Optical and magneto-optical properties of the simple cubic phase of the C$_{60}$ crystal

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Abstract
Using the Hartree–Fock and single configuration interaction model in conjunction with the local field method, the dielectric tensor, refractive index, circular dichroism, birefringence coefficient and the effects of spatial dispersion on the spectrum of the transverse normal polariton waves of the simple cubic phase of the C_{60} crystal are calculated. Our results on magneto-optical circular dichroism in the energy range 3–4 eV almost reproduces the reported experimental results. Also, our results on the effect of spatial dispersion, compared with the non-dispersive case, indicate that the first branch of the transverse normal polariton in the C_{60} crystal is due to the coupling of the second excitonic state of the C_{60} molecule with the electromagnetic field and the first excitonic state has very weak coupling.

1. Introduction

Since the discovery of the fullerene C_{60} and related materials [1, 2] many theories and experiments on the structural and optical properties of this molecule have been carried out. The high-temperature superconducting transition [3, 4], high third harmonic generation (THG) [5, 6], strong Coulomb interaction effects in its angular spectrum [7] and the existence of soft ferromagnetism [8] have been observed in doped and undoped C_{60} fullerenes. The theoretical investigations on the effects of the Coulomb interactions of the electrons within a single C_{60} molecule, as well as lattice fluctuation and anisotropy effects on the linear and nonlinear optical properties [9, 10], indicates that the C_{60} molecule is a strongly correlated electron system. Shirly *et al* [11] used a molecular orbital model to study the excitonic energy spectrum of solid C_{60}. Bechstedt *et al* [12] used the same method to obtain excitonic effects on the linear and nonlinear optical properties of a single C_{60} molecule. In a series of articles, Harigaya *et al* [9, 10], used the Hartree–Fock (HF) approximation and single configuration interaction (CI) to include the effects of excitonic Coulomb interaction on the linear and nonlinear optical properties of a C_{60} molecule. Eder *et al* [13] presented dispersion of Frenkel-type excitons in the low-temperature phase of solid C_{60} by an exchange-like two-step process where an electron–hole pair on a C_{60} molecule is split by the intermolecular

kinetic energy and recombines on a neighbouring molecule. Fagerström and Stafström [14] studied fundamental excitations in the C_{60} molecule by using a Pariser–Parr–Pople (PPP)-like Hamiltonian in combination with limited single and double configuration integration methods.

It is now well known that pristine solid C_{60} is a van der Waals bonded molecular solid whose optical properties are strongly connected to the properties of the molecule itself. The icosahedral (I_h) symmetry of the isolated molecule, which has 120 point group operations for the 60 carbon atoms located at corners of the 20 hexagonal and 12 pentagonal faces of a truncated icosahedron is unique among molecular crystals. Therefore, understanding the optical properties of this interesting material is extremely important (for an extensive review on properties of fullerenes see [15]). The optical measurements on C_{60} show three strong absorption band in the 2–6 eV region. The experimental spectra of molecular and solid C_{60} are similar. There is also a fair agreement between experimental results and theoretical calculations concerning the transition energies. The differences are typically less than 300 meV [15–17]. In solid form C_{60} molecules crystallize into two distinct dense phases [15, 18], one with a simple cubic (sc) structure low-temperature phase, and the other with a face centred cubic (fcc) structure room-temperature phase, with a lattice constant of 14.17 Å and nearest-neighbour C_{60}–C_{60} distance of 10.02 Å [15]. The C–C bond lengths for each C_{60} molecule in the solid phase are essentially the same as in the gas phase. At room temperature the four C_{60} molecules in the unit cell of the fcc pristine solid have been shown by nuclear magnetic resonance (NMR) [15] to be rotating rapidly with three degrees of rotational freedom [19]. Since the molecules are spinning rapidly about their lattice positions there is no orientational order (i.e. random orientations) and all molecules are equivalent. Below a critical temperature, $T_c \approx 261$ K, the solid undergoes a first-order transition and the C_{60} molecules lose two of their degrees of rotational freedom. This stabilization is induced by long-range orientational correlations between the C_{60} molecules, so the rotational motion occurs only around the four ⟨111⟩ axis [20–24].

Each molecule, where the experimental results indicate, is rotated by 22°–26° from the standard orientation about the ⟨111⟩ axis [15, 25]. Therefore the structure of solid C_{60} above $T_c \approx 261$ K is fcc, $Fm\bar{3}m$, with one molecule per unit cell and below T_c is sc with space group $Pa3$ [25–28] with the same lattice constant and four nonequivalent C_{60} molecules per unit cell.

On the theoretical side, three different theoretical approaches have been applied for calculating the optical dielectric function of the fcc phase of solid C_{60} [15, 16]. The first approach is based on a first principles electronic band structure calculation, using an orthogonalized linear combination of atomic orbitals (OLCAO) in the local density approximation (LDA) [29, 30]. The second approach considers the solid as being composed of weekly coupled molecules with an intermolecular hopping integral $t_\omega \simeq 0.1t$, where t is a C–C hopping integral on a single molecule [31]. In the third approach the sum of Lorentz oscillators profiles [32] is used, and the parameters of the model are fixed by fitting to the experimental data, such as reflectance and transmittance. Since the measured spectral shapes of the absorptive part of dielectric function exhibit distinctly flatter maxima compared to the model of Lorentzian profiles, Hora *et al* [17] used the sum of a Gauss–Lorentz oscillator profile to resolve this problem. Recently, time-dependent density functional theory (TDDFT) was applied to a description of optically allowed electronic transitions for C_{60} [33].

