and the first electric-dipole transition by Fermi’s Golden Rule gives $\tau^{-1} \simeq r_{\text{ball}}^2 \cdot G \cdot \rho_{\text{final}}$, where $r_{\text{ball}}$ is the radius of the $C_{60}$ molecule, $G$ is the energy current of the laser pulse and $\rho_{\text{final}}$ is the DOS of the final states (with one electron in the $t^{(5)}_{\text{LL}}$ (LUMO) and one hole in the $h^{(5)}_g$ (HOMO − 1), the second highest-occupied molecular orbital). We choose $\rho_{\text{final}} = W^{-1}$ where $W \sim 0.5$ eV is the band width of LUMO or HOMO − 1. At $T = 300$ K we find $\tau_{\text{rot}} \simeq \tau \simeq 10^{-11}$ s. This means that, in the time spent between the first and second transition a given $C_{60}$ molecule can perform a full rotation. Since the rotation of the different molecules is uncorrelated, this leads to strong ($T_2^*$) dephasing and to a decreasing of the second-harmonic intensity. We note, however, that electron-phonon interactions can play a similar role in the observed temperature dependence. A strong temperature dependence of the intensity can also be found in photoluminescence experiments. There, the increase in intensity occurs at a somewhat lower temperature compared with the phase transition and the interpretation is still controversial [113, 114, 115, 116, 94].

Liu et al. have also done temperature-dependent SHG of $C_{60}$ films, and they also observe a jump in the second-harmonic intensity around the orientational phase transition [117]. Their increase of the second-harmonic intensity for decreasing temperature is much less than what we observe. This is probably because they have done the SHG experiment using a fixed frequency (1064 nm) which involves other transitions well off the double resonance as found by Wilk et al. [98]. Their second-harmonic intensity might also contain a change due to a shift of the exciton states on going through the phase-transition temperature of 260 K as we have described above.

### 4.4 SFG

As already discussed in the previous sections (2.2.5 and 3.1), a sum-frequency generation (SFG) experiment can provide more information about a system than a SHG
experiment. For instance, by mixing different wavelengths, additional wavelength regions can be reached. Furthermore, a SFG experiment provides additional ways to identify excitations. In particular, a SFG measurement allows to decide whether a second-harmonic resonance is one-photon or two-photon resonant. This can be done in two ways: (1) using two tunable lasers, or (2) by combining a tunable laser with one at a fixed wavelength.

In the first case (1), the frequencies of both lasers are varied simultaneously, in such a way that their sum frequency remains constant. When the second-harmonic resonance is a two-photon resonance, a SFG measurement should yield a constant signal as a function of the incident frequency. On the other hand, if the resonance is at a one-photon frequency, a maximum in the frequency spectrum will be observed, resembling the corresponding SHG spectrum.

When two tunable lasers are unavailable, it is also possible to perform a SFG experiment with one laser at a fixed wavelength, combined with a tunable laser (case 2). In this case, if the SFG resonance is due to a one-photon resonance, it will appear at the same fundamental frequency as in the SHG measurement. A two-photon resonance will give rise to identical features at the detected, two-photon frequency [118].

We have performed SFG measurements in both ways, and our first goal was to find the exact frequency of the $h_u^{(5)} \rightarrow t_{1g}^{(6)}$ transition (see Fig. 4.7 for illustration and Table 4.1), i.e., the $2\hbar\omega$ transition ($2^1T_{1u}$ state) in the measurement described in section 4.3. The second goal was to find the electric-quadrupole-allowed transition to the $^1H_g$ excitonic state (see Fig. 4.6 and Table 4.1).

### 4.4.1 Motivation

The $^1H_g$ state is of particular interest to be studied, because Koopmans et al. predicted that the surface and bulk contributions of the electric-quadrupole-allowed transition $^1A_g \rightarrow ^1H_g$ should be roughly of equal magnitude, due to the electric-field gradient at the surface [96]. From thickness-dependent SHG measurements performed at various frequencies close to the magnetic-dipole-induced resonance we have noticed, that the surface contribution ($\chi^{(D)}_S$) to the SHG is small, but shows a steady increase toward higher energies (Fig. 4.12). On the contrary, the bulk contribution ($\chi^{(Q)}_A$) decreases upon moving away from the resonance. Indeed, Wilk et al. have shown from their SHG measurements [98], in which they probed this electric-quadrupole transition, that surface contributions are equally important as the bulk contributions. By performing a second-harmonic thickness-dependent measurement at the electric-quadrupole resonance, using different polarization combinations, all second-harmonic susceptibility tensor components can be resolved, as Koopmans et al. did for the 1.8 eV resonance [63]. All surface, interface and bulk contributions to
this resonance can subsequently be determined, providing a nice tool to study the \( C_{60} \) surface.

