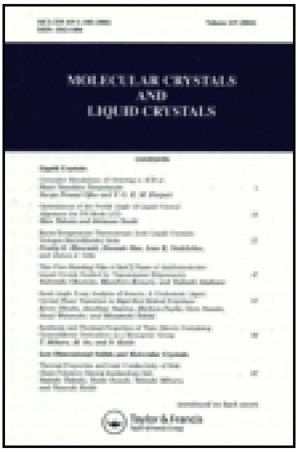

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Theoretical Investigation of the Magnetic Dipole and Electric Quadrupole Contributions to the Second-Harmonic Generation in C_{60} and C_{70}

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THEORETICAL INVESTIGATION OF THE MAGNETIC DIPOLE AND ELECTRIC QUADRUPOLE CONTRIBUTIONS TO THE SECOND-HARMONIC GENERATION IN C_{60} AND C_{70}

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ABSTRACT We develop the Valence Effective Hamiltonian method to calculate the magnetic dipole (MD) and electric quadrupole (EQ) contributions to the hyperpolarizability β of molecular systems. For both the C_{60} and C_{70} molecules, we find that the MD contribution leads to a β value which is several times larger than that of the EQ contribution. Taking into account the local field correction factor for C_{60} in solid state, we calculate $\chi^{(2)}$ susceptibility values that are in excellent agreement with recent experimental data.

INTRODUCTION

Recently, an intense interest has been devoted to the study of the nonlinear optical (NLO) properties of fullerenes[1-7]. In addition to third-order NLO effects, several groups have reported the observation of a second-harmonic generation signal in solid C_{60} films[1-3]. In contrast to C_{60}, Kajzar et al. have not found any SHG signal from C_{70} films[3]. Since C_{60} has central symmetry, the bulk second-order susceptibility cannot originate in electric dipole (ED) contributions; furthermore, it has been shown from measurements on C_{60} films that the surface and interface contributions are negligible[1,2]. Koopmans et al. therefore attribute the SHG signal to a bulk magnetic dipole contribution[1]. However, we note that Guyot-Sionnest and Shen have argued that generally the bulk $\chi^{(2)}$ of a central symmetric system is dominated by electric quadrupole (EQ), rather than magnetic dipole (MD) contributions[8]. In this contribution, we review our theoretical approach to calculate the MD- and EQ-induced second-order susceptibilities of molecules and describe the results of our calculations of the second-harmonic-generation spectra for the C_{60} and C_{70} fullerene molecules[9].

METHODOLOGY

The following Hamiltonian describes a molecule interacting with an external electromagnetic wave:

$$H=H_0-\underline{\mu}\cdot\underline{E}-\underline{m}\cdot\underline{B}-\underline{\underline{Q}}:(\nabla\underline{E})+\cdots \tag{1}$$

where H_0 is the unperturbed Hamiltonian; $\underline{E}$ and $\underline{B}$ denote the electric and magnetic fields of the radiation; $\underline{\mu}$, $\underline{m}$, and $\underline{\underline{Q}}$ correspond to the ED, MD, and EQ moments; the ED, MD, and EQ operators are as follows, respectively:

$$\underline{\mu}=-e\sum_i \underline{r_i}$$

$$\underline{m}=\frac{ie\hbar}{2m_e}\sum_i \underline{r_i}\times\underline{\nabla_i}$$

$$Q_{\alpha\beta}=-\frac{1}{6}e\sum_i\left[3r_{i\alpha}r_{i\beta}-r_i^2\delta_{\alpha\beta}\right]$$

where α and β indices in $\underline{\underline{Q}}$ are Cartesian indices (x,y,z). We have adopted the physicist's convention to write $\underline{\underline{Q}}$ in a traceless form.

According to the general perturbation formula for second-order polarization due to Orr and Ward (Sum-Over-States)[10], we can write the following β tensor for MD:

$$\beta_{ijk}^{MD}(-2\omega;\omega,\omega)=\frac{1}{2}\sum_{r,s}{}'\{\frac{\mu_{gr}^{i}m_{rs}^{k}\mu_{sg}^{j}}{\Omega_1}+\frac{\mu_{gr}^{i}\mu_{rs}^{j}m_{sg}^{k}}{\Omega_1}+$$