There are also number of theoretical and experimental reports on magneto-optical properties of fullerenes. Yabana and Bertsch [34] used TDDFT for calculating the magnetic circular dichroism and optical rotation of C_{76}. Experiments [35] shows that C_{76} has a very large optical rotatory power and significant circular dichroism in the visible and ultraviolet. Gasyna *et al* [36] also used C_{60} isolated in Ar matrices at 5 K to measure magnetic circular dichroism spectra in the visible and near-ultraviolet range.

To the best of our knowledge, no theoretical report on the dielectric tensor, magneto-optical properties and the effects of spatial dispersion on the transverse normal polariton waves of the sc phase of the C_{60} crystal, considering the effect of Coulomb interaction within the molecules, using the local field method has been reported yet. In this paper using the HF–CI model in conjunction with the local field method, we compute the aforementioned properties of the sc phase of the crystal. The outline of this paper is as follows. In section 2, we briefly present the HF–CI method at zero and non-zero magnetic field and derive the necessary formulae for the calculation of the polarizability tensor of the C_{60} molecule. In section 3, the formalism of the local field method is presented. In section 4, the calculated dielectric tensor, refractive index, circular dichroism, birefringence coefficient and the dispersion relation of transverse normal polariton of the sc phase of the C_{60} crystal are presented with discussions and comparisons with other works. Finally, we conclude the paper with a summary.

2. The Hartree–Fock configuration–interaction method

To find the dielectric tensor and the magneto-optical properties of the C_{60} crystal, we need to calculate the polarizability of each C_{60} molecule in zero and non-zero magnetic fields. We use the following Hamiltonian for the C_{60} molecule:

$$H = H_0 + H_{int} \tag{1}$$

where the first term is the tight binding Hamiltonian given by

$$H_0 = \sum_{\langle ij \rangle, s} (-t_D)(c_{is}^\dagger c_{js} + \text{h.c.}) + \sum_{\langle ij \rangle, s} (-t_S)(c_{is}^\dagger c_{js} + \text{h.c.}) \tag{2}$$

where $c_{is}^\dagger$ and c_{is} are, respectively, the creation and annihilation operators of a π electron at the ith carbon atom with spin s, t_D and t_S are the hopping integrals of double and single bonds with $t_D = t + (2/3)t'$ and $t_S = t - (1/3)t'$ which $t' = 0.1t$ and $t = 1.8$ eV [9, 10]. The second term, H_{int}, presents the electron–electron interactions between π electrons which has the form [9]

$$H_{int} = U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \tfrac{1}{2})(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \tfrac{1}{2})$$

$$+ \sum_{\langle ij \rangle, i \neq j} W(r_{i,j}) \left(\sum_\sigma c_{i,\sigma}^\dagger c_{i,\sigma} - 1 \right) \left(\sum_\tau c_{j,\tau}^\dagger c_{j,\tau} - 1 \right) \tag{3}$$

where $r_{i,j}$ is the distance between the ith and jth sites and

$$W(r) = \frac{1}{\sqrt{(1/U)^2 + (r/r_0 V)^2}} \tag{4}$$

is the Ohno potential [37] where U is the strength of onsite interaction, V is the strength of long-range Coulomb interaction and r_0 is the average bond length.

If we write the HF ground state, $|g\rangle = \prod_{\lambda = \text{occ}} c_{\lambda,\uparrow}^\dagger c_{\lambda,\downarrow} |0\rangle$, and the single electron–hole excitation states, $|\mu\lambda\rangle = c_{\mu,\sigma}^\dagger c_{\lambda,\tau} |g\rangle$, where λ and μ are occupied and unoccupied states, we can divide the total Hamiltonian (1) into $H = H_{HF} + H'$ where H' is given by

$$H' = U \sum_i (c_{i,\uparrow}^\dagger c_{i,\uparrow} - \rho_{i,\uparrow})(c_{i,\downarrow}^\dagger c_{i,\downarrow} - \rho_{i,\downarrow})$$

$$+ \sum_{\langle ij \rangle, i \neq j} W(r_{i,j}) \Bigg[\sum_\sigma (c_{i,\sigma}^\dagger c_{i,\sigma} - \rho_{i,\sigma}) \sum_\tau (c_{j,\tau}^\dagger c_{j,\tau} - \rho_{j,\tau})$$

$$+ \sum_\sigma (\tau_{i,j,\sigma} c_{j,\sigma}^\dagger c_{i,\sigma} + \tau_{j,i,\sigma} c_{i,\sigma}^\dagger c_{j,\sigma} - \tau_{i,j,\sigma} \tau_{j,i,\sigma}) \Bigg] \tag{5}$$

where $\rho_{i,\sigma} = \langle c_{i,\sigma}^{\dagger} c_{i,\sigma} \rangle$ and $\tau_{i,j,\sigma} = \langle c_{i,\sigma}^{\dagger} c_{j,\sigma} \rangle$. The matrix elements of $\boldsymbol{H}_{\text{HF}}$ and $\boldsymbol{H}'$ with respect to the electron–hole states are equal to

$$\langle \mu'\lambda'|(\boldsymbol{H}_{\text{HF}} - \langle \boldsymbol{H}_{\text{HF}}\rangle)|\mu\lambda\rangle = \delta_{\mu',\mu}\delta_{\lambda'\lambda}(E_\mu - E_\lambda) \tag{6}$$

and

$$\langle \mu'\lambda'|(\boldsymbol{H}' - \langle \boldsymbol{H}'\rangle)|\mu\lambda\rangle = 2J\delta_{\text{S}} - K \tag{7}$$

where E_μ is the HF state energy and $\delta_{\text{S}} = 1$ for the spin singlet and $\delta_{\text{S}} = 0$ for the triplet states. The J and K terms in equation (7) have the following forms [9]:

$$J(\mu', \lambda'; \mu, \lambda) = \sum_{i,j} V_{i,j}\langle \mu'|i\rangle\langle \lambda'|i\rangle\langle j|\mu\rangle\langle j|\lambda\rangle \tag{8}$$

$$K(\mu', \lambda'; \mu, \lambda) = \sum_{i,j} V_{i,j}\langle \mu'|j\rangle\langle \lambda'|i\rangle\langle j|\mu\rangle\langle i|\lambda\rangle \tag{9}$$

where $V_{i,i} = U$ and $V_{i,j} = W(r_{i,j})$ for $i \neq j$ and $U = 2V = 4t$. The diagonalization of the total Hamiltonian, $\boldsymbol{H}$, gives the singlet and triplet excitonic states of the C_{60} molecule. In the presence of a magnetic field, we can write the hopping terms as

$$t_{i,j}^{(S,D)} \rightarrow t_{i,j}^{(S,D)} f_{ij} \tag{10}$$

for single and double bonds, where $f_{ij} = e^{i2\pi\phi_{ij}}$ is the change in the phase of the hopping integral due to the magnetic field [38] which is related to the vector potential $\vec{A}(\vec{r})$ by

$$\phi_{ij} = \frac{e}{ch} \int_{\bar{R}_i}^{\bar{R}_j} \vec{A} \cdot \vec{d\ell}. \tag{11}$$

In equation (11) the lower and upper limits of integration are the positions of the nearest neighbour carbon atoms. For a uniform magnetic field the ϕ_{ij} are

$$\phi_{ij} = \frac{eB}{2ch}[\alpha(y_i + y_j)(z_i - z_j) + \beta(z_i + z_j)(x_i - x_j) + \gamma(x_i + x_j)(y_i - y_j)] \tag{12}$$

where B is the magnetic field strength, c is the velocity of light, h is the Planck constant, e is the electron charge and (α, β, γ) are the directional cosines of the magnetic field $\vec{B}$. In the presence of a magnetic field we must also include the Zeeman term, $\frac{e}{mc}\vec{S} \cdot \vec{B}$, for each of the HF states in equation (6). The linear polarizability of each C_{60} molecule in this scheme, $\alpha(\omega)$, is given by

$$\alpha_{ij}(\omega) = \sum_k \mu_i^k \mu_j^k \left(\frac{1}{\varepsilon_k' - \omega} + \frac{1}{\varepsilon_k' + \omega} \right) \tag{13}$$

where ε_k' are the excitonic eigenenergies of the total Hamiltonian and μ_i^k is the ith component of the dipole transition matrix of the singlet excitonic states. In the HF–CI model the dipole matrix element μ_i^k is given by

$$\mu_i^k = \sum_{j,s}' Z_{k,s}^*(j)(-e\xi_i)Z_{k,s}(j) \tag{14}$$

where ξ_i is ith component of the expectation value of the dipole operator with respect to the atomic orbitals of carbon [39]. In actual numerical calculation a lifetime broadening factor η should be included in the denominator of equation (13) which limits the height of resonant peaks. In our calculations we have set η equal $0.01t$. For the sc phase of the C_{60} crystal we have four C_{60} molecules in a unit cell with different orientations. Consequently, the polarizability tensor for each of the four molecules must be determined separately. To compute the polarizability tensors, we have used the coordinates generator algorithm for solid

C_{60} given in [25]. All the coordinates of four C_{60} molecules in the sc phase have been generated by this algorithm. Since the C_{60} molecule is a large cluster, the self-interaction or self-screening of this molecule has a sizable effect on its polarizability tensor. Using the relation between the volume integral of the field produced by a dipole and the strength of the dipole [40, 41]

$$\int_{\upsilon} \vec{E}(\vec{x}) \, \mathrm{d}^3 x = -\frac{4\pi}{3} \vec{P} \tag{15}$$

where υ is the volume taken by the charge distribution, for the self-field, we have

$$\vec{E}^{\text{self}} = -\frac{4\pi}{3\upsilon} \vec{P}. \tag{16}$$

Substituting the self-field in the equation

$$P_i = \sum_j \alpha_{ij} (E_j^{\text{ext}} + E_j^{\text{self}}) \tag{17}$$

we obtain the following relation for the screened polarizability tensor:

$$\alpha_{ij}^{\text{screened}} = \left[\frac{\alpha}{1 + \frac{4\pi}{3\upsilon}\alpha} \right]_{ij} \tag{18}$$

where α is given by (13).

3. Local field method

Many of the observed optical properties of solids are expressed in term of the second rank complex optical dielectric tensor, $\varepsilon_{ij}(\omega, \vec{k})$, where i and j are for (x, y, z) coordinates. In the principal dielectric axis of the crystal, this tensor is diagonal and for each direction we can define the complex refractive index

$$N_\delta(\omega, \vec{k}) = [n_\delta(\omega, \vec{k}) + \mathrm{i}\kappa_\delta(\omega, \vec{k})] = \sqrt{\varepsilon_\delta(\omega, \vec{k})} \tag{19}$$

where $\varepsilon_\delta(\omega, \vec{k})$ is the complex dielectric function of the δth principal dielectric axis, $n_\delta(\omega, \vec{k})$ is real part of the refractive index and $\kappa_\delta(\omega, \vec{k})$ is related to the absorption coefficient by $\alpha_\delta(\omega, \vec{k}) = 2(\frac{\omega}{c})\kappa_\delta(\omega, \vec{k})$. The magneto-optical properties of solids in the presence of the magnetic field, $\vec{B}$, are described by the circular dichroism, CD, and birefringence coefficient, θ. These two functions are defined in terms of real, $n_\pm(\omega, \vec{k})$, and the imaginary, $\kappa_\pm(\omega, \vec{k})$, parts of the refractive indices for left and right polarizations in the plane perpendicular to the magnetic field by the following equations:

$$CD(\omega, \vec{k}, \vec{B}) = \frac{\omega}{2c}[\kappa_+(\omega, \vec{k}, \vec{B}) - \kappa_-(\omega, \vec{k}, \vec{B})] \tag{20}$$

and

$$\theta(\omega, \vec{k}, \vec{B}) = \frac{\omega}{2c}[n_+(\omega, \vec{k}, \vec{B}) - n_-(\omega, \vec{k}, \vec{B})]. \tag{21}$$

