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Electronic structure and nonlinear optical properties of the fullerenes C_{60} and C_{70}: A valence-effective-Hamiltonian study

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Based on the geometries optimized by the AM1 semiempirical technique (Austin Model 1 of Dewar *et al.*), we exploit the valence-effective-Hamiltonian (VEH) method to study the electronic structures of C_{60} and C_{70}. The valence-electronic density of states (DOS) calculated is found to be in excellent agreement with the high-resolution energy-distribution curves obtained from synchrotron-photoemission experiments in terms of both positions and relative intensities of the peaks. The maximum difference in peak position between theory and experiment is 0.4 eV. This shows that the VEH method provides a very reasonable description of these two fullerenes. We then apply the VEH-SOS (sum-over-states) approach to study the nonlinear optical response of C_{60} and C_{70}. We obtain that the off-resonance third-order susceptibility $\chi^{(3)}$ is on the order of 10^{-12} esu. Our results are fully consistent with the electric-field-induced second-harmonic generation and third-harmonic-generation (THG) measurements by Wang and Cheng and the degenerate-four-wave-mixing measurements by Kafafi *et al.*, but about three to four orders of magnitude lower than the data reported by Blau *et al.* and by Yang *et al.* The static $\chi^{(3)}$ values of C_{60} and C_{70} are compared to those of polyacetylene. We also investigate the dynamic nonlinear optical response by calculating the THG spectrum. We find that the lowest two-photon and three-photon resonances occur at almost the same frequency for C_{60}, because of the symmetry of the molecule.

I. INTRODUCTION

The recent discovery of the carbon-cage C_{60} fullerenes in solid form[1] has led to intense scientific interest. The earlier proposition about the spheroid-shaped C_{60} molecule, obtained in graphite vaporization experiments, has been confirmed by electron and x-ray-diffraction, infrared spectrum, and NMR studies.[1,2] Conductivity and superconductivity in doped solid fullerenes have been reported[3] and have led to numerous investigations of the electronic properties of fullerenes and fullerides.[4] The theoretical electronic structures,[4] based on the remarkable fullerenes geometries, are generally consistent with the experimental data.

Fullerenes possess highly delocalized electrons and exhibit interesting nonlinear optical behaviors.[5-8] Degenerate-four-wave-mixing (DFWM) measurements for C_{60} in benzene solution, carried out by Blau *et al.*,[7] and for C_{70} in toluene solution by Yang *et al.*,[8] have been interpreted in terms that the off-resonance third-order polarizability γ values are around 10^{-30} esu; this leads to a macroscopic third-order susceptibility $\chi^{(3)}$ on the order of 10^{-8} esu, i.e., a value even larger than that reported for polyacetylene chains.[9] However, more recently, Wang and Cheng[5] have performed electric-field-induced second-harmonic-generation (SHG) measurements on fullerenes, both in toluene solution and in the form of fullerene-DEA [where DEA denotes (*N*,*N*-diethylaniline)] charge-transfer complexes. They deduced the γ values, after a standard local field treatment,[10] to be $(7.5\pm2)\times10^{-34}$ esu and $(1.3\pm0.3)\times10^{-33}$ esu for C_{60} and for C_{70}, respectively (in toluene solution). Kafafi *et al.* have carried out DFWM measurements on C_{60} and found the $\chi^{(3)}$ value to be 7×10^{-12} esu.[6] These figures are three to four orders of magnitude smaller than the experimental data reported in Refs. 7 and 8, and generally appear to be more reasonable. So far, all the measurements have been performed at fixed frequency; full dispersion spectra are not available yet.

In this work, we apply the valence-effective-Hamiltonian (VEH) approach to study the electronic structures of the fullerene molecules C_{60} and C_{70}. We then exploit the VEH-SOS (sum-over-states) approach, as developed by the present authors,[11] to investigate the static and dynamic nonlinear optical properties of fullerenes, in order to shed light on the experimental controversies.