Another prediction made by Koopmans et al. is that the electric-quadrupole-induced susceptibility is only 10% of the magnetic-dipole-induced susceptibility, meaning that the resonant intensities could be different by as much as two orders of magnitude [63, 81]. This holds, assuming a SFG experiment in which the \( 2\omega \) resonance is the same as in the magnetic-dipole-induced SHG experiment, thus for the transition \( h_4^{(4)} \rightarrow t_{1u}^{(5)} \) at about 3.6 eV (see Fig. 4.7 and Table 4.1). Performing SHG with the fundamental frequency matching the \( 1H_g \) excitation (at about 2.3 eV [98]), could in fact be a double resonance measurement as well. There is, namely, a strong electric-dipole-allowed transition \( (h_u^{(5)} \rightarrow h_y^{(6)}) \) at 4.56 eV [102]. We attempted this SHG measurement while scanning \( \hbar\omega \) from 2.12 - 2.38 eV (521 - 585 nm) at 78 K, but no SHG was detected. There are several ways to explain this negative result. It could be that (1) the \( 1H_g \) state is not lying in the range 2.12 - 2.38 eV, (2) we are not sensitive enough, or (3) the \( 1H_g \) state is not exactly in resonance with the \( 2\omega \) state \( (h_u^{(5)} \rightarrow h_y^{(6)}) \). The latter possibility would be in agreement with other measurements. Multiple groups using different experimental techniques assign the \( (h_u^{(5)} \rightarrow h_y^{(6)}) \) transition to different energies varying from 4.45 eV by Milani et al. using ellipsometry [119] to 4.8 eV by Gensterblum et al. in a HREELS experiment [89].

The SHG signal will be reduced when the experiment is not performed on double resonance conditions, as can be seen from the results obtained by Wilk et al. [98]. They performed \textit{in-situ} optical SHG measurements using 1.064 \( \mu \)m (1.17 eV) wave-
length laser pulses on a $C_{60}$ film during growth. They suggest that the second-harmonic frequency ($2\hbar\omega = 2.33$ eV) is singly resonant with the $^1A_g$ to $^1H_g$ electric-quadrupole transition (of the $h_{1u}^{[5]} \rightarrow t_{1u}^{[5]}$ multiplet) and that the input field at $\hbar\omega = 1.17$ eV is resonant with the broad $h_{1u}^{[5]} \rightarrow t_{1g}^{[6]}$ electric-dipole-allowed transition at 2.7 eV (see Fig. 4.7) and the vibration-assisted $h_{1u}^{[5]} \rightarrow t_{1u}^{[5]}$ electric-dipole transitions. They estimated that $\chi_3^Q \approx 9.1 \cdot 10^{-15}$ esu, whereas Koopmans et al. [63] obtained a value of $\chi_3^Q \approx 1.35 \cdot 10^{-13}$ esu from their double resonance experiment. Compared to the resonant magnetic-dipole susceptibility, the resonant electric-quadrupole susceptibility is even smaller than the order of magnitude predicted by Koopmans [81, 96]. We attribute this difference to the off double resonance conditions in the case of Wilk et al.

In order to perform the best possible SFG experiment, with the fundamental frequency resonant to the $^1H_g$ state and the sum-frequency resonant to the $^2^1T_{1u}$ (of the $h_{g}^{[4]} \rightarrow t_{1u}^{[5]}$ transition), we first tried to make an accurate frequency determination of the $^2^1T_{1u}$ state. Looking for the exact position of the $^2^1T_{1u}$ state, the $2\omega$ resonance described before in the 1.8 eV second-harmonic resonance experiment, we found an $\hbar\omega$ resonance at 2.0 eV, involving the $^1T_{1g}$ state.

### 4.4.2 Search for the $^2^1T_{1u}$ state

Several experiments are reported in the literature, in which the electric-dipole allowed $h_{g}^{[4]} \rightarrow t_{1u}^{[5]}$ transition is observed at room temperature (see Fig. 4.7 and Table 4.1). Two independent ellipsometry measurements, performed on $C_{60}$ films, determined the $h_{g}^{[4]} \rightarrow t_{1u}^{[5]}$ transition to be at 3.56 eV [102] and 3.5 eV [120] respectively. Hess et al. studied electroabsorption in both $C_{60}$ films and dispersed $C_{60}$ molecules and they found the $^2^1T_{1u}$ state at 3.6 and 3.7 eV, respectively [121].

The 100 meV solid-state red shift, can be used to "translate" the optical absorption data of $C_{60}$ in solution measured by Leach et al.: they found the $h_{g}^{[4]} \rightarrow t_{1u}^{[5]}$ transition to be at 3.78 eV [86], corresponding to a transition for solid $C_{60}$ at 3.68 eV. High-resolution electron-energy-loss spectroscopy (HREELS) on $C_{60}$ films exhibits a peak at 3.7 eV [89]. Theoretical calculations, such as the work of Bertsch et al. [101] support the assumption that the resonance, in general found between 3.5 - 3.7 eV, is indeed due to the $h_{g}^{[4]} \rightarrow t_{1u}^{[5]}$ transition. The small shifts in peak position of the $^2^1T_{1u}$ state can be attributed to the differences in techniques used: ellipsometry measures a peak in $\varepsilon_2$, whereas HREELS measures $-\text{Im}[\varepsilon(\omega) + 1]^{-1}$. However, the exact position of the $^2^1T_{1u}$ state is not unambiguously established. Although the

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7Wilk et al. use a different notation than Koopmans et al. Wilk and Koopmans use $\chi_3^P$ and $\chi_3^Q$ respectively. We use $\chi_3^P$.