For the magnetic field in the z-direction the real and imaginary parts of the refractive indices for left and right polarizations are determined from the following equations:

$$[n_\pm(\omega, \vec{k}, \vec{B}) + \mathrm{i}\kappa_\pm(\omega, \vec{k}, \vec{B})]^2 = \varepsilon_\pm(\omega, \vec{k}, \vec{B}) \tag{22}$$

and

$$\varepsilon_\pm(\omega, \vec{k}, \vec{B}) = \varepsilon_{xx}(\omega, \vec{k}, \vec{B}) \pm \mathrm{i}\varepsilon_{xy}(\omega, \vec{k}, \vec{B}) \tag{23}$$

where $\varepsilon_{xx}(\omega, \vec{k}, \vec{B})$ and $\varepsilon_{xy}(\omega, \vec{k}, \vec{B})$ are the xx and xy elements of dielectric tensor in the presence of a magnetic field. To calculate these parameters we must determine the frequency and magnetic field-dependent dielectric tensor.

The C_{60} crystal is a nearly ideal molecular solid [15, 42, 43]. Its sc phase has four C_{60} molecules per unit cell. When an external electromagnetic field, $E^{\text{ext}}(\omega, \vec{k})$, propagates in the crystal, the total electric field, $E^\alpha(\omega, \vec{k})$, acting on the αth molecule is equal to [44]

$$E_i^\alpha = E_i^{\text{ext}} + \sum_{\beta j} Q_{ij}^{\alpha\beta}(\omega, \vec{k}) p_j^\beta \tag{24}$$

where P_j^α are the cartesian components of the dipole moment induced in the molecule of α species and $Q_{ij}^{\alpha\beta}$ are the elements of the internal or local field coefficients, which are determined by the arrangement of the molecules in the crystal. The second term in equation (24) is the total induced electric field of the molecules acting on the αth molecule, in the dipole approximation [45, 46]. If a_{ij}^α is the molecular polarizability tensor of the αth molecule, the induced dipole moment is

$$p_i^\alpha = \sum_j a_{ij}^\alpha E_j^\alpha \tag{25}$$

Substitution of equation (25) into (24) yields

$$E_i^\alpha = E_i^{\text{ext}} + \sum_{\beta j_1} Q_{ij_1}^{\alpha\beta}(\omega, \vec{k}) a_{j_1 j}^\beta E_j^\beta \tag{26}$$

or

$$E_i^\alpha = \sum_j A_{ij}^\alpha E_j^{\text{ext}} \tag{27}$$

where $i, j = 1, 2, 3$ and

$$A_{ij}^\alpha(\omega, \vec{k}) = \sum_\beta (\delta_{ij}^{\alpha\beta} - \sum_{j_1} Q_{ij_1}^{\alpha\beta}(\omega, \vec{k}) a_{j_1 j}^\beta(\omega))^{-1}. \tag{28}$$

Since the polarization per unit volume is defined by

$$p_i = \frac{1}{\upsilon} \sum_\alpha p_i^\alpha = \frac{1}{\upsilon} \sum_{\alpha j_1} a_{ij_1}^\alpha E_{j_1}^\alpha \tag{29}$$

we have

$$p_i = \frac{1}{\upsilon} \sum_{\alpha j_1} a_{ij_1}^\alpha A_{j_1 j}^\alpha E_j^{\text{ext}} \tag{30}$$

where υ is the volume of unit cell. Using equation (30) the dielectric tensor is given by

$$\varepsilon_{ij}(\omega, \vec{k}) = \delta_{ij} + \frac{4\pi}{\upsilon} \sum_{\alpha j_1} a_{ij_1}^\alpha A_{j_1 j}^\alpha(\omega, \vec{k}). \tag{31}$$

The wavevector and frequency-dependent internal field tensor, $Q_{ij}^{\alpha\beta}(k_0, \vec{k})$, is defined by the Fourier transform of [44]

$$Q^{\alpha\beta}(\vec{R}) = -(\vec{\nabla}\vec{\nabla} + k_0^2 \boldsymbol{I}) \frac{\text{e}^{\text{i}k_0|\vec{R}+\vec{R}_{\alpha\beta}|}}{|\vec{R} + \vec{R}_{\alpha\beta}|} \tag{32}$$

where $\boldsymbol{I}$ is the unit tensor, $k_0 = \frac{\omega}{c}$ and $\vec{R}_{\alpha\beta} = \vec{R}_\alpha - \vec{R}_\beta$ is the distance between the αth and βth molecules. Since

$$\frac{\text{e}^{\text{i}k_0|\vec{R}+\vec{R}_{\alpha\beta}|}}{|\vec{R} + \vec{R}_{\alpha\beta}|} = \int \frac{\text{d}^3 q}{(2\pi)^3} \frac{\text{e}^{\text{i}\vec{q}\cdot(\vec{R}+\vec{R}_{\alpha\beta})}}{q^2 - k_0^2 - \text{i}\epsilon} \tag{33}$$

we can insert (33) into (32) to get

$$Q^{\alpha\beta}(\vec{R}) = \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \frac{(-\vec{q}\vec{q} + k_0^2 \boldsymbol{I})}{q^2 - k_0^2 - \mathrm{i}\epsilon} \mathrm{e}^{\mathrm{i}\vec{q}\cdot(\vec{R}+\vec{R}_{\alpha\beta})}. \tag{34}$$