II. METHODOLOGY

A. Valence effective Hamiltonian

The VEH method was originally developed for molecules by Nicolas and Durand[12] and extended and largely exploited for polymers by André *et al.*[13] and Brédas and co-workers.[14] The method is based on the use of an effective Fock Hamiltonian F_{eff} which combines a kinetic term and a summation over atomic potentials V_A:

$$F_{\text{eff}}=-\frac{\Delta}{2}+\sum_{A} V_A \ , \tag{1a}$$

$$V_A=\sum_{l,m,i,j} C^{A}_{i,j,l,m}\,|\chi^{A}_{i,l,m}\rangle\langle\chi^{A}_{j,l,m}| \ , \tag{1b}$$

where the summation over l and m define the angular dependence of V_A. The numerical coefficients $C_{i,j,l,m}$ are independent of m in the case of spherical symmetry, which we usually consider. In order to achieve double-ζ quality, the summation over i and j extend up to 2. The $\chi_{i,l,m}$'s are normalized Gaussian functions:

$$\chi_{i,l,m}=N_i r^l \exp(-\alpha_i r^2) Y_{l,m}(\theta,\phi) \; , \tag{2}$$

where N_i is the normalization factor and $Y_{l,m}(\theta,\phi)$ denotes usual spherical harmonics. Only 1s and 2p Gaussian Cartesian functions are used. The atomic potentials V_A are optimized on model molecules in order to minimize the difference between F_{eff} and the Fock Hamiltonian built from Hartree-Fock *ab initio* double-ζ calculations. In this way, the VEH method is completely nonempirical. For carbon atoms, the model molecules include ethane, butadiene, and acetylene.[14] The atomic basis set was chosen to be of minimal type (STO-3G) but, in conjunction with the parametrization of the atomic potentials, such as to produce one-electron energy levels of double-ζ quality. Only valence electrons are explicitly considered and one-electron integrals need to be evaluated, which allows one to carry out calculations on large-size molecules.

B. VEH density of states

The density of states (DOS) curves are obtained from the VEH one-electron levels:

$$\rho(E)=\sum_i \delta(E-\varepsilon_i) \; ,$$

where ε_i is the one-electron energy. By performing a Gaussian convolution on the Dirac δ function, we have

$$\rho(E)=\sum_i \frac{1}{\sqrt{2\pi}\,\eta(E)} \exp\left[-\left[\frac{E-\varepsilon_i}{2\eta(E)}\right]^2\right] \; . \tag{3}$$

The full width at half maximum (FWHM) Γ is related to the above η:

$$\Gamma(E)=2\sqrt{2\ln 2}\,\eta(E)\approx 2.355\,\eta(E)$$

and we adopt an energy-dependent broadening: $\Gamma(E)=0.25\,\text{eV}+0.05|E-E_{\text{HOMO}}|$ for all the calculations.

C. Sum-over-states evaluation for hyperpolarizability

In terms of nonlinear optical properties, we have implemented the SOS procedure into the VEH approach and have studied several conjugated polymers.[11(b)] For the third-harmonic-generation (THG) process, the standard Orr-Ward perturbation formula[15] for third-order polarizability $\gamma(-3\omega;\omega,\omega,\omega)$ is expressed in terms of VEH one-electron levels and can be written as [see Fig. 2 of Ref. 11(b), taking into account six diagrams in total]:

$$\gamma(-3\omega;\omega,\omega,\omega)=\gamma_2+\gamma_3+\gamma_1+\gamma_4+\gamma_7+\gamma_8 \; , \tag{4}$$

where

$$\gamma_2(-3\omega;\omega,\omega,\omega) =2\sum_{a\in\text{unocc};\,i,j,k\in\text{occ}} \mu_{ai}\mu_{ij}\mu_{jk}\mu_{ka}S_2(\omega) \; . \tag{5}$$