8Ren et al. plotted $1/(\varepsilon + 1)$ from the experimental $k$ values of a $C_{60}$ film on a Si(100) substrate. The plot shows a peak at 3.73 eV [102], whereas $\varepsilon_2$ peaks at 3.56 eV. This difference in peak position represents the longitudinal - transverse optical splitting.
full width at half maximum (FWHM) is 460 meV [102], a more precise determination of the energy of the $2^3T_{1u}$ state is required in order to carry out an optimized SFG experiment at the electric-quadrupole-allowed $^1H_g$ state.

In an attempt to find the $2^3T_{1u}$ state we first performed a SFG experiment with the OPO fixed at either $\hbar \omega_1 = 1.865$ eV (665 nm), or 1.922 eV (645 nm). We scanned the dye laser over the range $\hbar \omega_2 = 1.68 - 1.77$ eV (700 - 738 nm) resulting in a $\hbar (\omega_1 + \omega_2)$ scan of 3.545 - 3.635 eV, and 3.602 - 3.692 eV respectively. The observed SFG spectrum, did not exhibit any peak revealing a resonance at $\hbar (\omega_1 + \omega_2)$, but showed the steep slope of the resonance at $\hbar \omega \approx 1.8$ eV (the magnetic-dipole-allowed transition).

Next we kept the dye laser fixed at $\hbar \omega_2 = 1.742$ eV (712 nm), thus at the other side of the magnetic-dipole-induced resonance, and scanned the OPO from $\hbar \omega_1 = 1.908 - 2.102$ eV (590 - 650 nm). A weak SFG peak was found at $\hbar \omega_1 \approx 2.02$ eV (615 nm) or at $\hbar (\omega_1 + \omega_2) \approx 3.76$ eV, (see Fig. 4.13).

![Graph](image.png)

**Fig. 4.13.** The SFG resonance (black dots) at about $\hbar \omega_1 \approx 2.02$ eV was found while scanning $\hbar \omega_1$, and keeping $\hbar \omega_2$ fixed at 1.742 eV. The white marks are the result of a SHG experiment, performed with the same $\hbar \omega_1$ frequency range as input frequency. The latter do not show any sign of a resonance.

In order to determine whether the resonance is at $\omega$ or at the sum frequency $\omega_1 + \omega_2$, we scanned both lasers together, such that the sum frequency remained constant at 3.757 eV (330 nm). The result is plotted in Fig. 4.14 (black dots). These points, measured at a constant sum frequency, overlap well with the data obtained at fixed $\hbar \omega_2$ and varying $\hbar \omega_1$. This proves that the resonance is at the fundamental frequency $\omega$ and not at the sum frequency $\omega_1 + \omega_2$. Around 1.97 - 2.0 eV the constant sum-frequency data are a slightly higher than the data measured
Fig. 4.14. The black dots are the SFG data obtained, when the two laser frequencies $\omega_1$ and $\omega_2$ are scanned simultaneously, such that $\hbar(\omega_1 + \omega_2)$ is constant at 3.757 eV. Their agreement with the SFG data, where only one laser was scanned (white marks), proves that this resonance is resonant at 2.02 eV, and not at 3.76 eV (see the two x-axes in Fig. 4.13).

at fixed $\hbar\omega_2$ (see Fig. 4.14). This is because in the constant sum-frequency case, $\hbar\omega_2$ is varied simultaneously with $\hbar\omega_1$. When $\hbar\omega_1$ is moving away from the 2.02 eV resonance, $\hbar\omega_2$ approaches the magnetic-dipole-induced transition at 1.81 eV, resulting in a SFG which is deceivingly constant.

What is the origin of this resonance around 2 eV? It could be a charge-transfer excitonic state, but Shirley et al. [92] calculated that the charge-transfer states lie close to the band edge and above the $^1\text{H}_g$ state. Also Minami and co-workers assign the charge-transfer states to energies around 2.3 eV and higher [122]. Another possibility could be the electric-quadrupole-allowed $^1\text{H}_g$ state, but Wilk et al. found indications in their SHG experiments, that the $^1\text{A}_g$ to $^1\text{H}_g$ electric-quadrupole transition is at about 2.33 eV [98]. Furthermore, Negri et al. calculated a multiplet splitting of about 0.35 eV [90], whereas Shirley et al. found a multiplet splitting of 50 - 70 meV [92] in their ab initio calculations, including electron-hole interactions. Assigning the $^1\text{H}_g$ state (the highest energy state of the multiplet splitting, see Fig. 4.6) to the 2 eV resonance would result in a multiplet splitting of 0.20 eV, far smaller than expected.

Hartmann and co-workers performed absorption measurements on single crystals of $C_{60}$ and found intrinsic transitions, which could be grouped in three pairs around 1.86 eV, 1.94 eV and 2.03 eV, and a broad structure at 2.3 eV [85]. They com-
pared these observed transitions with the calculated density of states for excitonic transitions of Shirley et al. [92], and thus associate them to $^1T_{2g}$, $^1T_{1g}$, $^1G_g$, and $^1H_g$ states, respectively. Shirley et al. and Hartmann et al. believe that vibrational effects are the reason that parity-forbidden excitons are observed by optical means. The additional lines also observed in the absorption spectra can be explained by vibrational effects as well, via the Herzberg-Teller mechanisms [92, 85].