For the Fourier transform of $Q^{\alpha\beta}(\vec{R})$, we have

$$Q^{\alpha\beta}(k_0, \vec{k}) = \sum_{\vec{R}\neq 0} Q^{\alpha\beta}(\vec{R}) \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{R}} \tag{35}$$

or

$$Q^{\alpha\beta}(k_0, \vec{k}) = \sum_{\vec{R}\neq 0} \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{R}} \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \frac{(-\vec{q}\vec{q} + k_0^2 \boldsymbol{I})}{q^2 - k_0^2 - \mathrm{i}\epsilon} \mathrm{e}^{\mathrm{i}\vec{q}\cdot(\vec{R}+\vec{R}_{\alpha\beta})}. \tag{36}$$

Since the above summation over the lattice sites of the crystal is slowly convergent, we make use of Ewald method that changes this sum to three fast converging terms [47, 48]:

$$Q_{ij}^{\alpha\beta}(k_0, \vec{k}) = Q_{ij}^{(1)\alpha\beta}(k_0, \vec{k}) + Q_{ij}^{(2)\alpha\beta}(k_0, \vec{k}) + Q_{ij}^{(3)\alpha\beta}(k_0, \vec{k}) \tag{37}$$

given by

$$Q_{ij}^{(1)\alpha\beta}(k_0, \vec{k}) = \frac{1}{\upsilon} \sum_{\vec{G}} \frac{[-(k_i + G_i)(k_j + G_j) + k_0^2 \delta_{ij}]}{|\vec{k} + \vec{G}|^2 - k_0^2 - \mathrm{i}\epsilon} \mathrm{e}^{-(|\vec{k}+\vec{G}|^2 - k_0^2)\chi} \mathrm{e}^{-\mathrm{i}(\vec{k}+\vec{G})\cdot\vec{R}_{\alpha\beta}} \tag{38}$$

$$Q_{ij}^{(2)\alpha\beta}(k_0, \vec{k}) = \frac{\mathrm{e}^{k_0^2 \chi}}{6\pi^2} \left[-\mathrm{i}\pi k_0^3 w(k_0\sqrt{\chi}) + \frac{\sqrt{\pi}}{4} \left(\frac{1}{\chi^{3/2}} - \frac{4k_0^2}{\sqrt{\chi}} \right) \right] \delta_{ij} \tag{39}$$

where

$$w(z) = \mathrm{e}^{z^2} \left(1 + \frac{2\mathrm{i}}{\sqrt{\pi}} \int_0^z \mathrm{e}^{t^2} \mathrm{d}t \right) \tag{40}$$

and

$$Q_{ij}^{(3)\alpha\beta}(k_0, \vec{k}) = \frac{1}{32\pi^{3/2}} \sum_{\vec{R}\neq 0} \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{R}} \int_{\frac{1}{\chi}}^{\infty} \left[(R_i + R_i^{\alpha\beta}) \right.$$

$$\left. \times (R_j + R_j^{\alpha\beta}) \eta^{3/2} + \left(-2\sqrt{\eta} + \frac{4k_0^2}{\sqrt{\eta}} \right) \delta_{ij} \right] \mathrm{e}^{-\frac{|\vec{R}+\vec{R}_{\alpha\beta}|^2}{4}\eta + \frac{k_0^2}{\eta}} \mathrm{d}\eta \tag{41}$$

where $\vec{R}$ are direct lattice vectors, $\vec{G}$ are the reciprocal lattice vectors, χ is the convergence parameter, $\vec{k}$ is the wavevector, and $k_0 = \frac{\omega}{c}$. These three sums converge much faster than the sum (36).