$$+\frac{\mu_{sg}^{i}m_{gr}^{k}\mu_{rs}^{j}}{\Omega_2}+\frac{\mu_{sg}^{i}\mu_{gr}^{j}m_{rs}^{k}}{\Omega_2}+\frac{\mu_{rs}^{i}m_{gr}^{k}\mu_{sg}^{j}}{\Omega_3}+\frac{\mu_{rs}^{i}\mu_{gr}^{j}m_{sg}^{k}}{\Omega_3}\} \tag{2}$$

where the summation over *r* and *s* runs over the electronic excited states of the molecule; *i*, *j*, and *k* denote Cartesian indices; the μ and *m* terms correspond to electric and magnetic transition dipole moments; and the Ω terms are the standard frequency denominators for SHG. A similar formula for $\beta_{ijll'}^{EQ}$ is obtained from the above expression by: (i) adding a factor ik_1, where k_1 is the wavevector of the incident light; and (ii) replacing the MD operator m^k by the EQ operator $Q^{ll'}$. We note that the MD transition moments are antisymmetric and β^{EQ} is proportional to the photon energy. As a result, the static values of both β^{MD} and β^{EQ} are zero.

The transition moments of ED (or similarly MD, EQ) are evaluated as:

$$\mu_{gr}=\sqrt{2}\int dr\psi_p^*(r)\, er\psi_a(r)$$

$$\mu_{rs}=\int dr\psi_p^*(r)\, er\psi_q(r)\,\delta_{ab}-\int dr\psi_a^*(r)\, er\psi_b(r)\,\delta_{pq}$$

where a, b (p, q) are occupied (virtual) molecular levels. Only singly excited configurations are taken into account since the doubly excited configurations do not contribute to the summation in Eq. (2) when ground state corresponds to a single determinant. We note that for third-order polarizability, the inclusion of doubly excited configurations is essential[11].

RESULTS AND DISCUSSION

The magnetic part of the radiation is:

$$\underline{B}=\frac{1}{c}\underline{n}\times\underline{E}$$

where $\underline{n}$ is the unit vector in the wave propagation direction. In this context, it is possible to estimate the typical MD- and EQ-induced nonlinear susceptibilities relative to the ED contribution to be: (i) for MD : $e\hbar/(2mcea_0)=e^2/2\hbar c=3.6\times10^{-3}$ (half the fine structure constant); and (ii) for EQ: $ea_0^2k/2ea_0=\pi a_0/\lambda=2.7\times10^{-4}$ where λ is taken to be 620 nm and a_0 is the Bohr radius. These ratios can, however, be increased by orders of magnitude when optimizing the molecular structures; for instance, in the case of the optically active helicene molecule, we have obtained β^{MD}/β^{ED} as high as 0.07[12] at a pump photon energy of 1.4 eV. The MD and EQ β values are imaginary; hereafter, for the sake of simplicity, we neglect the factor *i*.

We have performed a valence effective Hamiltonian (VEH)[13] electronic structure calculation for C_{60} and C_{70}, based on the geometry optimized by the semiempirical AM1 approach[7]. The transition moments for the MD and EQ operators are then evaluated with the VEH method[7,12]. The I_h symmetry of C_{60} gives: for MD, $\beta_{xyz}=\beta_{yzx}=\beta_{zxy}=-\beta_{xzy}=-\beta_{yxz}=-\beta_{zyx}$ and all other components are zero; and for EQ, $\beta_{xyxy}=\beta_{xzxz}=\beta_{yxxy}=\beta_{yzyz}=\beta_{zxxz}=\beta_{zyyz}$, $\beta_{xxxx}=\beta_{yyyy}=\beta_{zzzz}$, and $\beta_{xxyy}=\beta_{xxzz}=\beta_{yyxx}=\beta_{yyzz}=\beta_{zzxx}=\beta_{zzyy}$, all others are zero. For C_{70} (with D_{5h} symmetry), the nonvanishing components are: for MD, $\beta_{xyz}=-\beta_{yxz}$, $\beta_{xzy}=-\beta_{yzx}$, $\beta_{zxy}=-\beta_{zyx}$; for EQ, β_{zzzz}, $\beta_{xxxx}=\beta_{yyyy}$, $\beta_{xyxy}=\beta_{yxxy}$, $\beta_{xzxz}=\beta_{yzyz}$, $\beta_{zzxx}=\beta_{zzyy}$, $\beta_{xxzz}=\beta_{yyzz}$, $\beta_{zxxz}=\beta_{zyyz}$. There is always symmetry in interchanging the last two indices for β^{EQ}. We calculate the energy dispersions of MD and EQ β values both for C_{60} and for C_{70}. In the case of C_{60}, the theoretical values off-resonance ($\hbar\omega=1.2$ eV) are: $\beta_{xyz}{}^{MD}=0.068\times10^{-30}$ esu, $\beta_{xyxy}{}^{EQ}=0.013\times10^{-30}$ esu, $\beta_{xxxx}{}^{EQ}=0.018\times10^{-30}$ esu, and $\beta_{xxyy}{}^{EQ}=0.009\times10^{-30}$ esu; this means that β^{MD} is about 5 times larger than the β^{EQ} component. At two-photon resonance, $\hbar\omega=1.8$ eV, $\beta_{xyz}{}^{MD}=0.74\times10^{-30}$ esu, $\beta_{xyxy}{}^{EQ}=0.24\times10^{-30}$ esu, $\beta_{xxxx}{}^{EQ}=0.32\times10^{-30}$ esu, and $\beta_{xxyy}{}^{EQ}=0.16\times10^{-30}$ esu; the MD contribution thus still dominates in C_{60}. The same situation is found in the C_{70} molecule. We depict the calculated dispersion curves of $\beta(-2\omega;\omega,\omega)$ in following figures.