The first three peaks of the absorption spectrum of Hartmann et al. [85] are in good agreement with the absorption data of Muccini et al. [112]. Muccini et al. found the true origin of the $^1T_{1g}$ state at 1.86 eV, and they assigned their peak at 2.03 eV to a $^1A_g \rightarrow ^1T_{1g}$ transition induced by the $t_{1u}$ phonon mode with 0.179 eV (1440 cm$^{-1}$) energy. This is in agreement with the quantum chemical calculations of Negri et al., which say that the most intense false origin in $T_{1g}$ is $\nu(t_{1u}) = 1437$ cm$^{-1}$ [90].

In our SHG experiment, the true origin of the $^1T_{1g}$ state at low temperature is not as clear as in Muccini’s case, due to the mixing of the $^1T_{1g}$ state with the $^1G_g$ state. We solved this problem already in section 4.3.1 of this chapter by taking the first moment of the entire spectrum, which results in a mean frequency, i.e., a weighted average peak position. We determine the true origin of the $^1T_{1g}$ state at 1.83 eV (Fig. 4.9(b)). A vibronic coupling with the $t_{1u}$-mode of 1440 cm$^{-1}$ would give rise to a peak at about 2.01 eV, in good agreement with our findings.

![Graph](image_url)

**Fig. 4.15.** SFG done at room (black dots) and liquid-nitrogen temperature (white squares). Notice that the increase in sum-frequency intensity is smaller than in the case of the 1.8 eV bulk resonance (Fig. 4.9(a)). The blue shift, however, is comparable (Fig. 4.9(b)).
If the 2 eV peak is due to the \( ^1T_{1g} \) state coupled to a \( t_{1u} \) phonon, the transition is no longer electric-dipole forbidden, hence we can expect that this SFG signal is coming from the surface and therefore surface sensitive. Indeed, we observed that a C\(_{60}\) film exhibited less SHG signal after aging. Also the temperature-dependent SFG measurements support the idea that the 2 eV peak is a surface resonance. Two SFG curves, measured at room- and liquid nitrogen temperature, are plotted in Fig. 4.15. The enhancement in second-harmonic intensity is much smaller than for the bulk 1.8 eV resonance (where the enhancement in second-harmonic intensity is a factor five on the same temperature range). In the intensity part of section 4.3.2 we discussed the strong relation between the degree of rotational motion of the C\(_{60}\) molecules and the second-harmonic intensity. When the rotation of the C\(_{60}\) molecules is minimal, the second-harmonic intensity is maximal. With this in mind, it is not surprising that a bulk second-harmonic (or sum frequency) resonance exhibits a stronger temperature dependency than a surface second-harmonic (or sum-frequency) resonance. As already discussed in the section on crystallographic properties (4.2.1), at temperatures below the orientational-ordering phase-transition temperature, the electrostatic interaction between the C\(_{60}\) molecules causes the C\(_{60}\) molecules to freeze in, i.e., it is blocking their rotational motion. In the bulk, a C\(_{60}\) molecule is surrounded by 12 neighbours, and the anisotropic field distribution, produced by these neighbours, is much stronger than at the surface, where a C\(_{60}\) molecule is surrounded by only 9 neighbours. A C\(_{60}\) molecule on the surface will therefore be less inclined to reduce its rotational motion. As a result, we might expect that the influence of the temperature on the rotation of the molecules, and consequently on the second-harmonic intensity, is higher in the bulk than at the surface.

Regarding the shift in peak position, we observe a blue shift of about 20 meV (from 2.00 to 2.02 eV) in going from room temperature to 78 K, which is approximately the same as the blue shift of the pure \( ^1T_{1g} \) state at 1.8 eV. In first order one expects a similar blue shift for the 1.8 eV peak as for the one at 2 eV, if we assume that the 2 eV resonance is indeed the \( ^1T_{1g} \) state coupled to the \( t_{1u} \) mode. In the last case, however, the situation could be more complicated, since the phonon involved can also affect the change in peak position as function of temperature.

The line shape of the two peaks at 1.8 eV and 2 eV is comparable. The asymmetric tail at low energies is most probably due to disorder and admixing of other states, because in the disordered state \( k \) is no longer a good quantum number.

The enhancement of the SFG, when it is resonant at \( (\omega_1 + \omega_2) \) as well, is clearly illustrated in the 2 eV sum-frequency resonance experiment. A SHG measurement carried out in the same region (\( \hbar \omega_1 = 1.9 - 2.05 \) eV, 605 - 653 nm) did not show any signal (white marks in Fig. 4.13). A clearly different response is shown by the black dots in the same figure, which represent the peak arising from a SFG measurement at \( \hbar \omega_1 = 1.9 - 2.05 \) and \( \hbar \omega_2 = 1.742 \) eV (712 nm) resulting in \( \hbar (\omega_1 + \omega_2) = 3.65 - 3.80 \) eV. This demonstrates that at 4 eV nothing or too little of the \( 2^1T_{1u} \) state is
probed, while at 3.75 eV a considerably larger portion of the 2^1T_{1u} state is probed.

