

Theory of nonlinear optical response of excitons in solid C_{60}

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We present a theoretical study of the dispersion of Frenkel-type excitons in the low-temperature $Pa\bar{3}$ phase of solid C_{60} . Exciton propagation is accomplished by an exchange-like two-step process, where an electron-hole pair on a given C_{60} molecule is split by the intermolecular kinetic energy and recombines on a neighboring molecule. We apply our results to the theoretical calculation of the nonlinear optical susceptibility for second-harmonic generation, for which we find reasonable agreement with experiment.

I. INTRODUCTION

Despite the large amount of research done on C_{60} and its compounds since its discovery,¹ the electronic structure and the importance of solid state band-structure effects remain controversial. In solid C_{60} the interaction between neighboring molecules is small as compared to the intramolecular energies. This suggests the presence of pronounced excitonic effects, whereby the excited states of a single molecule are broadened into bands. The complicated crystal structure of the low-temperature $Pa\bar{3}$ phase² with its four C_{60} molecules/unit cell, as well as the high degeneracy of the highest occupied molecular orbital (HOMO, fivefold degenerate) and lowest unoccupied molecular orbital (LUMO, three-fold degenerate) of a single C_{60} molecule³ thereby imply the existence of a large number of excitonic bands. The experimental observation of these excitons, however, is complicated due to symmetry reasons: both the HOMO and LUMO of an isolated C_{60} molecule have *ungerade* character, so that none of the low-lying particle-hole states can be excited by an electric dipole transition. This prohibits the optical observation of the excitons, and necessitates the use of electron-energy-loss spectroscopy (EELS) or nonlinear optical techniques.⁴⁻⁶ It is the purpose of the present work to provide a minimum-effort theoretical description of the exciton bands in solid C_{60} and to apply this simple theory to the computation of nonlinear susceptibilities which may be compared to nonlinear optical experiments.

To understand the basic requirements that a successful theory must meet, it is useful to recall the various energy scales present in the problem. The gap between HOMO and LUMO derived bands in solid C_{60} is ≈ 2.3 eV.⁸ This may roughly measure the difference of the single-particle energies of HOMO and LUMO of an isolated C_{60} molecule. This “single-particle contribution” to the energy of an electron-hole pair is reduced appreciably by the Coulomb attraction between electron and hole: in an *isolated* C_{60} molecule, the lowest singlet states are found at an excitation energy of ≈ 1.91 eV;^{9,10} a quantum chemical estimate for the splitting in energy of the different electron-hole multiplets is 0.35 eV.¹¹ Next, the lowest singlet excitonic states in *solid* C_{60} are found between 1.81 (Ref. 4) and 1.85 eV;⁵ this “solid-state red-shift” of $\approx 60-100$ meV represents the combined effect of band formation and the crystal-field-like splitting of

the particle-hole multiplets of a C_{60} molecule in an fcc lattice. We also note that EELS experiments on solid C_{60} (Ref. 7) have detected states with an excitation energy of ≈ 1.5 eV, i.e., still lower than the optically observed singlet excitons. This suggests to interpret these states as $S=1$ excitons. It is obvious from the above that an adequate treatment of the intramolecular Coulomb interaction and the resulting multiplet splitting is of crucial importance for a realistic discussion of the exciton states.

The multiplet splitting is important for yet another reason: the relative smallness of the solid-state effects as compared to the estimated multiplet splitting suggests that one may find exciton bands with a reasonably well-defined “multiplet parentage.” The weak coupling between the C_{60} molecules, moreover, implies that transitions that take place within a single molecule are by far the dominant ones, so that the symmetry of the “parent multiplet” will largely decide the “observability” of the respective exciton band. Then, of the singlet states corresponding to the four possible *gerade* representations of the icosahedral point group, $^1T_{1g}$ can be reached by a magnetic dipole transition from the 1A_g ground state and 1H_g can be reached by an electric quadrupole transition. Excitation of the remaining two representations, $^1T_{2g}$ and 1G_g , would require even higher multipoles, so that bands which originate from these multiplets remain unobservable at all.

The plan of the paper is as follows: In Sec. II, we briefly review the excitation spectrum of an isolated C_{60} molecule, thereby focusing on the multiplet splitting in the subspace of HOMO \rightarrow LUMO electron-hole excitations, which is the first crucial ingredient for the theoretical description of the excitons. Section III outlines the formalism for treating the exciton dispersion and presents results for the obtained band structure. In Sec. IV we calculate the nonlinear optical susceptibility for second-harmonic generation and briefly discuss the cross section for two-photon absorption. We conclude with a discussion of our results.