Hereafter, a,r,s denote unoccupied molecular levels, and i,j,k denote occupied ones. The $S_2(\omega)$ function is defined as

$$S_2(\omega)=\frac{1}{(\varepsilon_{ai}-3\omega)(\varepsilon_{aj}-2\omega)(\varepsilon_{ak}-\omega)}+\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{aj}+2\omega)(\varepsilon_{ak}-\omega)}+\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{aj}-2\omega)(\varepsilon_{ak}-\omega)} +\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{aj}+2\omega)(\varepsilon_{ak}+3\omega)} \; ,$$

where $\varepsilon_{ai}=\varepsilon_a-\varepsilon_i$. The other terms are

$$\gamma_3(-3\omega;\omega,\omega,\omega) =2\sum_{a,r,s,\in\text{unocc};\,i\in\text{occ}} \mu_{ia}\mu_{ar}\mu_{rs}\mu_{si}S_3(\omega) \; , \tag{6}$$

where $S_3(\omega)$ is analogous to $S_2(\omega)$ with substitutions of ε_{aj} by ε_{ri}, and ε_{ak} by ε_{si};

$$\gamma_1(-3\omega;\omega,\omega,\omega) =-2\sum_{a,r\in\text{unocc};\,i,j\in\text{occ}} \mu_{ia}\mu_{ar}\mu_{ji}\mu_{rj}S_1(\omega) \; , \tag{7}$$

with S_1 corresponding to S_2 with substitutions of ε_{aj} by ε_{ri}, and ε_{ak} by ε_{rj};

$$\gamma_4(-3\omega;\omega,\omega,\omega) =-2\sum_{a,r\in\text{unocc};\,i,j\in\text{occ}} \mu_{ia}\mu_{ji}\mu_{ar}\mu_{rj}S_4(\omega) \; , \tag{8}$$

with S_4 corresponding to S_2 with substitution of ε_{ak} by ε_{rj};

$$\gamma_7(-3\omega;\omega,\omega,\omega) =-2\sum_{a,r\in\text{unocc};\,i,j\in\text{occ}} \mu_{ia}\mu_{rj}\mu_{aj}\mu_{ri}S_7(\omega) \; . \tag{9}$$

with S_7 corresponding to S_2 with substitutions of ε_{aj} by $\varepsilon_{ai}+\varepsilon_{rj}$, and ε_{ak} by ε_{aj};

$$\gamma_8(-3\omega;\omega,\omega,\omega) =-2\sum_{a,r\in\text{unocc};\,i,j\in\text{occ}} \mu_{ia}\mu_{rj}\mu_{aj}\mu_{ri}S_8(\omega) \; , \tag{10}$$

with S_8 corresponding to S_2 with substitutions of ε_{aj} by $\varepsilon_{ai}+\varepsilon_{rj}$, and ε_{ak} by ε_{ri}. The double excitation channels $\gamma_7+\gamma_8$ can be cast into a single term after simple algebra (by noting $\varepsilon_{ai}+\varepsilon_{rj}=\varepsilon_{aj}+\varepsilon_{ri}$):

$$\gamma_7+\gamma_8=-2\sum_{a,r\in\text{unocc};\,i,j\in\text{occ}}\mu_{ia}\mu_{rj}\mu_{aj}\mu_{ir}\times\left[\frac{1}{(\varepsilon_{ai}-3\omega)(\varepsilon_{aj}-\omega)(\varepsilon_{ri}-\omega)}+\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{rj}+\omega)(\omega_{aj}+3\omega)}+\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{rj}+\omega)(\varepsilon_{ri}-\omega)}+\frac{1}{(\varepsilon_{ai}+\omega)(\varepsilon_{aj}-\omega)(\varepsilon_{ri}-\omega)}\right]. \tag{11}$$

The linear polarizability $\alpha(\omega)$ is expressed as

$$\alpha(\omega)=2\sum_{a\in\text{unocc};\,i\in\text{occ}}\mu_{ia}\mu_{ai}\left[\frac{1}{\varepsilon_{ai}-\omega}+\frac{1}{\varepsilon_{ai}+\omega}\right]. \tag{12}$$