Hampered somewhat by the lack of the appropriate dye for the right frequency, we chose the LDS867 dye solution, being the most efficient IR dye. Fixing the OPO at a particular frequency (2.3 eV, 540 nm) we scanned the dye laser over the LDS867 frequency range in order to find the maximum in \( \hbar(\omega_1 + \omega_2) \). The result of this measurement is plotted in Fig. 4.16. In the dye laser range (1.39 - 1.44 eV, 860 - 890 nm) no C_{60} resonance is present (even the lowest triplet state is higher in energy), therefore any maximum showing up in Fig. 4.16 would reveal a \( \hbar(\omega_1 + \omega_2) \) resonance. A shallow \( \hbar(\omega_1 + \omega_2) \) resonance (thus corresponding to the 2^1T_{1u} state) appears to be present at about 3.71 eV. However, great care has to be taken, because the sum-frequency intensity is low, the error bars are fairly large, and not many points were measured.

![Graph](image)

**Fig. 4.16.** SFG measurement, where \( \hbar\omega_2 \) is kept fixed at 2.297 eV, and \( \hbar\omega_1 \) is varied. Because the energy range of \( \hbar\omega_1 \) is even lower than the lowest triplet state of C_{60}, the peak structure observed in this plot can be assigned to the 2^1T_{1u} state.

### 4.4.3 Search for the \( ^1H_{1g} \) state

A SHG experiment in the energy range \( \hbar\omega = 2.12 - 2.38 \) eV (520 - 585 nm), where in general the electric-quadrupole-allowed \( ^1H_g \) state is assumed to be, yielded no detectable signal. We therefore tried a SFG experiment with \( \hbar\omega_1 \) in the expected energy range, and with \( \hbar\omega_2 \) such that \( \hbar(\omega_1 + \omega_2) \) reached the \( h_g^{(4)} \rightarrow t_{1u}^{(5)} \) transition, the 2\( \hbar\omega \) transition (the 2^1T_{1u} state) probed in the magnetic-dipole-induced SHG diagram.

Hoping that with the IR dye laser \( \hbar\omega_2 \) fixed at 1.425 eV (870 nm) the 2^1T_{1u} state is probed resonantly, the OPO was scanned over the range \( \hbar\omega_1 = 2.12 - 2.38 \) eV
Chapter 4. Excitons in C\textsubscript{60} studied by SHG and SFG

Fig. 4.17. Spectroscopic SHG (gray) and SFG (black and white) from a C\textsubscript{60} film. All these resonances are resonant at the fundamental $\hbar \omega_1$ energy. The corresponding second-harmonic and sum-frequency energy for each experiment is indicated in the upper x-axis. At $\hbar \omega_1 = 1.826$ eV (gray marks), the excitonic $^1T_{1g}$ state is present (magnetic-dipole-allowed). Due to mixing of this state with the (nearly) degenerate $^1G_g$ state a second peak at 1.866 eV arises (also gray marks). We assign the resonance at 2.02 eV (white circles) to the $^1T_{1g}$ state coupled with the $t_{1u}$-phonon mode, and the one at 2.3 eV (black marks) to the excitonic $^1H_g$ state (electric-quadrupole allowed).

(520 - 585 nm). In this case, we indeed found a small but well discernible resonance at 2.3 eV (540 nm). The result of this measurement, performed at the cryostat temperature of 4 K in the $m \rightarrow p$ polarization geometry, is shown in the inset of Fig. 4.17.

The sum-frequency signal was too weak to be able to do any thickness-dependent measurements. This is rather unfortunate, because this would have allowed us to resolve all sum-frequency susceptibility tensor components at this resonance, in order to establish whether this 2.3 eV resonance is indeed the electric-quadrupole-induced $^1H_g$ transition, and to determine the surface, interface and bulk contributions, separately.

Without any further measurements we can say the following about the 2.3 eV peak.
First of all, we noticed that this sum-frequency resonance is also more surface sensitive than the bulk-induced SHG from the magnetic-dipole-allowed transition. After having exposed the sample to a bad vacuum, the weak SFG at 2.3 eV was no longer detectable. For the bulk-sensitive SHG at 1.8 eV, a bad vacuum had no measurable consequence. One needs to be very careful with drawing the conclusion that the SFG is (partly) from the surface, on the basis of a decrease in SFG due to surface coverage. However, in first order this observation points in that direction.

Secondly, if we try to establish the microscopic origin of the 2.3 eV resonance, there are three possibilities that have to be considered: it is either the excitonic $^1H_g$ state we were looking for, it is a charge-transfer state, or it corresponds to an interband transition. Based on the temperature-dependent second-harmonic intensity analysis of the 1.8 eV resonance, where a strong relation between the coherence of the excitonic state and its second-harmonic intensity was found, it is more likely that the origin is an excitonic state (the $^1H_g$ or a charge-transfer state) rather than an interband transition. In the case of an interband transition, a free electron and hole will be created. This excitation, involving two independent charged particles, will be more susceptible to scattering processes, and thus to dephasing circumstances, than an exciton, since the latter is a bound electron-hole pair, i.e., one charge-neutral particle.