II. SINGLE-MOLECULE EXCITATIONS

The low-energy single-electron levels of an isolated C_{60} molecule can be described by restricting the Hilbert space to the 60 “radial” carbon $2p$ orbitals, one of them on each carbon atom.³ The ν th single-electron level in this Hilbert space can be expanded as

$$\phi_{\nu,\sigma} = \sum_{i=1}^{60} \alpha_{\nu,i} p_{i,\sigma}^{\dagger} |vac\rangle, \quad (1)$$

where $p_{i,\sigma}^{\dagger}$ creates an electron in the p orbital pointing in the radial direction on the carbon atom with index i . The coefficients $\alpha_{\nu,i}$ are determined from the Schrödinger equation with the Hamiltonian

$$H_{\text{kin}} = \sum_{i,j,\sigma} t_{i,j} p_{i,\sigma}^{\dagger} p_{j,\sigma}, \quad (2)$$

where $t_{i,j} = -2.59$ eV if i and j are connected by a pentagon edge and $t_{i,j} = -2.78$ eV if i and j are nearest neighbors along a hexagon edge (we are using the parameter values of Satpathy *et al.*¹²). Filling the lowest 30 levels with one electron/spin direction gives a fivefold degenerate HOMO with h_u symmetry and a threefold degenerate LUMO with t_{1u} symmetry.³ In the following we denote the creation operators for an electron in the μ th HOMO (ν th LUMO) $h_{\mu,\sigma}^{\dagger}$ ($l_{\nu,\sigma}^{\dagger}$); when dealing with more than one C_{60} molecule we will subscribe the wave functions and operators also by the position vector \mathbf{R} of the center of gravity of the molecule, e.g., $\phi_{\mathbf{R},\nu,\sigma}$. We now consider the lowest particle-hole excitations of an isolated molecule. Taking only single-particle energies into account, there are $3 \times 5 = 15$ degenerate lowest-energy configurations obtained by exciting an electron from the μ th HOMO into the ν th LUMO. The degeneracy is lifted by the Coulomb interaction between electron and hole, which gives rise to a multiplet splitting. We can make the following ansatz for the n th member of the multiplet ${}^1\Gamma$:

$$|\Phi_n^{\Gamma}\rangle = \sum_{\nu=1}^3 \sum_{\mu=1}^5 \alpha_n^{\Gamma}(\nu,\mu) (l_{\nu,\uparrow}^{\dagger} h_{\mu,\uparrow} + l_{\nu,\downarrow}^{\dagger} h_{\mu,\downarrow}) |0\rangle, \quad (3)$$

where $|0\rangle$ denotes the ‘‘half-filled’’ A_{1g} ground state of the molecule. The determination of the coefficients $\alpha_n^{\Gamma}(\nu,\mu)$ represents a complicated many-body problem,¹¹ because the ‘‘dressing’’ of the electron-hole pair by ‘‘virtual’’ particle-hole excitations has to be taken into account. In order to circumvent a demanding quantum-chemical calculation, we proceed as follows: using the group theoretical identity

$$t_{1,u} \otimes h_u = T_{1g} + T_{2g} + G_g + H_g, \quad (4)$$

one finds that the 15-dimensional product representation of a singlet LUMO-HOMO electron-hole pair splits up into the three-dimensional ${}^1T_{1g}$ and ${}^1T_{2g}$ representations, the four-dimensional 1G_g representation and the five-dimensional 1H_g representation. Since each of the irreducible representations appears precisely once, the coefficients $\alpha_n^{\Gamma}(\nu,\mu)$ are determined completely by symmetry, i.e., they can in principle be obtained by the Clebsch-Gordan decomposition of the product representation. The entire intramolecular Coulomb interaction thus can be parametrized completely by the energies $E_{1\Gamma}$ of the four symmetry-different $S=0$ multiplets and the coefficients $\alpha_n^{\Gamma}(\nu,\mu)$ can be determined by a simple

calculation with, e.g., an unscreened Coulomb interaction, thereby neglecting all many-body effects. Within the framework of the above ansatz, these many-body effects are then completely absorbed into the ‘‘renormalization’’ of the multiplet energies $E_{1\Gamma}$ so that within the singlet subspace the entire intramolecular electron-hole interaction can be parametrized as

$$H_{\text{intra}} = \sum_{\Gamma} \sum_{n=1}^{N_{\Gamma}} |\Phi_n^{\Gamma}\rangle E_{1\Gamma} \langle \Phi_n^{\Gamma}|. \quad (5)$$

Quantum-chemical calculations¹¹ indicate that the ${}^1T_{1g}$, ${}^1T_{2g}$, and 1G_g multiplets are quasidegenerate, whereas the 1H_g multiplet is well separated by an energy of ≈ 350 meV. Experimentally, there is consensus that the lowest $S=0$ state is ${}^1T_{1g}$,^{9,10} at an energy of ≈ 1.91 eV in dissolved and gas phase samples. Conclusive information about the energies of the remaining multiplets is not available at present; we will therefore treat their energies $E_{1\Gamma}$ as adjustable parameters and try to infer estimates for their values by comparison with experiment. Having adjusted these energies, the Hamiltonian (5) may be expected to provide a reasonable description of the intramolecular interaction of the electron-hole pair, at least within our approximation. We also note that by using the energies of the triplet excitons, $E_{3\Gamma}$, our formalism would treat these excitons in the same way.

III. EXCITON DISPERSION

We proceed to the case of solid C_{60} and consider the broadening of the molecular levels into bands. In solid C_{60} the centers of gravity of the individual C_{60} molecules form a fcc lattice. Below $T_c = 259$ K the molecules order orientationally with a larger unit cell, so that the actual crystal structure is sc with four C_{60} molecules/unit cell.² We write the position vector of the i th C_{60} molecule as $\mathbf{r}_i = \mathbf{R}_{j(i)} + \mathbf{s}_{l(i)}$, where \mathbf{R}_j with $j = 1, \dots, N$ denotes the position of the unit cell of the sc lattice to which the C_{60} molecule belongs and \mathbf{s}_l , with $l = 1, \dots, 4$ labels the position within the unit cell. In addition, we introduce the vectors δ_i , with $i = 1, 12$, which point from a site of the fcc lattice to one of its 12 nearest neighbors.