In the above formula, an overall factor of 2 comes from spin-singlet summation, μ_{ai} is the dipole transition matrix between molecular orbital Ψ_a and Ψ_i:

$$\mu_{ai}=\int dr\,\Psi_a^*(r)(-er)\Psi_i(r) \tag{13}$$

and Ψ_k is expanded within the linear-combination-of-atomic-orbitals (LCAO) approximation:

$$\Psi_k(r)=\sum_n C_{kn}\chi_n(r-r_n)\ . \tag{14}$$

χ_n is an atomic basis function (of STO-3G type within the VEH technique). In this way, the dipole transition moments between molecular levels can be written as

$$\mu_{ai}=\sum_{k,k'}C_{ak}^*C_{ik'}\int\chi_k(r-r_k)(-er)\chi_{k'}(r-r_{k'})dr\ . \tag{15}$$

In fact, in the above formulation, the total wave functions of the molecular electronic states are approximated as single determinants from VEH one-electron levels. Note that the electron-electron interactions (but not the correlation effects) are incorporated in the parametrization of the atomic potentials. It is emphasized that in the VEH technique, the term *atomic potential* refers to the potential of an atom in its chemical environment and not to the potential of an isolated atom.

Note that in Eqs. (1) and (2), the effective Fock operator is constructed to reproduce double-ζ *ab initio* results only for the *occupied levels;* no information pertaining to the unoccupied levels is included in the atomic potentials. In that way, the unoccupied valence electronic levels do not suffer from the usual Hartree-Fock deficiencies.[14] Furthermore, all the one-electron wave functions coming from a VEH calculations form a complete set. In the SOS formulation, the perturbed molecular wave function are expanded within the wave function of the unperturbed system. In doing so, the completeness of the basis is of prime importance. Previous calculations[11,14] have shown that VEH can offer a good description for the π-π^* transitions and the hyperpolarizability in conjugated systems. The VEH-SOS approach is thus expected to provide reliable results for the nonlinear optical coefficients of fullerenes.

III. RESULTS AND DISCUSSION

We optimize the geometric structures of C_{60} and C_{70} via the Hartree-Fock semiemipirical AM1 (Austin Model 1) method.[16] The single and double-bonds lengths for C_{60} are found, respectively to be 1.464 and 1.385 Å; for C_{70}, we find there are eight types of bonds [see Fig. 1(b)] with $r_1=1.456$ Å, $r_2=1.380$ Å, $r_3=1.459$ Å, $r_4=1.383$ Å, $r_5=1.468$ Å, $r_6=1.447$ Å, $r_7=1.413$ Å, and $r_8=1.461$ Å. These results are in good agreement with the corresponding experimental values obtained by McKenzie *et al.*[17] on the basis of electron-diffraction measurements: (from r_1 to r_8 in Å) 1.464±0.009, 1.37±0.01, 1.47±0.01, 1.37±0.01, 1.46±0.01, $1.47^{+0.01}_{-0.03}$, 1.39±0.01, and $1.41^{+0.03}_{-0.01}$.

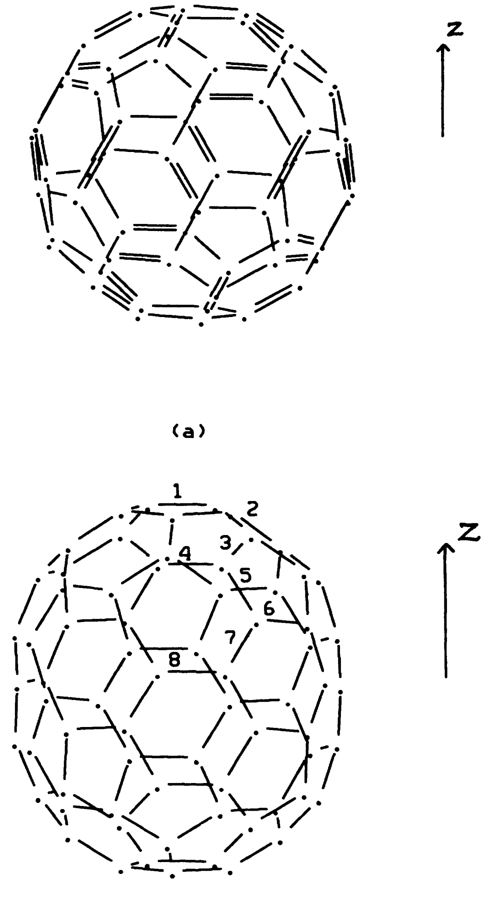

FIG. 1. Geometric structures of (a) C_{60} and (b) C_{70} (the eight different types of bonds are indicated).