It will be difficult to discriminate between a charge-transfer exciton, and the $^1H_g$ excitonic state without a detailed analysis of the second-harmonic susceptibility tensor components. However, based on the following arguments, we are slightly more inclined to assign the 2.3 eV resonance to the $^1H_g$ state. Shirley et al. [92] found from their calculations, that the charge-transfer states are positioned above the $^1H_g$ state. We did not observe any resonance between the 2 eV and the 2.3 eV, neither did other people such as Hartmann et al. [85], and Muccini et al. [112, 94]. In the previous section we already discussed and discarded the possibility that the 2 eV resonance is due to the electric-quadrupole-induced transition. In conjunction with the intensity discussion here below, we believe that the 2.3 eV resonance can be attributed to the $^1H_g$ state, although we are aware that on the basis of these arguments a charge-transfer excitonic state can not be ruled out.

In Fig. 4.17 all SHG and SFG spectra are plotted together. Due to some changes in the laser set-up introduced with the arrival of the OPO, the SFG data, marked in Fig. 4.17 by the circles, are scaled by a factor of 3.5, ensuring that the 1.8 eV SFG data coincide with the 1.8 eV SHG spectra taken earlier, marked by squares. Both 1.8 eV spectra were measured at 80 K as is the 2 eV peak. The electric-quadrupole-induced resonance at 2.3 eV was taken at 4 K on a three-day old C$_{60}$ film, and these data coincide with the data taken at the same resonance at 80 K on a freshly evaporated film. Thus, all spectra can be directly compared.

From Fig. 4.17 we see that the intensity of the electric-quadrupole-induced reso-
Fig. 4.18. The SHG reflection coefficient for $\hbar \omega = 1.8$ eV as measured in-situ as function of the evaporated C$_{60}$ film thickness with different polarization combinations. These data show how a frequency-dependent SHG measurement performed on a C$_{60}$ film (of a certain thickness) could be affected by dispersive interference. From Koopmans et al. [63].

nance differs almost by two orders of magnitude from to the magnetic-dipole-induced one. That this difference is somewhat smaller than the two orders of magnitude predicted by Koopmans et al. [63] could be due to two reasons. A first possible explanation is based on the observation that the magnetic-dipole-allowed transition is at $2\hbar \omega = 3.65$ eV, whereas the electric-quadrupole-allowed transition is at $\hbar (\omega_1 + \omega_2) = 3.71$ eV. The measurements reported in Fig. 4.16 suggest that the sum frequency in the SFG measurement, in which the electric-quadrupole-induced resonance was probed, is closer to resonance, and therefore more enhanced, than the double frequency in the SHG experiment, in which the magnetic-dipole-induced resonance was measured. However, taking into account that the $2^1T_{1u}$ state has a FWHM of 460 meV [102], one can argue that this slight shift in double frequency resonance does not affect the difference in the second-harmonic and sum-frequency intensity very strongly.

A second explanation is that C$_{60}$ is evaporated on a MgO substrate up to a thickness of about 250 nm. This thickness corresponds to the first broad minimum in the $m \rightarrow p$ polarization combination thickness scan at 1.8 eV (690 nm) (see Fig. 4.18, after Ref. [63]). We have done this to avoid dispersive interference effect while tuning the fundamental frequency. However, in order to probe the electric-quadrupole-induced transition, the fundamental frequency has to be tuned so far
from 1.8 eV, that the SFG can not remain constant in spite of the broadness of the minimum. (This $m \rightarrow p$ minimum allows a tuning in frequency in the range of 1.7 - 1.9 eV). Considering the interference pattern for the magnetic-dipole-induced SHG (Fig. 4.18) we can say that a measurement performed on a 250 nm thick film at 2.3 eV actually has a maximum in SHG (or SFG) in the $m \rightarrow p$ geometry due to the dispersive interference effect. The interference pattern for the electric-quadrupole-induced SHG is different. In Fig. 4.19 we show the predicted result from Koopmans [81] for a $p \rightarrow p$ thickness scan for a magnetic-dipole- (solid line) and an electric-quadrupole- (dotted line) induced SHG scan. The electric-quadrupole curve uses identical parameters as the magnetic-dipole one, except that it assumes that $\chi_4^{(Q)} = \chi_3^{(Q)}$ instead of $\chi_4^{(Q)} = -\chi_3^{(Q)}$, where the latter holds for the magnetic-dipole case. In the $m \rightarrow p$ geometry the second-harmonic output is given by a coherent mixture of the $p \rightarrow p$ and the $s \rightarrow p$ geometry. Therefore, a different behaviour of these two cases (magnetic-dipole and electric-quadrupole) in the $m \rightarrow p$ interference pattern as function of film thickness can be expected. This different behaviour can easily account for the relatively small discrepancy in second-harmonic intensity between theory and experiment, mentioned in the beginning of this discussion.