4. Results and discussions

Using the HF single CI model we have determined the electron–hole excitation energies without spin flip, i.e. singlet excitonic states of C$_{60}$ molecules, both at zero and non-zero magnetic fields. We have then calculated the screened polarizability tensors of the four C$_{60}$ molecules of the unit cell of the sc phase of the C$_{60}$ crystal. Then the real and imaginary parts of the dielectric tensor of the crystal are calculated using equation (28), where A_{ij}^{α} are determined by the Ewald method. We have also calculated the dielectric constant of the fcc phase of the C$_{60}$ crystal at zero temperature, with and without spatial dispersion. The difference in the dielectric constants of the two phases is of the order of 10^{-3}. We have also carried out the computation for a different orientational angle of the C$_{60}$ molecules in the unit cell. Our results indicate that the dielectric constant is almost independent of the orientational C$_{60}$ angles. This is due to the symmetry
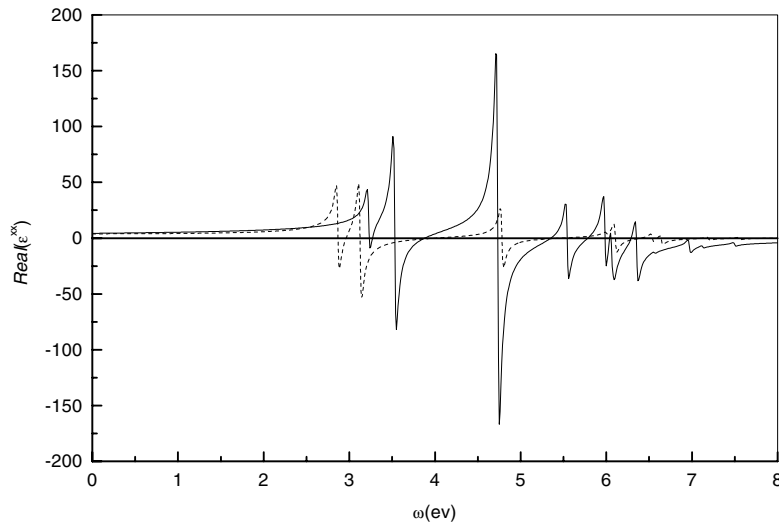
Figure 1. The real part of the dielectric constant with, $U = 2V = 4t$, $t = 1.8$ eV, (solid plot) and without, $U = V = 0$, (dashed plot) Coulomb interaction effect of the sc phase at zero magnetic field.
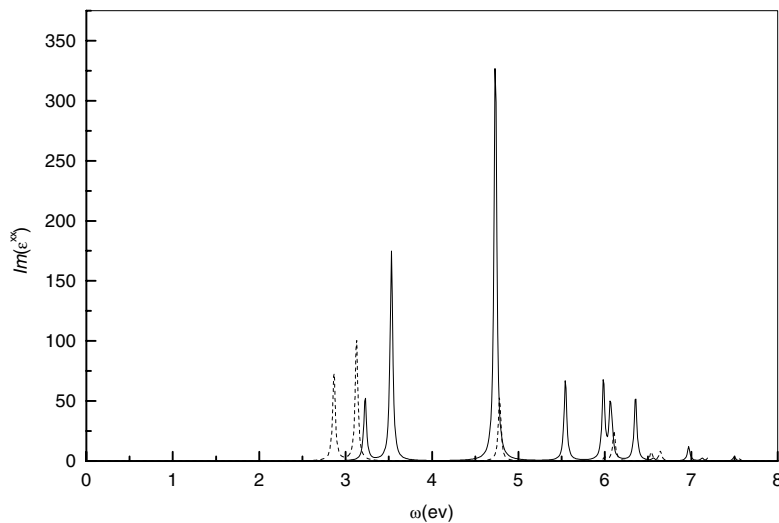
Figure 2. The imaginary part of the dielectric constant with, $U = 2V = 4t$, $t = 1.8$ eV, (solid plot) and without, $U = V = 0$, (dashed plot) the Coulomb interaction effect of the sc phase at zero magnetic field.

property of the C_{60} molecule. The C_{60} molecule, having a high-symmetry icosahedral group with 120 elements, behaves as an almost spherical molecule.

At zero magnetic field, because of the cubic symmetry of the crystal, the dielectric tensor is diagonal. Figures 1 and 2, respectively, represents the computed real and imaginary parts of the dielectric constant for the sc phase with and without Coulomb interaction not considering the spatial dispersion. The parameters for the Ohno potential were chosen at $U = 2V = 4t$, $t = 1.8$ eV. We have also presented the index of refraction, $n(\omega, \vec{k})$, as a function of ω and
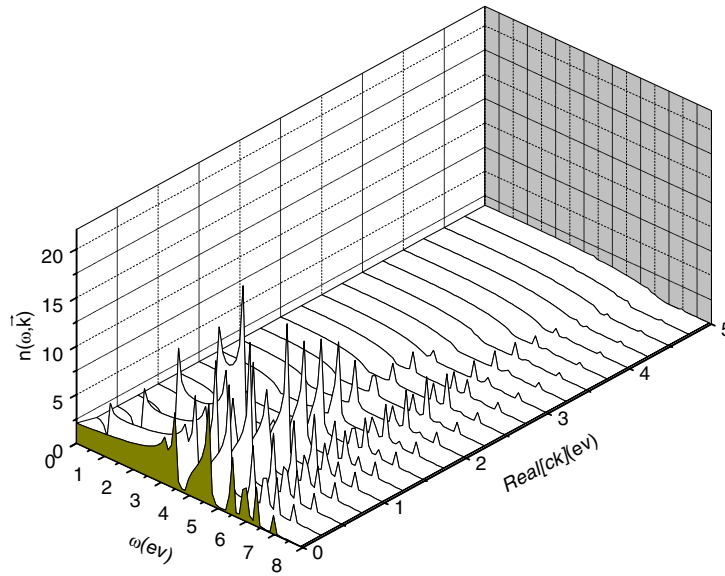
Figure 3. The refractive index of the sc phase at zero magnetic field, $U = 2V = 4t$, $t = 1.8$ eV.

Table 1. Excitation energies of absorption in eV for T$_{1u}$ symmetry species.