We first consider the propagation of a single electron in the LUMO or a single hole in the HOMO. Using the molecular single-electron levels defined in (1) the hybridization matrix element is given by

$$T_{\nu,\mu}(\mathbf{r}_i, \mathbf{r}_j) = \langle \phi_{\mathbf{r}_i, \nu, \sigma} | H_{\text{single}} | \phi_{\mathbf{r}_j, \mu, \sigma} \rangle, \quad (6)$$

where $H_{\text{single}} = p^2/2m + V$ is the one-electron part of the Hamiltonian. Using the expansion (1) of the molecular orbitals in terms of the radial p orbitals on the individual molecules, we can express the $T_{\nu,\mu}(\mathbf{r}_i, \mathbf{r}_j)$ in terms of matrix elements between radial p orbitals. The latter in turn are parametrized following Satpathy *et al.*¹² Since the solutions of (2) always can be chosen real, the hopping integrals $T_{\nu,\mu}(\mathbf{r}_i, \mathbf{r}_j)$ also can be chosen purely real. Due to the complicated node structure of the HOMO and LUMO (which

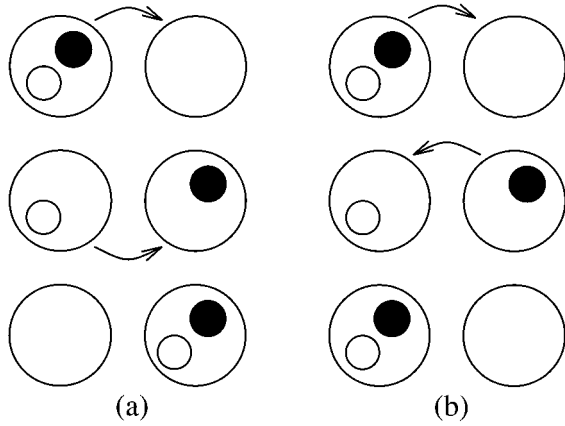


FIG. 1. Different hopping processes which couple neighboring C_{60} molecules. The light circle denotes the hole, the dark one the electron. The two-step process shown in (a) leads to a propagation of the electron-hole-pair. The ‘‘virtual’’ back and forth hopping shown in (b) gives an exchange-like lowering of the multiplet energies as well as a crystal-field-like mixing of the multiplets.

correspond to angular momentum $l=5$), the magnitude and sign of the hopping integrals will depend sensitively on the relative orientations of the two C_{60} molecules in question.

Numerical evaluation shows that the hopping integrals between the neighboring molecules are fairly small; as a measure of the hopping strength we may, for example, take the trace of the hopping matrix between HOMOs-LUMOs on neighboring molecules, divided by the degeneracy of the level, n_{deg} :

$$\bar{T} = \frac{1}{n_{\text{deg}}} \sum_{\nu} T_{i,j}^{\nu,\nu} \quad (7)$$

where the sums over ν run over the orbitals of the LUMO or HOMO, respectively. Numerical evaluation shows that the \bar{T} are less than 10 meV for both HOMO and LUMO. These relatively small hybridization energies have to be compared to the energy Δ required to break an intramolecular electron-hole pair by transferring either electron or hole to a nearest neighbor. This energy can be estimated as follows: Auger spectroscopy on solid C_{60} (Ref. 8) shows that two holes on the same C_{60} molecule repel each other with an energy of $U \approx (1.5 \pm 0.1)$ eV, which is practically independent of the molecular orbitals into which the holes are put. This suggests that an attractive energy between an electron and a hole on the same molecule be $-U$. Similarly, the attractive energy for an electron-hole pair on nearest neighbors should be $-V$, where V is the repulsive energy between two electrons on nearest neighbor molecules. The latter has been estimated to be (0.9 ± 0.4) eV.¹³ The resulting value for $\Delta = U - V$ has a large uncertainty, but in any way is large as compared to the average hybridization energy. This suggests to model the exciton propagation entirely by two-step processes:¹⁴ in the first step either electron or hole jumps to a nearest neighbor, which process raises the energy by the (relatively large) charge transfer energy Δ ; in the second step the remaining

hole or electron follows straight up. This mechanism for exciton propagation is also supported by the fact that the states seen in EELS at ≈ 1.5 eV (which we interpret as triplet excitons) also seem to have a considerable dispersional broadening;¹⁵ this would be hard to explain by the ‘‘conventional’’ mechanism for exciton propagation via intramolecular dipole-dipole transitions.