Based on the above geometries, we carry out the VEH electronic structure calculations for molecules C_{60} and C_{70}. The ionization potentials (IP's) are calculated to be 7.52 and 7.39 eV for C_{60} and for C_{70}, respectively. These values are in excellent agreement with the synchrotron radiation experiments of Hertel *et al.*: 7.54 ± 0.04 and 7.3 ± 0.2 eV, respectively.[18] (Note that the IP values obtained from AM1 are too large, 9.64 eV for C_{60} and 9.07 eV for C_{70}.)

We illustrate the VEH density of valence electronic states spectra in Fig. 2. For comparison, we also display schematically the synchrotron high-resolution photoemission data for C_{60} at $h\nu=50$ eV, by Weaver *et al.*[19] in Fig. 2(a). We set the energy origin of the theoretical curves to be at highest occupied molecular orbital (HOMO). Both the peak positions and relative intensities of theoretical curves are in good agreement with experiment. To be more precise, we compare the theoretical and experimental positions in Table I. We observe that the largest discrepancy is only on the order of 0.4 eV, the experimental resolution being 0.2 eV. This demonstrates that VEH can provide a very good description of the electronic structures in fullerenes, as it does in conjugated polymers.[14] Furthermore, these results indicate that the intermolecular coupling in solid C_{60} (van der Waals forces) is relatively weak, so that a molecular approach suffices for the descriptions of the electronic properties, as mentioned previously.[4]

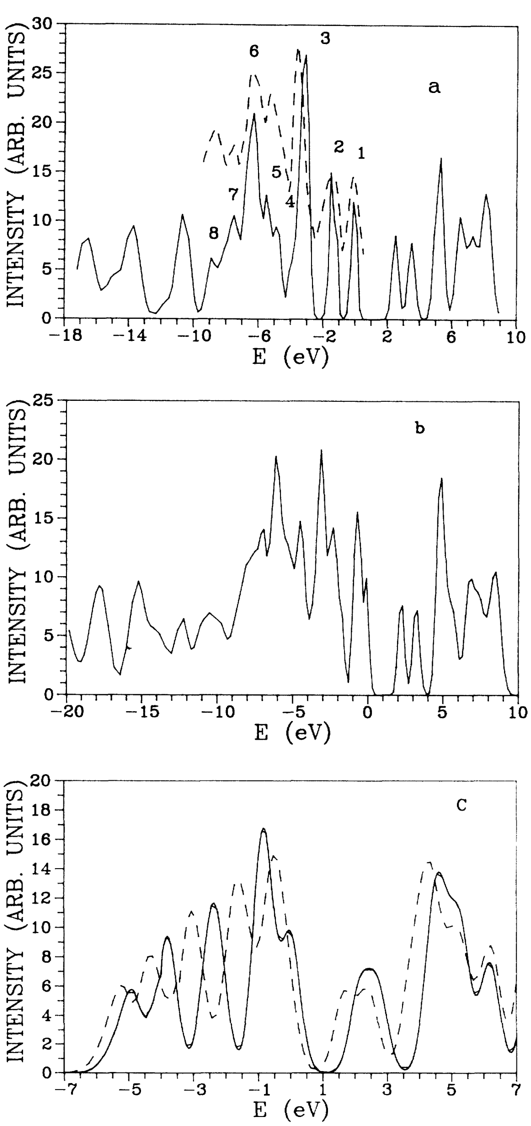

FIG. 2. (a) VEH DOS curve for C_{60} (solid line) compared to the synchrotron-photoemission data (dashed line) from Ref. 19 (a schematic plot); (b) VEH DOS curves for C_{70}; (c) DOS curves from the LHS model: solid line for C_{60}, dashed line for C_{70}. The energy origins in all cases are set at HOMO. [Since there are only π electrons considered in case (c), the range and scale there are different.]