Present work[a]		LDA[b]		TDDFT[c]		Exp. 1[d]		Exp. 2[e]	
Assignmt	E_{calc}	Assignmt	E_{calc}	Assignmt	E_{calc}	Assignmt	E_{obs}	Assignmt	E_{obs}
h$_u$ → t$_{1g}$,	3.23	h$_u$ → t$_{1g}$,	2.7	h$_u$ → t$_{1g}$	2.82	h$_u$ → t$_{1g}$	2.73	h$_u$ → t$_{1g}$	3.04
		g$_g$, h$_g$ → t$_{1u}$							
h$_g$ → t$_{1u}$	3.53	h$_u$ → t$_{2u}$,	4.3	h$_g$ → t$_{1u}$	3.51	g$_g$, h$_g$ → t$_{1u}$	3.56	h$_g$ → t$_{1u}$	3.30
		g$_g$, h$_g$ → t$_{1g}$							
h$_u$ → h$_g$	4.73	h$_u$ → h$_g$,	5.3	h$_u$ → h$_g$	4.48	h$_u$ → h$_g$	4.56	h$_u$ → h$_g$	3.78
		g$_g$, h$_g$ → t$_{2u}$							
g$_g$, h$_g$ → t$_{2u}$	5.54		6.3	h$_g$ → t$_{1u}$	5.02	g$_g$, h$_g$ → t$_{2u}$	5.6	h$_g$ → t$_{1u}$	4.06
h$_u$ → t$_{1g}$	6.03			g$_g$ → t$_{2u}$	5.10			g$_g$ → t$_{2u}$	4.35
	6.36			h$_g$ → t$_{2u}$	5.47			h$_g$ → t$_{2u}$	4.84
				h$_u$ → t$_{1g}$	5.72			h$_u$ → t$_{1g}$	5.46
				h$_u$ → g$_g$	5.98			h$_u$ → g$_g$	5.88
									6.36

[a] Present work for the sc phase of solid C$_{60}$.
[b] LDA calculation for the fcc phase of solid C$_{60}$ [30].
[c] TDDFT calculations for the C$_{60}$ molecule [33].
[d] Experimental result for a solid C$_{60}$ thin film [16, 17].
[e] Experimental result of C$_{60}$ solution in n-hexane at 300 K [49].

$\vec{k}$ in figure 3. In table 1, we present the absorption spectra peaks of the allowed excitation energies of T$_{1u}$ symmetry species for this work, the OLCAO method in LDA for the fcc phase of the C$_{60}$ crystal [30], TDDFT for the C$_{60}$ molecule [33], and two different experimental results for C$_{60}$ molecules in n-hexane solution [49] and a solid C$_{60}$ thin film grown on a substrate [16, 17]. Since our calculated excitons are of interamolecular Frenkel-type without consideration being taken of the intermolecular charge transfer (CT), we do not observe the first absorption peak at 2.73 eV [16, 17] or 2.7 eV [30], as recent measurements of the fullerene
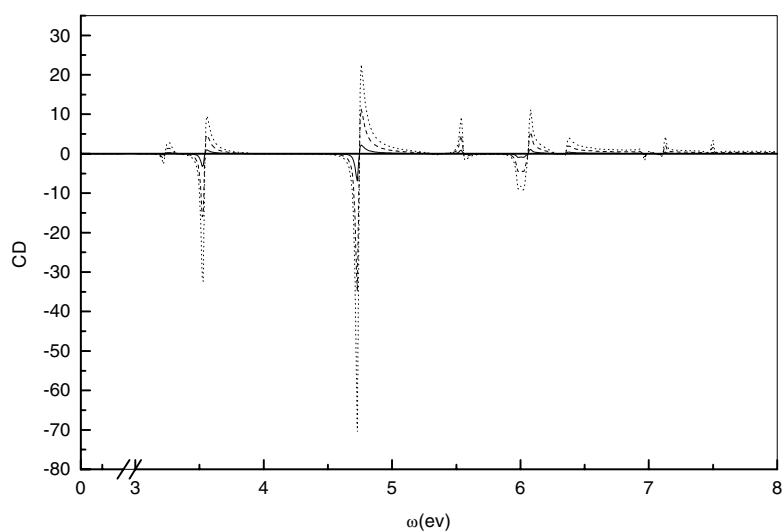
Figure 4. Circular dichroism (in 10^{-5}) of the sc phase at 1(——plot), 5(– – –plot) and 10(·····plot) T, $U = 2V = 4t$, $t = 1.8$ eV.
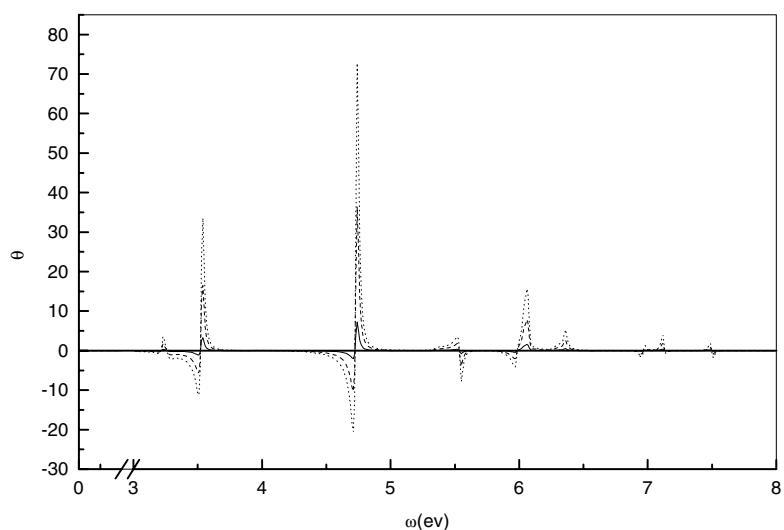
Figure 5. The birefringence coefficient (in 10^{-5}) of the sc phase at 1(——plot), 5(– – –plot) and 10(·····plot) T, $U = 2V = 4t$, $t = 1.8$ eV.

electroabsorption (EA) spectrum in a polymethyl-methacrylate (PMMA) matrix and in the film [50] and results of Pac *et al* [51] show that this first excitation peak is due to intermolecular CT excitons through transferral of an electron from the HOMO (highest occupied molecular orbital) of one molecule to the LUMO (lowest unoccupied molecular orbital) of another one. For the static dielectric constant with Coulomb interaction we obtain $\varepsilon_1(0) \simeq 4.3$, compared to the experimental result 4.08 [16] and 4.4 of LDA [30] calculations.