The possibility that the peak at 2.3 eV is not a real resonance, but simply due to interference effects, can be discarded on the basis of the following SFG experiment that we performed. Again tuning $\hbar \omega_1 = 2.12 - 2.38$ eV (520 - 585 nm), but now with another fixed frequency for $\hbar \omega_2$, namely 1.610 eV (770 nm), we measured a weak SFG peak at about 2.3 eV. If this peak would have been purely due to interference effects, the peak should have been observed at a different frequency (Fig. 4.20). The much lower sum-frequency intensity is most probably because this experiment was performed in the $s \rightarrow p$ instead of $m \rightarrow p$ geometry.

**Fig. 4.19.** A $p \rightarrow p$ thickness scan for a magnetic-dipole (solid line), and an electric-quadrupole (dotted line) induced SHG diagram. From by Koopmans [81].
Fig. 4.20. Two measurements showing the sum-frequency resonance at $\hbar \omega_1 \approx 2.3$ eV. In each case a different fixed $\hbar \omega_2$ was used. This proves that the peak at 2.3 eV is really a $\hbar \omega_1$ resonance, and no interference effect.

### 4.5 Photopolymerization

In 1993 Rao and co-workers discovered that fcc C$_{60}$ films irradiated with visible or ultraviolet light transform to polymer segments with up to ten covalently bonded C$_{60}$ molecules [27]. Zhou et al. proposed that this photopolymerization of pristine solid C$_{60}$ is driven by a photochemical '2+2 cyclo addition', where parallel double bonds from adjacent C$_{60}$ molecules are broken and reformed as a four-sided ring [123], as depicted in Fig. 4.21. This mechanism is active in molecular solids where the two parallel carbon double bonds are separated by less than about 4.2 Å [123]. Solid C$_{60}$ satisfies this topochemical requirement, but only for $T > 260$ K, thus, above the rotational-ordering phase-transition temperature. Below this temperature, the double bonds on adjacent molecules avoid each other (Fig. 4.4), and the reaction is suppressed. Above 260 K, as the temperature is increased, the frequency at which these favorable alignments occur increases, and the reaction rate per incident photon should increase as well [123]. Above 373 K the photopolymers thermally decompose, and pristine C$_{60}$ can be retained [124, 125].

This was exactly what we observed during our frequency-dependent room- and high-temperature SHG measurements. A decrease of the second-harmonic intensity in time was seen which was especially pronounced at high temperatures (around 350 K). On the other hand, after measurements carried out at 450 K, the SHG at room temperature was higher then at the start of the measurements.

Photoluminescence (PL) spectra taken by Wang et al. [95], show that a $\sim$330
cm$^{-1}$ (40 meV) spectral red shift and peak broadening of the vibronic transitions throughout the entire low-energy spectrum is observed upon phototransformation. The red shift of the PL features for the polymer relative to the peak energies for the pristine film is consistent with the luminescence red shifts observed with oligomerization (i.e., monomer $\rightarrow$ dimer, dimer $\rightarrow$ trimer etc.).

Once we were aware of the photopolymerization of C$_{60}$, we did most measurements below the orientational-ordering phase-transition temperature, and those measurements done at room or high temperature were carried out on a fresh sample or corrections were made to account for the polymerization.

In order to investigate the influence of photopolymerized C$_{60}$ on the second-harmonic resonance at 1.8 eV, we measured this resonance from 1.75 eV to 1.85 eV before and after irradiating the C$_{60}$ film for several hours with the visible light of a halogen lamp (50 Watt). The results are plotted in Fig. 4.22. An increase in irradiation time leads to a decrease of pristine C$_{60}$ molecules, and hence a decrease of second-harmonic intensity, because the photopolymerized C$_{60}$ is not giving any SHG in this frequency range.

It is not known, whether photopolymerized C$_{60}$ produces SHG at any frequency. If that would be the case, then, assuming the same red shift as in the PL data of Wang et al. [95], some second-harmonic signal is expected at 1.75 eV in the photopolymerized phase; however from Fig. 4.22 we see that no particular signal is detected at this energy. We did not perform a broad frequency scan to see whether the photopolymerized C$_{60}$ exhibits SHG somewhere else.

From the data in Fig. 4.22 we can calculate the photopolymerization rate constant of the dimerization process: $^3M^* + M \rightarrow \text{D}$, where M stands for monomer
Chapter 4. *Excitons in C$_{60}$ studied by SHG and SFG*

![Graph showing SH intensity vs. energy](image)

**Fig. 4.22.** (a) The second-harmonic resonance at $\hbar\omega \approx 1.8$ eV measured on the same C$_{60}$ film after irradiation with visible light for different time periods. The decrease of the second-harmonic intensity as a function of irradiation time reflects the disappearance of pristine C$_{60}$ molecules due to photopolymerization.