TABLE I. Comparison of the DOS peak positions coming from the VEH theoretical simulation and the synchrotron-photoemission data of Ref. 19 [see Fig. 2(a), where the peaks are labeled as in the table].

	1	2	3	4	5	6	7	8
VEH	0	1.4	3.2	4.8	5.4	6.4	7.5	8.8
Expt.	0	1.4	3.6		5.3	6.5	7.5	8.6

We stress that, from the analysis of the VEH LCAO coefficients, we find that even for the HOMO and lowest unoccupied molecular orbital (LUMO) levels in fullerenes, the wave functions contain significant contributions from σ atomic orbitals. This is of course due to the three-dimensional (3D) spherical structures, so that σ-π mixing always exists. For comparison, we have also carried out Hückel-type Longuet-Higgins–Salem (LHS) calculations.[20] We used the parameters adopted for polyacetylene[21] and optimized the molecular structures. Though the bond lengths we find are in good agreement with experiment, the resulting electronic structures (e.g., the DOS curves) are not accurate [see Fig. 2(c)], both the peak positions and relative intensities being markedly different from measurements.

The linear and nonlinear polarizabilities α and γ are calculated based on the VEH electronic structure. The theoretical status value[22] are listed in Table II, where the spatial averages are defined as $\alpha_{\rm av}=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$; and $\gamma_{\rm av}=(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\gamma_{xxyy}+2\gamma_{yyzz}+2\gamma_{zzxx})/5$. The z axis, both for C_{60} and C_{70}, is along the direction from pentagon at bottom to pentagon at top, as shown in Fig. 1. In this way, the x and y directions are identical. For C_{60}, there is a very slight difference between the z and x (or y) α (or γ) components, since it is not strictly a sphere; for C_{70}, this difference is much more pronounced. For comparison, we also present the VEH-SOS results for an all *-trans* planar polyacetylene chain containing 60 carbons. The data in Table II are fully consistent with the results from the measurement of Wang and Cheng.[5] These authors reported the electric-field-induced SHG nonresonant ($h\nu=0.65$ eV) $\gamma(-2\omega;\omega,\omega,0)$ values to be $(7.5\pm2)\times10^{-34}$ esu and $(1.3\pm0.3)\times10^{-33}$ esu for C_{60} and C_{70} in toluene solution, respectively. The corresponding macroscopic susceptibility $\chi^{(3)}$ then is on the

TABLE II. VEH-SOS theoretical static first-order polarizability α (in Å^3) and third-order polarizability γ (in 10^{-36} esu) tensor components for C_{60}, C_{70}, and the $C_{60}H_{62}$ polyene.

Polarizability	C_{60}	C_{70}	$C_{60}H_{62}$
α_{xx}	153.2	222.8	1332.3
α_{yy}	153.2	222.8	26.7
α_{zz}	155.6	197.4	
α_{av}	154.0	214.3	453.0
γ_{xxxx}	212.8	516.3	4×10^5
γ_{yyyy}	212.8	516.3	-6.1
γ_{zzzz}	226.1	816.5	
γ_{xxyy}	62.5	141.1	-627
γ_{yyzz}	58.6	543.5	
γ_{zzxx}	58.6	543.5	
γ_{av}	202.0	862.3	8×10^4

order of 10^{-12}–10^{-13} esu (the precise value depending on the statistical model and the local field correction used[10]). Other experimental data come from Kafafi *et al.*,[6] who obtained a third-order susceptibility $\chi^{(3)}$ value of 7×10^{-12} esu for C_{60} from a DFWM experiment; this gives a γ value around 3×10^{-34} esu, very close to our theoretical value, 2×10^{-34} esu. We note that Blau *et al.*[7] and Yang *et al.*[8] reported DFWM-measured $\chi^{(3)}$ values for fullerenes to be around 10^{-8} esu, i.e., 3 or 4 orders of magnitude larger than our theoretical results or the data from Refs. 5 and 6. These authors utilized the particle-in-a-box model developed by Rustagi and Ducuing[23] to justify such a huge value. However, as we pointed out previously,[11(b)] this model does not allow one to obtain a correct saturation behavior in the case of large systems; furthermore, due to their peculiar symmetries, fullerenes are rather different from a "box" character, in terms of their electronic structure.

