

Nonlinear Optical Properties of the C₆₀ Molecule: Theoretical and Experimental Studies

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Frequency-dependent molecular linear polarizability, α , and the second hyperpolarizability, γ , of the C₆₀ molecule have been calculated by the time-dependent coupled-perturbed Hartree-Fock method within extended basis intermediate neglect of diatomic differential overlap approach. The orientationally averaged values of α and γ for C₆₀ are respectively about 13 and 30-34 times larger than those for benzene. The α and γ tensors appear to be isotropic, indicating a spherically symmetric charge distribution in C₆₀. Experimental observations of third-order optical nonlinearity of C₆₀ by the degenerate four-wave mixing technique at the wavelength of 602 nm and by optical Kerr gate measurements at the wavelength of 620 nm indicate its ultrafast response time. The experimentally measured optical second hyperpolarizability is a complex number for which $\gamma^r = -(5 \pm 2) \times 10^{-33}$ esu and $\gamma^i = (9 \pm 1) \times 10^{-33}$ esu.

Introduction

The recent success in isolating and purifying macroscopic quantities of C₆₀ clusters¹⁻⁴ has generated unprecedented interest in the chemical and physical properties of this molecule.⁵⁻⁷ The highly symmetric π -electron cloud on the surface of the icosahedral C₆₀ cage results in interesting magnetic and electric properties^{7,11} of this fullerene. The inherent spherical delocalization of π -electrons is also expected to considerably enhance linear and nonlinear optical (NLO) responses of C₆₀. Indeed, recent measurements in solution and in films indicate a large value of $\chi^{(3)}$ for C₆₀.¹²⁻¹⁴ There have been a number of theoretical studies, at both the ab initio^{7,15,16} and the semiempirical¹⁷ levels, related with the structure, excited states, and magnetic properties of this molecule. However, to the best of our knowledge, the nonlinear optical properties of the C₆₀ molecule have not yet been investigated by quantum mechanical methods.

Calculation of the NLO properties of macromolecules such as C₆₀ by first principle based quantum chemical methods is not practical due to computational limitations. Fortunately, much of the useful information pertaining to the optical nonlinearity of large organic structures can be extracted from calculations based on semiempirical quantum chemical techniques, provided that such techniques have been calibrated and tested against nonempirical methods. Recently, we have implemented the time-dependent coupled-perturbed Hartree-Fock (TDCPHF) approach¹⁸ in the intermediate neglect of diatomic differential overlap (INDO) molecular orbital (MO) method¹⁹ that relies on the explicit computation of the resonance integrals β^o and applied it to study the NLO properties of a number of substituted benzene molecules.²⁰ The initial results, though not always in quantitative agreement with experiment, consistently reproduce the trends in the dispersion of NLO properties shown by ab initio methods. An advantage of using this particular INDO approach is the possibility of extending the atomic functions beyond the minimal set. Using these features of our multiple-zeta (MZ) INDO approach, we have calculated for C₆₀ the linear polarizability, α , at two fundamental wavelengths, 1.37 and 0.685 μm , and the second hyperpolarizability, γ (the first hyperpolarizability, β , is zero for C₆₀), at a fundamental wavelength, $\lambda = 1.37 \mu\text{m}$. The results, which are presented in this communication, indicate that the α and γ values of C₆₀ are respectively 13 and 30-34 times larger than the corresponding values for benzene.

In order to verify the theoretical predictions, we have also measured the molecular second hyperpolarizability, γ , of the C₆₀ molecule in solution by the degenerate four-wave mixing (DFWM) technique at a fundamental wavelength of 0.602 μm and by the

TABLE I: INDO-TDCPHF Calculated Values of α (10^{-24} esu) for the C₆₀ Molecule

λ (μm)	∞	1.37	0.685
$\hbar\omega$ (eV)	0	0.905	1.81
α_{xx}	81.69	82.64	85.81
α_{yy}	81.79	82.75	85.93
α_{zz}	81.58	82.53	85.70
$\langle\alpha\rangle$	81.69	82.64	85.82

optical Kerr gate (OKG) experiment at a fundamental wavelength of 0.620 μm . The measured values of γ are 3 orders of magnitude larger than those predicted by the INDO-TDCPHF calculations.