As our central approximation for dealing with the exciton dispersion we therefore restrict the Hilbert space to configurations where electron and hole are either on the same or on immediately adjacent molecules. We define the following Bloch states:

$$|\psi_{\mu,\nu,s,\sigma}(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} l_{\mathbf{R}_j+s,\mu,\sigma}^\dagger h_{\mathbf{R}_j+s,\nu,\sigma} |0\rangle, \quad (8)$$

$$|\psi_{\mu,\nu,s,\delta,\sigma}(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j} l_{\mathbf{R}_j+s+\delta,\mu,\sigma}^\dagger h_{\mathbf{R}_j+s,\nu,\sigma} |0\rangle. \quad (9)$$

With a threefold degenerate LUMO, a fivefold degenerate LUMO, and 4 molecules/unit cell there are 60 functions of the type (8) and since each C_{60} molecule has 12 nearest neighbors there are 720 states of the type (9). Our truncation of the Hilbert space may be expected to be an accurate approximation only for $T/\Delta \rightarrow 0$; one may expect, however, that the wave functions obtained in this way do incorporate the symmetries of the multiplets, the dependence of the signs of hopping integrals on the orientation of the C_{60} molecules, etc. Solving the exciton propagation with the above ansatz one thus may hope to obtain wave functions with the proper *symmetry*, which in turn determines, e.g., the magnitude of transition probabilities or whether two given multiplets mix strongly due to intermolecular hopping or not.

The numerical effort may be reduced considerably if we treat the intermolecular hopping in second-order perturbation theory. To that end, we start with Bloch states composed of multiplets on individual molecules, so that the intramolecular part of the Hamiltonian, H_{intra} , is already diagonal. Neglecting the difference between the multiplet energies E_Γ as compared to the charge transfer energy Δ , processes of the type shown schematically in Fig. 1(a) give rise to an ‘‘effective hopping’’ between two multiplet-states at the sites \mathbf{r} and $\mathbf{r} + \delta$

$$t_{(n,\Gamma),(n',\Gamma')} = 2 \sum_{\mu,\nu} \sum_{\mu',\nu'} \alpha_n^\Gamma(\mu,\nu) \times \frac{T_{\mu,\mu'}(\mathbf{r},\mathbf{r}+\delta) T_{\nu',\nu}(\mathbf{r}+\delta,\mathbf{r})}{\Delta} \alpha_{n'}^{\Gamma'}(\mu',\nu'). \quad (10)$$

Hopping processes shown schematically in Fig. 1(b) do not lead to true propagation of the electron-hole pair, but result in a (diagonal) shift of the multiplets to lower energies as well as a crystal-field-like mixing of the multiplets on a single molecule at position \mathbf{r} .

$$m_{(n,\Gamma),(n',\Gamma')} = - \sum_{\mu,\nu} \sum_{\delta} \alpha_n^{\Gamma}(\mu,\nu) \left(\sum_{\mu',\mu''} \frac{T_{\mu,\mu'}(\mathbf{r},\mathbf{r}+\delta) T_{\mu',\mu''}(\mathbf{r}+\delta,\mathbf{r})}{\Delta} \alpha_{n'}^{\Gamma'}(\mu'',\nu) + \sum_{\nu',\nu''} \frac{T_{\nu',\nu}(\mathbf{r}+\delta,\mathbf{r}) T_{\nu'',\nu'}(\mathbf{r},\mathbf{r}+\delta)}{\Delta} \alpha_{n'}^{\Gamma'}(\mu,\nu'') \right). \quad (11)$$

We now present some results obtained by the above procedure. Figure 2 shows the exciton dispersion obtained by the second-order perturbation scheme. Thereby an infinite energy separation between multiplets has been assumed. With the reasonably realistic value $\Delta=0.5$ eV we find an average redshift of the ${}^1T_{1g}$ derived bands of ≈ 60 meV [originating from the “crystal field contribution” (11)] and an additional “dispersional redshift” of the lower band edge at $\Gamma \approx 40$ meV. It should be noted that the perturbation theory tends to overestimate these energy shifts, particularly

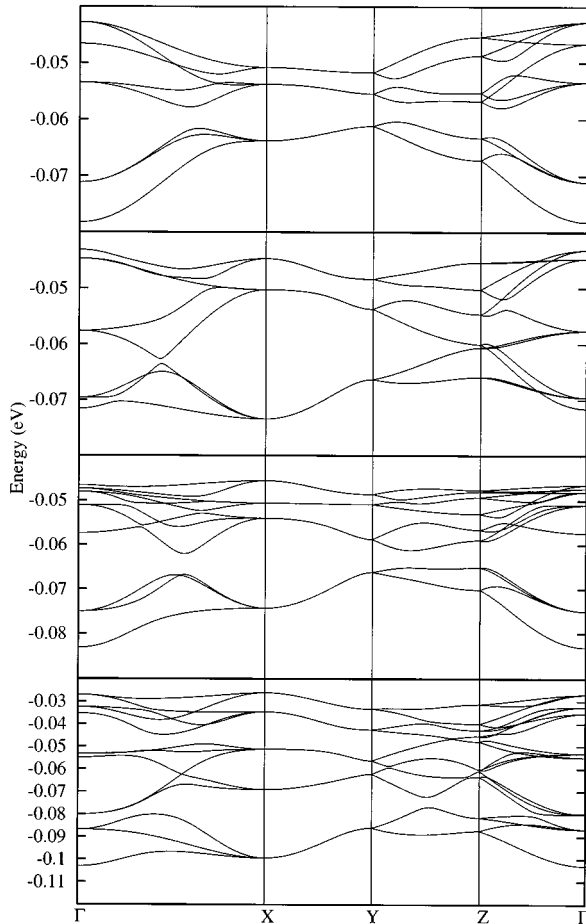


FIG. 2. Exciton band structures derived from the individual multiplets of a C_{60} molecule. From top to bottom the “parent multiplet” is ${}^1T_{1g}$, ${}^1T_{2g}$, 1G_g , and 1H_g . In the calculation, the energy of the respective multiplet was chosen as the zero of energy, the energies of the other multiplets were taken to be $+\infty$. The bands are obtained by the second-order perturbation scheme with $\Delta=0.5$ eV. The high-symmetry k points of the sc lattice are $\Gamma=(0,0,0)$, $X=(\pi/a,\pi/a,\pi/a)$, $Y=(\pi/a,\pi/a,0)$, and $Z=(\pi/a,0,0)$.