The VEH-SOS approach gives a γ value for a polyacetylene chain containing 60 carbon atoms which is two to three orders of magnitude bigger than that of the fullerenes. This result is actually in agreement with THG measurements on polyacetylene by Halvorson *et al.* which indicate an off-resonant $\chi^{(3)}$ value for polyacetylene on the order of 10^{-10} esu and even larger for well-oriented samples, 10^{-8}–10^{-9} esu.[9(b)] This is due to the fact that electron delocalization in one dimension significantly increases the nonlinear optical susceptibility,[24] as discussed widely in recent years.[25] The relatively large susceptibility in fullerenes is due to strong electron delocalization, but is hampered by the three-dimensional character of the molecules.

We have also investigated the dynamic optical response of fullerenes. We present the dispersion of the linear polarizability $\alpha(\omega)$ of C_{60} and C_{70} in Fig. 3, and the third-harmonic-generation dispersion spectrum γ_{THG} in Fig. 4. We have adopted the same excitation-dependent broadening as before, i.e., we have set the damping equal to 0.05 times the excitation energy.[11] Note that due to the symmetry of C_{60}, the lowest electronic excitation is one-photon forbidden.[4] As a consequence, the lowest two-photon and three-photon resonances occur at almost the same position. In Fig. 4(a), the first (and highest) peak contains both resonance contributions, one at 1.17 eV (three-photon), and the other at 1.22 eV (two-photon), the energy difference being within the range of broadening. In Fig. 4(b), for C_{70}, the first peak (≈ 0.7 eV) is due to three-photon resonance to the HOMO-LUMO transition and the second (highest) peak at 1.17 eV is a two-photon resonance. We note that the experiments of both Blau *et al.*[7] and Yang *et al.*[8] were carried out at $\omega = 1.17$ eV and that in the DFWM process, there can occur two-photon resonances, which can of course increase the nonlinear optical response; as a result, the γ values of Refs. 7 and 8 are expected to be larger than those of Ref. 5, but not by three or four orders of magnitude. The experimental data analysis by Blau *et al.*[7] has been criticized by Knize and Partanen.[26]

Our theoretical static α value for C_{60} (154 Å^3) is larger than that from the quantum-chemistry calculations of Fowler, Lazaretti, and Zanasi.[27] These authors reported an α value of 65 Å^3, using an extended basis set. Lambin