Theoretical Calculations

For a spherically symmetric molecule like C₆₀, the induced dipole moment, p , in the presence of an external field, E , can be written as²¹

$$p = \alpha \cdot E + \gamma : EEE + \dots \quad (1)$$

where the Einstein summation convention has been used; coefficients α and γ are the linear polarizability and the second hyperpolarizability tensors, respectively, and can be obtained in the coupled-perturbed Hartree-Fock approach as¹⁸

$$\alpha(-\omega; \omega) = -\text{Tr} [\mathbf{MD}^{(1)}(\omega)] \quad (2)$$

$$\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = -\text{Tr} [\mathbf{MD}^{(3)}(\omega_1, \omega_2, \omega_3)] \quad (3)$$

where $\omega, \omega_1, \omega_2, \dots$ are optical frequencies and $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$; \mathbf{M} is the dipole moment matrix, $\mathbf{D}^{(n)}$ is the n th-order perturbed density matrix, and Tr stands for the trace of the matrix in the bracket. Thus, the elements of α and γ tensors can be calculated from the knowledge of \mathbf{M} and $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(3)}$, respectively. A detailed description of our MZINDO approach, which uses the method of Lipinski and Leszczynski²² to calculate the resonance integrals, β^o , over atomic functions is given in ref 20. The ab initio optimized double-zeta exponents of Clementi and Roetti²³ are used for the carbon valence shell. Calculated values of the elements of α and γ tensors, along with their mean scalar values obtained as

$$\langle\alpha\rangle = (1/3) \sum_i (\alpha_{ii}); \quad i = x, y, z \quad (4)$$

$$\langle\gamma\rangle = (1/5) \sum_{i,j} (\gamma_{ijj} + \gamma_{ijj} + \gamma_{ijj}); \quad i, j = x, y, z \quad (5)$$

are listed in Tables I and II, respectively. The spherically symmetric charge distribution of C₆₀ is clearly noted from the isotropic nature of α (Table I). Between the static limit ($\lambda = \infty$) and the optical wavelength $\lambda = 0.685 \mu\text{m}$ ($\hbar\omega = 1.81 \text{ eV}$), a dispersion of about 5% is observed in the values of α . It should be noted that the calculated values of $\langle\alpha\rangle$ (Table I) for C₆₀ are about 13 times larger than the corresponding values of 6.134, 6.181, and

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TABLE II: INDO-TDCPHF Calculated Values of γ (10^{-36} esu) for Various Third-Order NLO Effect in C_{60} at $\lambda = 1.37 \mu\text{m}$ ($\hbar\omega = 0.905$ eV)

γ	(0;0,0,0)	($-\omega$;0,0, ω)	(-2ω ;0, ω , ω)	($-\omega$; ω , ω , $-\omega$)
xxxx	4.93	5.02	5.64	5.50
xyyy	1.64	1.66	1.59	2.00
xxzz	1.67	1.68	1.62	2.02
xyyx	1.64	1.70	2.03	1.53
xzzx	1.67	1.73	2.06	1.57
yxxy	1.64	1.70	2.03	1.51
yyxx	1.64	1.66	1.59	2.00
yyyy	4.93	5.02	5.64	5.50
yyzz	1.68	1.69	1.63	2.03
yzzy	1.68	1.74	2.07	1.58
zxzx	1.67	1.73	2.05	1.54
zyyz	1.68	1.74	2.07	1.55
zzxx	1.67	1.68	1.62	2.00
zzyy	1.68	1.69	1.63	2.02
zzzz	4.90	4.99	5.60	5.46
$\langle\gamma\rangle$	4.95	5.04	5.49	5.52

6.328 (in units of 10^{-24} esu) calculated for benzene at $\lambda = \infty$ (static field), $1.37 \mu\text{m}$, and $0.685 \mu\text{m}$, respectively.²⁰ It is informative to rescale the values of calculated linear polarizability, α , taking into account the number of effective π -bonds in benzene and C_{60} (3 vs 30, respectively). It appears that due to cooperative effects the normalized α increases by a factor of ca. 1.3 when going from benzene to C_{60} molecule.

The calculated values of γ also indicate a highly symmetric nature of the charge distribution around C_{60} . As seen from Table II, the γ values for various third-order processes at $\lambda = 1.37 \mu\text{m}$ have the following order, $\gamma(-\omega;\omega,\omega,-\omega) > \gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;0,0,\omega) > \gamma(0;0,0,0)$, which is slightly different from the corresponding order in benzene,²⁰ where $\gamma(-2\omega;0,\omega,\omega) > \gamma(-\omega;\omega,\omega,-\omega)$. The calculated value of $\gamma(-\omega;\omega,\omega,-\omega)$, though larger than other γ values, is much smaller (by about 8 orders of magnitude) than the corresponding solution measured DFWM value as reported by Blau et al.¹⁴ These authors report a value of $|\gamma| \approx 1.07 \times 10^{-28}$ esu! One of the reasons for such a large discrepancy between theory and experiment could be the difference in the optical wavelength; the DFWM measurements were performed at $\lambda = 1.064 \mu\text{m}$ while the theoretical calculations were made at $\lambda = 1.37 \mu\text{m}$. However, a dispersion of such a large magnitude in the value of $\gamma(-\omega;\omega,\omega,-\omega)$ in going from $\lambda = 1.37 \mu\text{m}$ to $\lambda = 0.602 \mu\text{m}$ does not seem plausible. Other important factors responsible for the noted difference could be the local field effects in the experimental measurements and the basis set as well as electron correlation effects in the theoretical calculations. Also, in comparing the theoretical results with the bulk measurements of nonlinear optical coefficients, one should remember that the former are purely electronic in nature while the latter may have contributions from complicated processes, such as molecular orientation, strong local field effects, cascading, etc.