for smaller values of Δ ; in the following discussion of the exciton optics, we therefore always use the full eigenvalue problem of dimension 720×720 .

A notable fact is the relatively strong broadening of the 1H_g level. Since 1H_g is accessible by an electric quadrupole transition from the A_{1g} ground state one may expect to observe pronounced nonlinear optic signals also from this band. From the energy of the molecular ${}^1T_{1g}$ energy, ≈ 1.9 eV,^{9,10} and the estimated energy splitting between ${}^1T_{1g}$ and 1H_g of $+0.35$ eV,¹¹ we expect the 1H_g derived bands at energies somewhat below 2.25 eV. Indeed, strong two-photon absorption has been found in this range of energies.⁵ Unfortunately the relatively high energy of the 1H_g multiplet renders the effective Δ for this multiplet very small (Δ represents the energy difference between the on-ball multiplet and an electron-hole pair on nearest neighbors). Our simplified theory therefore most probably is inadequate for the description of the 1H_g derived exciton bands.

IV. OPTICAL PROPERTIES OF THE EXCITONS

Due to the multitude of bands and the resulting complexity, the full exciton dispersion clearly does not represent very useful information. We therefore proceed to the study of optical properties of the excitons, which allow for comparison with experiment. As already stated this requires a study of nonlinear optical effects: starting from the totally symmetric “half-filled” ground state, none of the multiplets of a single molecule has the proper symmetry to be excited by an electric dipole transition, so that the excitons cannot be observed by conventional optical experiments. However, the ${}^1T_{1g}$ multiplet is accessible by a magnetic dipole transition, and the 1H_g multiplet by an electric quadrupole transition. Since the expected excitation energy of the ${}^1T_{1g}$ derived excitons

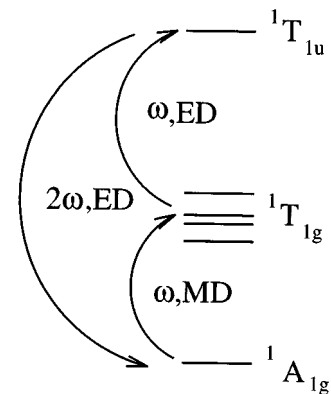


FIG. 3. A resonant second-harmonic generation process connecting the lowest single electron levels of the C_{60} molecule.

(~ 1.9 eV) is approximately one-half times the energy separation between the second highest occupied molecular orbital, the h_g HOMO', and the t_{1u} LUMO, there arises the possibility to observe them via a near-resonant second-harmonic generation (SHG) process,⁴ shown in Fig. 3: in the first step, the ${}^1T_{1g}$ multiplet (consisting of h_u/t_{1u} electron-hole pairs) is excited by magnetic dipole transition from the ground state. Next, the hole in the h_u HOMO can be transferred to the h_g HOMO' by an electric dipole transition (the product $t_{1u} \otimes h_g$ contains ${}^1T_{1u}$). In the last step, the hole in the h_g HOMO' and the electron in the t_{1g} LUMO recombine, and a photon of 2ω is emitted. Recent second-harmonic generation experiments⁶ have shown a two-peaked structure in the second-harmonic reflectivity at an excitation energy of ≈ 1.84 eV. This structure appears only below the transition temperature to the rotationally ordered low-temperature phase and becomes the more pronounced the lower the temperature. This temperature dependence strongly suggests to associate the observed structure with band effects on the molecular ${}^1T_{1g}$ multiplet.

We proceed to the calculation of the relevant nonlinear response function. Second-order perturbation theory gives the 2ω Fourier component of the electric polarization P induced by monochromatic light of frequency ω as¹⁶

$$\begin{aligned} \langle P \rangle(2\omega) = & \sum_{m,n} \left(\frac{\langle 0|H_1|m\rangle\langle m|H_1|n\rangle\langle n|P|0\rangle}{(E_m - E_0 + \omega)(E_n - E_0 + 2\omega)} \right. \\ & + \frac{\langle 0|H_1|m\rangle\langle m|P|n\rangle\langle n|H_1|0\rangle}{(E_m - E_0 + \omega)(E_n - E_0 - \omega)} \\ & \left. + \frac{\langle 0|P|m\rangle\langle m|H_1|n\rangle\langle n|H_1|0\rangle}{(E_m - E_0 - 2\omega)(E_n - E_0 - \omega)} \right), \quad (12) \end{aligned}$$