(a, C$_{60}$ molecule), and D stands for dimer. It turns out that the photonexcitation of the monomer is the rate determining step, so that the polymerization is a pseudo first-order process, in which the polymerization rate $k$ is linearly dependent on the photon flux $\phi$. Since the second-harmonic intensity is proportional to the number of free C$_{60}$ molecules squared, we can say:

$$I_{\text{SHG}}(t) \approx I_{\text{SHG}}(0) e^{(-k t)}$$

(4.5)

with $t$ being the time. For $I_{\text{SHG}}(t)$ we took the surface below each curve in Fig. 4.22 (zeroth-order moment). Plotting $\ln[I_{\text{SHG}}(0) / I_{\text{SHG}}(t)]$ against time gives a straight line (see Fig. 4.23), where the slope is determined by $k$. Using visible light, we obtain a photodimerization rate of $k \approx 2.16 \cdot 10^{-5}$ s$^{-1}$ for $\phi_0 \approx 5$ mW/mm$^2$ at room temperature.

Wang *et al.* also studied the photodimerization kinetics of solid C$_{60}$. They used 488 nm radiation, and found $k \approx 1.5 \cdot 10^{-3}$ s$^{-1}$ for $\phi_0 \approx 40$ W/mm$^2$ [124, 125]. It is not surprising that they find a higher photodimerization rate, since they used light closer to the UV (it was observed that UV light is more effective than visible light in the photo-induced transformation [126]) and they had a higher radiation flux.

The main point, however, in this section is not the obtained value for $k$, but the fact that a SHG experiment can be used to probe a resonance very selectively, thereby providing a means to investigate and determine the photopolymerization rate.
Fig. 4.23. The logarithm decrease of the ratio in the second-harmonic intensity of the 1.8 eV resonance as function of the irradiation time (see also Fig. 4.22). The polymerization rate constant $k$, appearing in Eq. (4.5), determines the slope of the straight line. (We find $k \simeq 2.16 \cdot 10^{-5}$ s$^{-1}$.)

### 4.6 Conclusions

We have studied the dynamics of the $^1T_{1g}$ Frenkel exciton at $\hbar\omega = 1.81$ eV with temperature-dependent SHG. We find a very strong temperature dependence of this resonance. Its second-harmonic intensity increases strongly close to the phase transition down to about 200 K. We explain this by correlating the rotational disorder of the $C_{60}$ molecules to a $T_2$ dephasing mechanism. Below the rotational ordering phase transition the second-harmonic resonance splits in two bands. Several ideas for the possible causes of this splitting have been discussed. Detailed exciton dispersion calculations taking into account the full symmetry, multiplet structure and crystal structure, yield large exciton dispersions with total band widths of about 100 meV and a Davydov splitting of the $^1T_{1g}$ state of 30 meV. The corresponding second-harmonic intensity is calculated to be concentrated to more than 90% in the lowest Davydov component in contradiction to the observed behaviour. The experimental data including the two component structure in the low temperature phase are, however, very well described by the theory if the full multiplet structure and mixing of the $^1T_{1g}$ and $^1G_g$ states due to the lowering of space group symmetry is included. The experimental data together with the theory strongly support the ideas that the excitons in solid $C_{60}$ are Frenkel like but propagate via virtually excited charge-transfer states described by Lof et al. [20]. This model is consistent with the total width, the splitting below the phase transition, the red shift relative to the gas phase and the blue shift of the $^1T_{1g}$ excitonic state component upon lowering the temperature, measured in our SHG experiment.

We have performed spectroscopic SFG, and found sum-frequency resonances at
about $\hbar \omega_1 \approx 2$ eV, and $\hbar \omega_1 \approx 2.3$ eV. The first resonance ($\hbar \omega_1 \approx 2$ eV) is presumably due to the $^{1}\text{T}_{1g}$ state, coupled to a $t_{1u}$ phonon. The second sum-frequency resonance ($\hbar \omega_1 \approx 2.3$ eV) can be assigned to either a charge-transfer exciton or to the $^{1}\text{H}_{g}$ excitonic state. For reasons discussed in this chapter we are more inclined to assign the 2.3 eV resonance to the excitonic $^{1}\text{H}_{g}$ state. In both experiments the sum-frequency intensity could only be measured when the sum frequency $\hbar (\omega_1 + \omega_2) \approx 3.75$ eV. SHG performed with the fundamental frequency $\hbar \omega_1$ in the 2 - 2.3 eV range gave no detectable second-harmonic signal. This, in conjunction with the SFG measurement shown in Fig. 4.16, indicates that the 2$^{1}\text{T}_{1u}$ state is at about 3.71 eV.

The results of spectroscopic SHG and SFG on a C$_{60}$ film are shown together in Fig. 4.17. Fig. 4.17 clearly shows that in a SHG or SFG experiment excitons are well probed, whereas no contribution from the interband transitions is observed. This is different from other techniques, such as linear optical absorption and two-photon absorption. A possible explanation is that an exciton, which is a bound electron-hole pair, will exhibit more second-harmonic intensity, than an interband transition, since SHG probes coherent processes. The latter case involves two charged and independently moving particles and will therefore be more susceptible to dephasing.

The exciton selectivity of a SHG experiment is also evident from the photopolymerization experiment on C$_{60}$. Upon irradiating a C$_{60}$ film with visible light we observed a decrease of second-harmonic intensity. This clearly reflects the disappearance of pristine C$_{60}$ due to the photopolymerization process. By virtue of the selectiveness of a SHG experiment we were able to determine the photopolymerization rate.

References

REFERENCES


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