It is important to note here that the calculated values of C_{60} (Table II) are about 30–34 times larger than the corresponding values for benzene. For the benzene molecule, the MZINDO-TDCPHF calculated values (in units of 10^{-36} esu) are 0.161, 0.167, 0.169, 0.174, and 0.189 for $\gamma(0;0,0,0)$, $\gamma(-\omega;0,0,\omega)$, $\gamma(-\omega;\omega,\omega,-\omega)$, $\gamma(-2\omega;0,\omega,\omega)$, and $\gamma(-3\omega;\omega,\omega,\omega)$, respectively. Thus, the theoretical calculations predict a considerably enhanced values of γ for the C_{60} molecule with respect to a single benzene molecule.

Experimental Section

In order to examine the NLO response and to further verify the theoretical predictions made in this study, the optical nonlinearity of C_{60} was also measured in our laboratory by DFWM and OKG techniques. The DFWM experiments were performed in the forward wave (folded boxcars) geometry employing nearly transform-limited 400-fs pulses at $0.602 \mu\text{m}$ with average energy of ~ 0.4 mJ per pulse. A detailed description of the employed experimental setup is given elsewhere.²⁴ The OKG measurements, described in detail in an earlier paper,²⁵ were carried out with a colliding pulse mode-locked laser system yielding 60-fs output

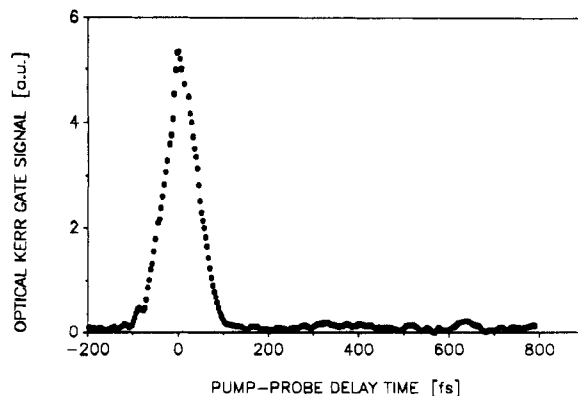


Figure 1. Time-resolved optical Kerr gate signal for benzene solution of C_{60} .

pulses centered at $0.620 \mu\text{m}$ with the average energy of $50 \mu\text{J}$ per pulse.

The compound (C_{60}) was purchased from Texas Fullerenes with a purity of about 90%, the remaining being mostly C_{70} , without further purification. Several organic solvents were tried to obtain good quality solutions of C_{60} . Unfortunately, none of the common organic solvents except benzene turned out to be a good choice. A solubility of up to 3.6 g/L was achieved in benzene.

The effective third-order susceptibilities, $\chi^{(3)}$, were obtained by comparing the intensities of the DFWM signals of the solution with a reference compound (which was pure benzene itself) according to²¹

$$\chi^{(3)} = \left(\frac{n}{n_R}\right)^2 \left(\frac{I}{I_R}\right)^{1/2} (I_R/I) \chi_R^{(3)} \mathcal{F} \quad (6)$$

where n is the refractive index, I is the intensity of the DFWM signal, I is the interaction length, and the subscript R refers to the reference. \mathcal{F} is the correction factor for the sample absorption taken as

$$\mathcal{F} = A[(1 - e^{-A})e^{-A/2}]^{-1} \quad (7)$$

where A is the sample absorbance at the working wavelength. In the presence of absorption the measured molecular hyperpolarizability, γ , is a complex quantity, and hence we treat the $\chi^{(3)}$ value as an effective quantity with contributions from both the solute and the solvent. The real and the imaginary components of the conjugated beam are $\pi/2$ out of phase with each other, and therefore the DFWM signal is proportional to their squares, so that

$$|\chi_{\text{eff}}^{(3)}| = \mathcal{L}^4 (N_s \gamma_s^r + N_{C_{60}} \gamma_{C_{60}}^r)^2 + (N_{C_{60}} \gamma_{C_{60}}^i)^2)^{1/2} \quad (8)$$

where the superscripts r and i represent the real and the imaginary parts, respectively, and the subscript s stands for the solvent (benzene) for which we assume no absorption ($\gamma_s^i = 0$). In eq 8, N represents the molecular concentration and \mathcal{L} is the local field correction, approximated by the Lorentz expression.²¹ From the $\chi_{\text{eff}}^{(3)}$ obtained from eq 6 at various concentrations, the γ value is obtained by means of least-squares fit to eq 3. Errors in the determination of γ are mainly related to the uncertainties associated with the intensities of the DFWM signals.