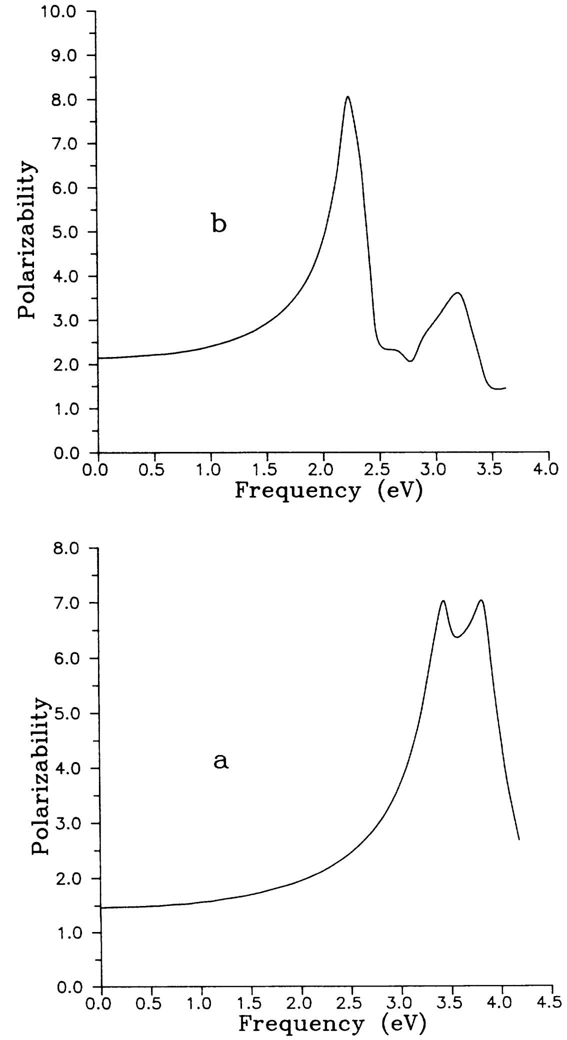

FIG. 3. VEH frequency dependence of polarizability $\alpha(\omega)$ (in Å^3): (a) C_{60}; (b) C_{70}.

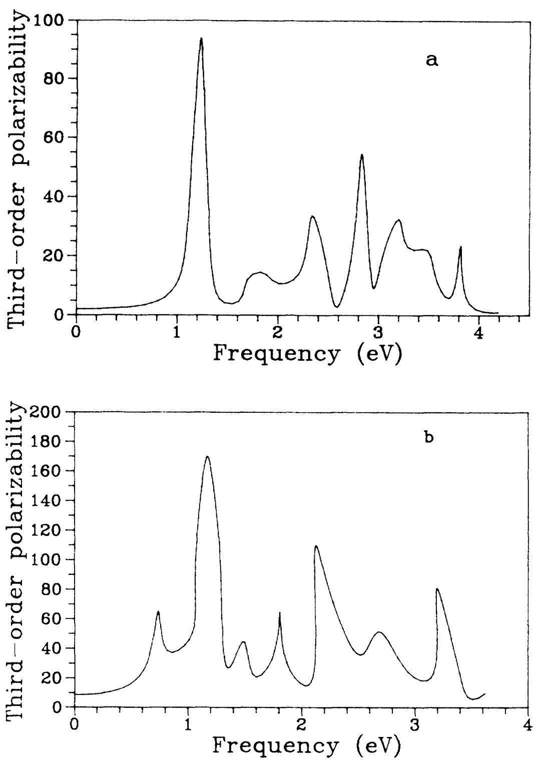

FIG. 4. VEH theoretical THG spectra of fullerenes (in 10^{-34} esu): (a) C_{60}; (b) C_{70}.

and co-workers have developed a model based on π and σ plasmon polarization, which yields an α value of roughly 53.3 Å^3.[28] Based on (i) the experimental static dielectric constant value $\epsilon \approx 4.4$ (Ref. 29) (which gives $\chi^{(1)}$ around 0.27 esu [$\epsilon = 1 + 4\pi\chi^{(1)}$]), (ii) the Clausius-Mossotti relation (i.e., considering the local field correction), and (iii) a C_{60} cluster density $N = 1/720$ Å^{-3}, one can estimate the polarizability α to be around 91.2 Å^3, (without local field correction, the α value would be 194.4 Å^3). The quantum-chemical calculations[27] thus underestimate the α value, while our VEH-SOS method overestimates it. For C_{70}, we calculate the static α to be about 50% larger than in C_{60}.

IV. SYNOPSIS

To summarize, we have performed VEH electronic structure and nonlinear optical response calculations on the fullerenes C_{60} and C_{70}. The ionization potentials and theoretical DOS spectra are found to be in excellent agreement with photoemission experiments, showing that VEH can give an accurate description of the electronic structure of fullerenes, as it does for conjugated polymers. We stress the importance of σ-π electron mixing in fullerenes due to the typical 3D spherelike geometries.

The large nonlinear optical response in fullerenes can be attributed to electron delocalization, much as in conjugated polymer chains; however, some limitation arises due to the three-dimensional character of the fullerene molecules. As a result, the γ values for fullerenes are about two orders of magnitude lower than those of linear polyenes containing a similar number of carbons. In terms of the dynamic response, we show that in C_{60} the two-photon and three-photon resonances occur at almost the same frequency in the THG spectrum, due to the symmetry of the molecule. Our theoretical values for γ are in good agreement with the experimental data of Wang and Cheng[5] and of Kafafi *et al.*[6]

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