where P denotes the electric dipole operator. For a bulk material with inversion symmetry the second-harmonic susceptibility vanishes due to symmetry if only electric dipole transitions are taken into account; consequently, we choose $H_1 = \sum_i (\mathbf{E} \cdot \mathbf{P}_i + \mathbf{H} \cdot \mathbf{M}_i)$, with the dipole operator \mathbf{P}_i for the i th molecule and $\mathbf{M}_i = (e\hbar/2mc)\mathbf{L}_i$, where \mathbf{L}_i denotes the operator of orbital angular momentum for molecule i . One of the two transitions induced by H_1 in (12) then has to be magnetic dipole; if for the moment we choose this to be the rightmost factor H_1 , the first term on the right hand side of (12) cannot contribute. The sum over n in this case can be restricted to the exciton states in question, the sum over m extends over states with a hole in the HOMO' and an electron in the LUMO; see Fig. 4. Next, the transition $m \rightarrow 0$, i.e., the electric dipole transition from the LUMO to the HOMO', corresponds to $E_m - E_0 \approx 3.56$ eV.¹⁷ For an incoming photon energy of ≈ 1.8 eV the energy denominator $(E_m - E_0 - 2\omega)$ in the third term thus becomes much smaller than that of the second term, so that the latter can be neglected. Next, the inverse lifetime Γ of the HOMO' \rightarrow LUMO transition has been estimated¹⁷ to be 0.46 eV, i.e., larger than the total width of the SHG signal of ≈ 100 meV,⁶ and most probably also larger than band effects and multiplet splitting for the LUMO-HOMO' electron-hole pair. If we therefore for sim-

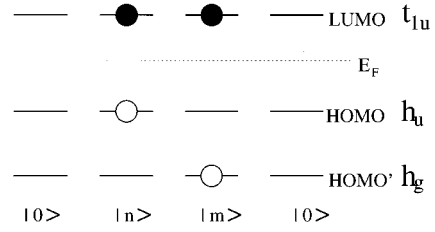


FIG. 4. Schematic representation of the states appearing in (12). The light circle denotes the electron, the dark one the hole.

plicity neglect the latter, we obtain the following expression for the nonlinear susceptibility tensor:

$$\chi(2\omega) = \sum_{m,n} \frac{\langle 0|P|m\rangle\langle m|P|n\rangle\langle n|M|0\rangle}{(E_n - E_0 - \omega) \cdot i\Gamma}. \quad (13)$$

This expression holds for $\omega > 0$ and can be extended to negative frequencies by the identity $\chi(-2\omega) = \chi^*(2\omega)$. We next discuss the tensorial structure of $\chi(2\omega)$ and note that the three members of the ${}^1T_{1g}$ multiplet transform like the three components of the pseudovector $M|0\rangle$. Since the only way to construct a scalar from the two vectors P and the pseudovector M is the product $(P \times P) \cdot M$, we can conclude that $\chi_{\alpha\beta\gamma}(2\omega) \sim \epsilon_{\alpha\beta\gamma}$ and moreover that in calculating χ_{xyz} up to factors of order unity we may replace

$$\sum_m |P_x|m\rangle\langle m|P_y \rightarrow \frac{1}{2} \frac{e^2 r^2}{\mu_B} L_z. \quad (14)$$

Dropping these overall factors of order unity we thus find that within our approximate scheme $\chi_{xyz}(2\omega)$ reduces to the dynamical correlation function of the operator of orbital angular momentum:

$$\chi_{xyz}(2\omega) \sim \sum_n \frac{\langle 0|L_z|n\rangle\langle n|L_z|0\rangle}{E_n - E_0 - \omega}, \quad (15)$$

which is readily evaluated with the known exciton energies and wave function E_n and $|n\rangle$.

Figure 5(a) then compares the resulting SHG intensity with the experimental result. It has been assumed that the ${}^1T_{1g}$ multiplet is well separated from the other multiplets, i.e., the energy of the ${}^1T_{1g}$ state has been set to 1.914 eV, those of the other multiplets to $+\infty$. The δ -peaks have been replaced by Lorentzians corresponding to an inverse lifetime of the exciton states of 10 meV. For the reasonable value $\Delta = 0.3$ eV we obtain a good estimate for the solid-state redshift, but a relatively small band splitting. Most important, however, the entire SHG weight is concentrated in one dominant peak near the lower edge of the exciton bands. This is a consequence of phase coherence: the respective state to good accuracy can be written as $(1/2\sqrt{N})\sum_i M_i|0\rangle$, i.e., a simple superposition of states generated by acting *in phase* with the magnetic dipole operator on each individual C_{60} molecule.