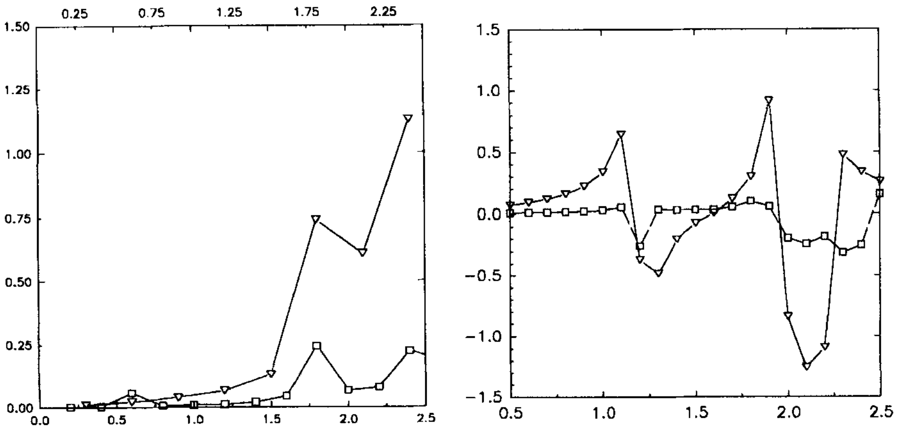

FIGURE 1 Theoretical molecular second-harmonic generation dispersion curve (real part, β in 10^{-30} esu) vs. fundamental photon energy in eV for C_{60} (left) and C_{70} (right). Squares depict $\beta_{xzxz}{}^{EQ}$ and triangles, $\beta_{xzy}{}^{MD}$.

For the C_{60} crystal (fcc), the number density is 1/720Å^3. The static dielectric constant of solid C_{60} is $\varepsilon=4.4$[14]. The local field correction factor is then estimated to be $f_L \approx ((2+\varepsilon)/3)^3 \approx 9.7$. Both the corrected theoretical SHG susceptibilities at $\hbar\omega=1.2$ and 1.8 eV and the experimental data are given in Table 1.

TABLE 1 Comparison between the theoretical and experimental $\chi^{(2)}$ values (in esu) for C_{60} (the experimental data at $\hbar\omega=1.2$ eV come from Refs. 1 and 3 and at $\hbar\omega=1.8$ eV from Ref. 2). The theoretical EQ contribution corresponds to the *xzxz* component.

$\hbar\omega$ (eV)	$\chi_{MD}^{(2)}$	$\chi_{EQ}^{(2)}$	$\chi_{exp}^{(2)}$
1.2	0.9×10^{-9}	0.2×10^{-9}	2.1×10^{-9} [1] 3.8×10^{-9} [3]
1.8	1.0×10^{-8}	0.3×10^{-8}	1.8×10^{-8} [2]

To conclude, we have extended the Sum-Over-States VEH method to calculate the ED, MD, and EQ transition moments and their contributions to nonlinear optical susceptibility. Our theoretical results for C_{60} agree well with different measurements, showing that the SHG signal in C_{60} is mainly induced by magnetic dipole interactions. Our results also suggest that SHG activity should be found in C_{70}; however, this has not been observed yet[3].

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