Following the above procedure, we obtained $\gamma(-\omega;\omega,\omega,-\omega) = -(5 \pm 2) \times 10^{-33}$ esu and $\gamma_{C_{60}}^i(-\omega;\omega,\omega,-\omega) = (9 \pm 1) \times 10^{-33}$ esu. The absolute value $|\gamma_{C_{60}}^i|$ is 3 orders of magnitude larger than the corresponding value of γ for benzene ($= (6.4 \pm 0.8) \times 10^{-36}$ esu) measured in our laboratory²⁶ under similar conditions. In terms of normalized γ (i.e., calculated per effective π -bond of a molecule), we observe a ca. 2 orders of magnitude higher hyperpolarizability in C_{60} as compared to that in the benzene molecule. Time-resolved OKG measurements carried out in the femtosecond regime revealed an ultrafast character of the dynamics responsible for the observed third-order nonlinearity. The decay of the nonlinearity occurred in the time domain shorter than 60 fs, i.e., the duration of the excitation (Figure 1). Within the experimental uncertainty, the value of the hyperpolarizability, γ_{OKG} , was found

to be of the same magnitude as in the case of DFWM. Taking 1.65 g/cm^3 for the density¹ and assuming a value of 2 for the refractive index, a value of $\chi^{(3)} = (2.2 \pm 0.3) \times 10^{-10}$ esu is obtained for C_{60} , which is in excellent agreement with $\chi^{(3)} = 2 \times 10^{-10}$ esu reported by Hoshi et al.¹² from the third harmonic generation (THG) in C_{60} films. Since the two results are obtained from two different techniques (DFWM vs THG) and in two different phases (solution vs film), the aforementioned agreement could very well be accidental. However, the close agreement between the values of $\chi^{(3)}$ in the two independent measurements, in addition to supporting the assumptions made in this study, asserts the fact that the third-order optical nonlinearity of the C_{60} molecule is quite large, being on the order of 10^{-10} esu.

The large discrepancy between the experimental and the theoretical values needs to be further investigated. At this point, we can only conjecture that this difference may be attributed to one or more of the following causes: (i) $\gamma(-\omega; \omega, \omega, -\omega)$ is calculated for $\lambda = 1.37 \mu\text{m}$ whereas our experimental studies of Kerr gate and degenerate four-wave mixing have been performed at wavelengths near $0.6 \mu\text{m}$. (ii) The calculation is performed for C_{60} whereas our sample for experimental studies contained ca. 10% of C_{70} . (iii) The calculated value of γ represents only the pure electronic four-photon parametric mixing contribution; the experimental study being conducted near one-photon resonance of C_{60} will contain incoherent $\chi^{(3)}$ contribution derived from excited-state population.²⁷ (iv) The basis set used for the calculation does not include diffuse and polarization functions and may not be adequate for the representation of third-order nonlinearity. Our previous studies have shown a strong basis set dependence of γ calculations.²⁸

Our measured value of γ_{DFWM} is about 5 orders of magnitude smaller than the corresponding value reported by Blau et al. Since both experiments employed a similar technique (DFWM), the greatly varying values of γ are somewhat surprising. Perhaps the difference in the optical wavelengths ($\lambda = 1.064 \mu\text{m}$ vs $0.602 \mu\text{m}$) may have some implications, since in the wavelength region of our measurements both coherent and incoherent mechanisms may play important roles with opposing effects due to absorption.¹⁷ The purity of the sample may also affect the measured values of γ substantially. On the other hand, the value of γ reported by Blau et al. seems inconsistent with their reported value of $\chi^{(3)}$.

Besides the greatly varying magnitude for the third-order molecular NLO coefficients obtained in the two DFWM measurements and that predicted by the quantum mechanical calculation, it is clear that the C_{60} molecule has large NLO coefficients and ultrafast response time. The large values of molecular second hyperpolarizability, γ , in C_{60} is consistent with its highly delocalized π -electron cloud around the spherical surface and lends additional support to the aromatic character of this molecule.

After this manuscript was completed, a $\chi^{(3)}$ measurement by degenerate four-wave mixing at the wavelength of 1064 nm was reported by Lindle et al.²⁹ Their value of $\chi^{(3)}(-\omega; \omega, \omega, -\omega) = 7 \times 10^{-12}$ esu yields an effective $\gamma(-\omega; \omega, \omega, -\omega)$ of ca. 10^{-35} esu at

this wavelength, which is far from one-photon resonance. Although this value is much closer to the theoretically computed value, it is still more than an order of magnitude higher than the theoretical value. Lindle et al. point out that there may be a contribution derived from two-photon excited species which may be responsible for this discrepancy.

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