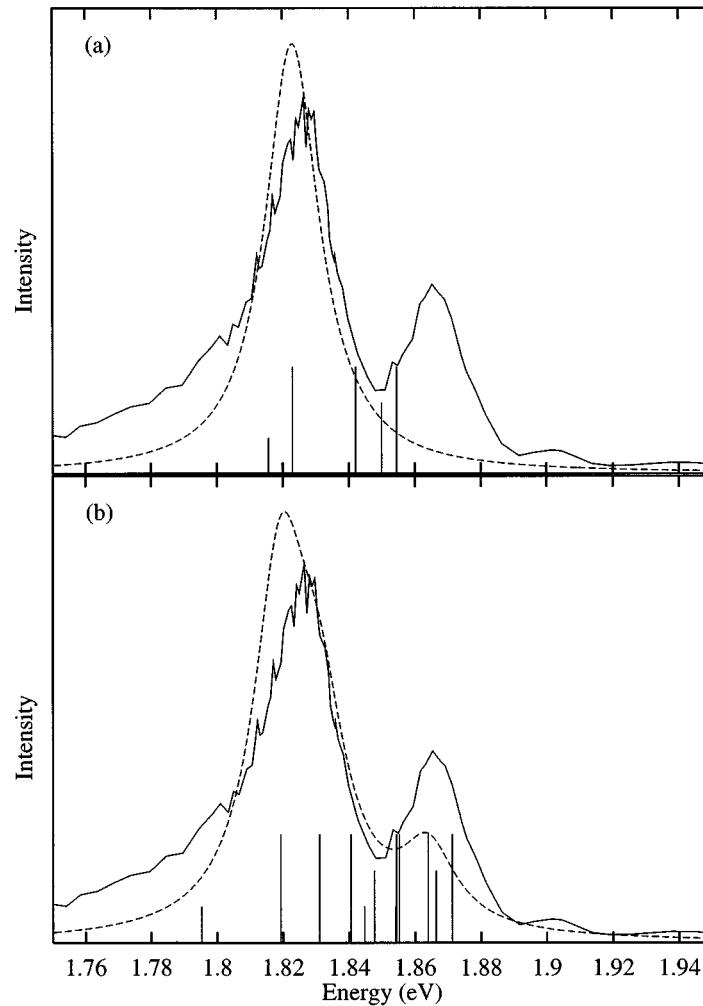


FIG. 5. Comparison of calculated SHG intensity (dashed line) and experimental result (full line) for an isolated ${}^1T_{1g}$ multiplet (a) and for degenerate ${}^1T_{1g}$ and 1G_g multiplets. The vertical bars indicate the positions of the exciton bands at Γ , the length of the bars thereby indicates the degeneracy of the level (1-, 2-, or 3-fold).

The other eigenstates, which necessarily have to be orthogonal to this particular state, consequently must be out-of-phase superpositions of exciton states on the four C_{60} molecules of a unit cell. These states therefore cannot couple to light, which acts coherently on each C_{60} molecule, so that these states remain unobservable. We therefore cannot explain the smaller peak in the SHG signal at ≈ 1.87 eV if we take into account only the ${}^1T_{1g}$ multiplet. On the other hand, the two-peak structure in the SHG signal has a pronounced temperature dependence, being absent in the rotationally disordered high-temperature phase and well-defined only at the lowest temperatures;⁶ this strongly suggests that the two-peak structure indeed originates from coherent exciton propagation. Then, the simplest assumption to explain the two-peaked shape of $I(2\omega)$ then is that the ${}^1T_{1g}$ multiplet *mixes* with one of the other multiplets; the dominant peak at 1.825 eV then would be the a band with predominantly ${}^1T_{1g}$ character, whereas the smaller peak at 1.87 eV could be interpreted as a band with only a minor admixture of ${}^1T_{1g}$ character. Since the SHG signal only measures the ${}^1T_{1g}$ component, this would readily explain the different intensities. Test calculations show that only the 1G_g multiplet mixes sufficiently strong with the ${}^1T_{1g}$ multiplet to produce such an effect (the

1H_g multiplet, moreover, can be excluded because both quantum-chemical calculation¹¹ as well as two-photon absorption experiments⁵ suggest that its energy is above 2 eV, i.e., far too high to influence the ${}^1T_{1g}$ derived bands). Figure 5(b) then shows the calculated SHG spectrum when the 1G_g multiplet is taken to be degenerate with the ${}^1T_{1g}$ multiplet at an energy of 1.914 eV; the value of $\Delta=0.35$ eV. Again, we obtain a good estimate for the redshift; in addition, there appears now a second peak at approximately the right frequency to explain the smaller high-energy peak in the experimental spectrum. The ratio of intensities between the two peaks is not yet satisfactorily reproduced by theory, but this may simply reflect the deficiencies of our purely single-particle wave functions. In the following, we therefore adopt the hypothesis that the ${}^1T_{1g}$ and 1G_g multiplets are (nearly) degenerate and proceed to the discussion of another nonlinear optics experiment, two-photon absorption.

To reach the low-lying exciton states by a two-photon process requires a photon energy of ≈ 1.9 eV/2=0.8 eV, so that one is in a strongly nonresonant situation. Second-order perturbation theory shows¹⁸ that the transition probability to a given state $|n\rangle$ is proportional to the matrix element of the operator M , defined as

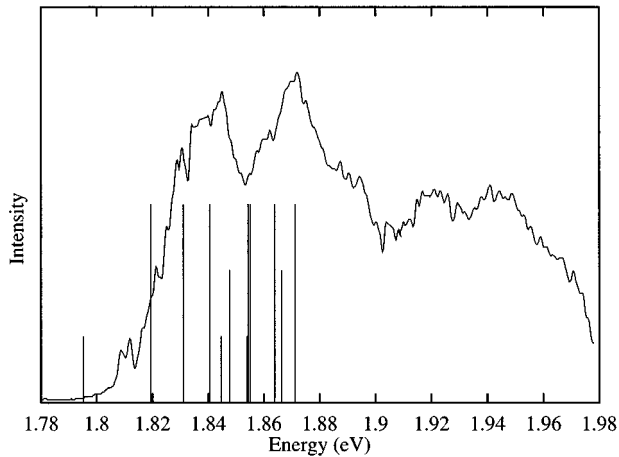


FIG. 6. Comparison of the experimental TPE intensity (full line) and calculated positions of the exciton bands at Γ (bars). The length of the bars indicates the degeneracy (1-, 2-, or 3-fold).