For non-zero magnetic field, we have calculated the circular dichroism, CD, and birefringence coefficients, θ. Figure 4 represents the CD coefficient for the magnetic field
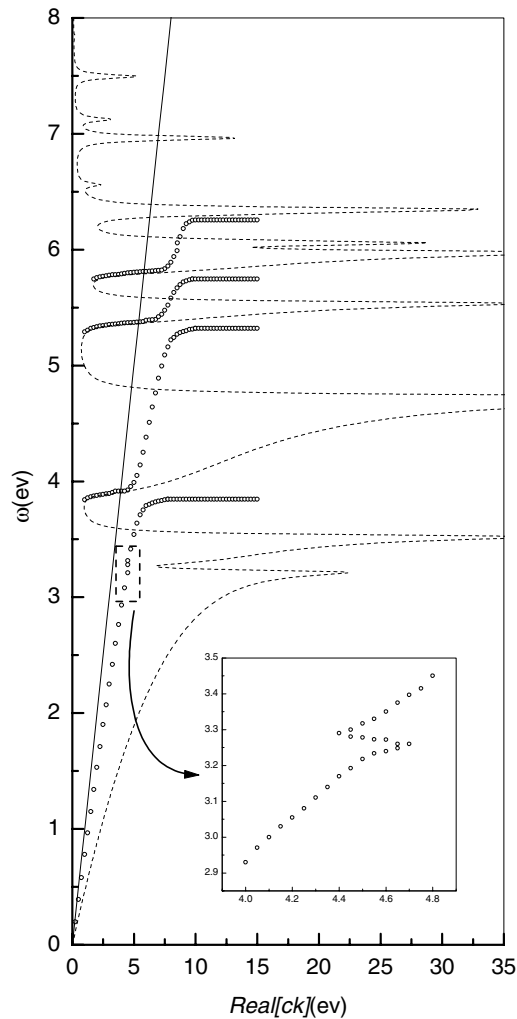
Figure 6. The dispersion relation for transverse normal polariton waves of the sc phase with (∘ ∘ ∘) and without (– – –plot) spatial dispersion, the solid line denotes $\omega = ck$, $U = 2V = 4t$, $t = 1.8$ eV.

in the z-direction with strength equal to 1, 5 and 10 T. The birefringence coefficients for the same field configurations are depicted in figure 5. The second, third and fifth excitonic states of the C_{60} crystal show the largest magneto-optical effects. In comparing CD with the experimental results of Gasyna *et al* [36], we did not find any optical activity below 3.23 eV which is due to vibrationally induced and spin triplet transitions [36] which we did not consider in our calculations. The first CD peak of our results is at 3.23 eV, the observed peak in the Gasyna experiment appears in the 400 nm ($\simeq 3.2$ eV) region. A large CD activity is observed at about 3.8 eV in the Gasyna *et al* experiment. We observe the same peak, but at 3.53 eV. Our calculation also show the CD patterns at 4.73, 5.54, 6.03 and 6.36 eV. For all the peaks we have a linear variation of θ and CD with respect to the strength of the external magnetic field. The aforementioned mechanical excitonic states which are singlets have zero total spin and this linear behaviour of θ and CD cannot be attributed to Zeeman splitting. Considering that

the magnetic fluxes through the faces of C_{60} molecule at field strengths 1, 5 and 10 T are small relative to the quantum flux, ch/e, the dominant term in the coupling of electron motion around the faces of the C_{60} molecule with the magnetic field is the linear term in the strength of the field which is proportional to $\frac{e}{ch}\sum_{i,j}t_{ij}\phi_{ij}$. This term causes the aforementioned behaviour. We have also calculated the dispersion relation of the transverse normal polariton waves with and without the spatial dispersion. The results are depicted in figure 6. The spatial dispersion have a profound effect on the ω–k relation of the transverse normal polariton. The coupling of the transverse electromagnetic field with the first excitonic states, 3.23 eV, is very weak and the first branch of transverse normal polariton is almost due to the second excitonic state of the C_{60} molecule. The first excitonic state which is due to the $h_u \rightarrow t_{1g}$ transition is a p-type exciton. For cubic crystals and $\vec{k} \neq 0$ along the [001] direction the triplet state breaks into Δ_1 (longitudinal) and Δ_2 (transverse) excitonic bands [52]. Considering that the total oscillatory strength of the first excitonic state is weak [12], the breaking of the band to Δ_1 and Δ_2 further reduces the coupling of the transverse electromagnetic field to almost $1/3$ of the total coupling.

In summary, we have calculated the dielectric tensor, birefringence coefficients, circular dichroism and effects of spatial dispersion on the transverse normal polariton waves of the sc phase of the C_{60} crystal using the HF single CI model in conjunction with local field effects, using the Ewald method. Our absorption spectra results show the allowed excitation energies for T_{1u} species in good agreement with experiments [16, 17, 49] and theoretical LDA and TDDFT [30, 33] calculations (see table 1). We do not observe the first absorption peaks [16, 17, 30] at 2.7 or 2.73 eV, since we did not consider the effects of CT excitations [50, 51]. The first two magneto-optical circular dichroism peaks, 3.23 and 3.53 eV, of our calculations are in good agreement with the limited experimental result of Gasyna *et al* [36]. Our calculations also determine circular dichroism activity peaks in the ultraviolet region. Our results also indicate that the coupling of the transverse electromagnetic field with the first excitonic state is weak and the first branch of the transverse normal polariton is almost due to the second excitonic state of the C_{60} molecule.

Acknowledgments

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