$$M = \sum_m \frac{H_1 |m\rangle \langle m| H_1}{E_m - E_0 - \omega}. \quad (16)$$

Choosing $H_1 = \mathbf{E} \cdot \mathbf{P}$, it is obvious that M can contain only symmetric combinations of the components of the vector \mathbf{P} , i.e., the form of M does not allow the construction of the pseudovector $\mathbf{P} \times \mathbf{P}$. In an *isolated* C_{60} molecule we therefore cannot reach the ${}^1T_{1g}$ multiplet (nor the ${}^1T_{2g}$ and 1G_g multiplets), but only the 1H_g multiplet. If the C_{60} molecule is embedded into a lattice, but still only transitions within the molecule are considered, the only change would be a weak splitting of the intermediate levels m , due to ‘‘crystal field effects’’ and band formation. The corrections to the matrix elements of M as compared to the case of an isolated molecule would be $\sim \Delta E / (E_m - E_0 - \omega)$, where ΔE is the width of the dispersional splitting. Assuming the results for the exciton bands in Fig. 2 to be representative, we estimate $\Delta E \sim 0.01$ eV– 0.1 eV so that the two-photon absorption associated with the low-lying exciton bands should be ~ 0.01 times that of the 1H_g derived bands; this indeed seems to be consistent with experiment,¹⁹ which shows strong two-photon absorption above ~ 2 eV, but only very weak absorption at the energies of the lowest excitons near 1.85 eV. For completeness we note that a simple estimate shows that intermolecular transitions are so strongly suppressed as compared to intramolecular dipole transitions that such processes are completely negligible, even compared to the weak ‘‘crystal field’’ contribution addressed above. Then, since a realistic discussion of multiplet splitting and band effects for all excited states of the C_{60} molecule is clearly out of reach for our simple formalism, there is no possibility for a realistic computation of the two-photon absorption cross section. We therefore restrict ourselves to a mere comparison of the calculated *level scheme* for the low-lying exciton bands to the experimental two-photon absorption. Figure 6 shows the experimental two-photon emission (TPE) spectrum compared to the level scheme obtained with degenerate ${}^1T_{1g}$ and 1G_g levels at 1.914 eV and $\Delta = 0.35$. Comparison with the SHG spectrum first shows that both

experiments actually seem to be observing different states at the low energy end of the spectra; this may indicate a relatively large number of states below ≈ 1.85 eV, which would be in good agreement with the level scheme for ‘‘mixed’’ ${}^1T_{1g}$ and 1G_g multiplets. In addition, the calculated level scheme shows a region of enhanced density of states above 1.85 eV, which may explain the broad structure in the TPE spectrum at these energies. We may conclude that our assumption of degenerate 1G_g and ${}^1T_{1g}$ multiplets seems to be consistent with both SHG and TPE results.

At energies ≈ 2 eV we, moreover, expect to find the 1H_g derived bands, and since this multiplet can be excited by an intramolecular quadrupole transition we expect a much stronger two-photon absorption in this frequency range, as is indeed the case.¹⁹ We note that the relatively high energy of the 1H_g multiplet probably makes our simplified theory (which assumes a large charge transfer energy Δ) inapplicable for a realistic discussion of these exciton bands.

V. CONCLUSION

In summary, we have presented a simple theory for exciton propagation in the low temperature $Pa\bar{3}$ phase of solid C_{60} . The key ingredient of the exciton dispersion thereby is the multiplet splitting in an isolated C_{60} molecule, which we treated as adjustable parameters. We found that assuming a (nearly) degenerate ${}^1T_{1g}$ and 1G_g level at an energy of ≈ 1.915 eV we could obtain a satisfactory fit of the lowest excitonic states as probed by nonlinear optical experiments. Solid-state redshift and energy differences between dominant features in second-harmonic generation and two-photon absorption seem to be consistent with our calculated level scheme and nonlinear susceptibilities. Adopting this interpretation, the lowest exciton bands are found to have mixed ${}^1T_{1g}$ - 1G_g character; the 1H_g multiplet is substantially higher in energy; we cannot make any reliable statement about the energy of the remaining ${}^1T_{2g}$ multiplet, because it cannot be observed itself and does not seem to mix appreciably with observable multiplets either. We note that the assumption of a degenerate ${}^1T_{1g}$ and 1G_g level may be somewhat problematic. Assignments in absorption spectra of isolated C_{60} molecules⁹ (which, however, may not be really conclusive) would indicate a larger separation between these two multiplets. Clearly, further experimental data are necessary to settle this question. Our calculations moreover provide an estimate for the energy Δ required to break an intramolecular electron-hole pair of 0.35 eV, which is in reasonable agreement with previous estimates.⁸

Recently we received unpublished data from Shirley, Benedict, and Louie,²⁰ who approached the exciton dispersion in C_{60} in a different way; their band structures for the individual multiplets are reasonably consistent with our above results.

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