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Large vibrational nonlinear optical properties of C_{60}: A combined Hartree-Fock/density-functional approach

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Vibrational contributions to the nonlinear optical properties of an isolated buckminsterfullerene molecule have been computed within the double harmonic oscillator and infinite optical frequency approximations. In our treatment, normal coordinates from density-functional theory are combined with Hartree-Fock electrical properties. Values obtained for the ratio of vibrational to static electronic contributions vary from 0.01 for second-harmonic generation to 0.64 for the electro-optic Kerr effect to 1.26 for degenerate four-wave mixing.

INTRODUCTION

The discovery of the stability of the C_{60} cage molecule,[1] buckminsterfullerene, and the development of methods for its bulk synthesis[2] has led to a huge amount of theoretical and experimental investigation. Quite a few studies have been devoted to the nonlinear optical (NLO) properties of C_{60}, no doubt stimulated by the possibility of technological applications.[3] As it happens, there is considerable scatter in the experimental data[4–7] as well as in the theoretical calculations[8–16] that have been done thus far.

Most of the theoretical treatments have been of the semiempirical variety.[8–13] On the other hand, van Gisbergen, Snijders, and Baerends[16] have obtained time-dependent density-functional theory (TDDFT) results for the NLO properties that support the relatively small experimental values found by Geng and Wright[7] in four-wave mixing (FWM) experiments. However, this TDDFT investigation—and all other studies as well—neglects vibrational and solvent effects. In typical π- (or σ-) conjugated systems such as the linear polyenes, there is often a large vibrational contribution to NLO properties associated with geometry relaxation [called nuclear relaxation (NR)] induced by an applied *static* (see later) electric field.[17] Although C_{60} belongs to a different class of compounds we will see that it also has large NR terms. In either case these terms are due to Raman-active vibrations that primarily affect the electro-optic Kerr effect (EOKE) and degenerate (or nearly degenerate) four-wave-mixing (DFWM) processes. However, in C_{60} the vibrations involved are different from those of the linear polyenes, and the vibrational contribution is larger in comparison with the static electronic hyperpolarizability.

In a recent study[18] we have assessed conventional DFT schemes for computing static polarizabilities and hyperpolarizabilities of linear polyenes. It was found that all common functionals fail for the linear and nonlinear responses: they lead to a substantial overestimate. This made us leery of applying a density-functional theory approach for the same properties of C_{60} even though the spherical shape of the latter—as opposed to extended linear polyenes—may work in favor of DFT. In contrast with electrical properties it is known[19] that DFT gives accurate harmonic force constants for C_{60}. Thus, it was decided to combine DFT normal coordinates with Hartree-Fock (HF) static polarizabilities and hyperpolarizabilities in a treatment of NR effects aimed at determining relative vibrational versus electronic contributions.

METHODOLOGY

From the exact sum-over-states expressions for the frequency-dependent polarizabilities and hyperpolarizabilities Bishop and Kirtman[20] have extracted the vibrational contribution by applying a clamped nucleus (CN) approximation in which electronic and vibrational motions are treated sequentially rather than simultaneously. Assuming nonresonant conditions, they write the vibrational linear polarizability tensor α^v and the second hyperpolarizability tensor γ^v in the form:

$$\alpha^v_{\zeta\eta}(-\omega_\sigma;\omega_1)=[\mu^2] \tag{1}$$

and

$$\gamma^v_{\zeta\eta\xi\chi}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=[\alpha^2]+[\mu\beta]+[\mu^2\alpha]+[\mu^4]. \tag{2}$$

Since C_{60} has a center of inversion the first hyperpolarizability tensor β^v vanishes and is, therefore, omitted here. The square-bracket quantities in Eqs. (1) and (2) involve summations over the vibrational manifold associated with the ground electronic state. For instance,

$$[\alpha^2]=\tfrac{1}{4}\sum P_{-\sigma,1,2,3}\sum_k{}'\frac{\langle 0|\alpha^e_{\zeta\eta}|k\rangle\langle k|\alpha^e_{\xi\chi}|0\rangle}{\omega_k-\omega_2-\omega_3}, \tag{3}$$

where the prime on the summation indicates exclusion of the ground vibrational state $|0\rangle$, $\hbar\omega_k$ is the vibrational excitation energy $0\rightarrow k$, $\Sigma P_{-\sigma,1,2,3}$ represents a summation over the 24 permutations of the pairs $(-\omega_\sigma,\zeta)$, (ω_1,η), (ω_2,ξ), and (ω_3,χ), and $\omega_\sigma=\omega_1+\omega_2+\omega_3$. The superscript e indicates

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that α^e is an electronic property which, nonetheless, is a function of the CN geometry. By expanding α^e about the equilibrium position one obtains a power series in the normal coordinates Q_a and the linear terms in this expansion constitute the harmonic approximation. Likewise, the vibrational potential—which determines both $|k\rangle$ and ω_k—may be expanded as a power series in Q_a. In this case the harmonic approximation is defined by retaining only the quadratic terms (the linear terms vanish at equilibrium). Using the double-harmonic approximation in Eq. (2), as we do in the treatment here,

$$\gamma^v_{\zeta\eta\xi\chi}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=[\alpha^2]^{0,0}+[\mu\beta]^{0,0} \tag{4}$$

in which the superscripts 0,0 refer to the order in electrical and mechanical anharmonicity, respectively. Note that $[\mu^2\alpha]^{0,0}=0=[\mu^4]^{0,0}$. In Eq. (4) the quantity $[\alpha^2]^{0,0}$ is given by the sum-over-modes (SOM) formula:

$$[\alpha^2]^{0,0}=\tfrac{1}{8}\sum P_{-\sigma,1,2,3}\sum_{a=1}^{3N-6}\frac{\left(\frac{\partial\alpha^e_{\zeta\eta}}{\partial Q_a}\right)_0\left(\frac{\partial\alpha^e_{\xi\chi}}{\partial Q_a}\right)_0}{\omega_a^2-(\omega_2+\omega_3)^2}, \tag{5}$$

where the subscript 0 refers to the equilibrium nuclear configuration. The SOM expression for $[\mu\beta]^{0,0}$ may be derived from $[\alpha^2]^{0,0}$ by making the correspondences $\frac{1}{8}\rightarrow\frac{1}{6}$, $\{\omega_a^2-(\omega_2+\omega_3)^2\}\rightarrow\{\omega_a^2-\omega_\sigma^2\}$, and

$$\left\{\left(\frac{\partial\alpha^e_{\zeta\eta}}{\partial Q_a}\right)_0\left(\frac{\partial\alpha^e_{\xi\chi}}{\partial Q_a}\right)_0\right\}\rightarrow\left\{\left(\frac{\partial\mu^e_{\zeta}}{\partial Q_a}\right)_0\left(\frac{\partial\beta^e_{\eta\xi\chi}}{\partial Q_a}\right)_0\right\}.$$

By invoking the same frequency correspondence, as well as

$$\left\{\left(\frac{\partial\alpha^e_{\zeta\eta}}{\partial Q_a}\right)_0\left(\frac{\partial\alpha^e_{\xi\chi}}{\partial Q_a}\right)_0\right\}\rightarrow\left\{\left(\frac{\partial\mu^e_{\zeta}}{\partial Q_a}\right)_0\left(\frac{\partial\mu^e_{\eta}}{\partial Q_a}\right)_0\right\}$$

and $\frac{1}{8}\rightarrow 1$, one can also obtain the expression for $[\mu^2]^{0,0}$.

For third-harmonic generation ($\omega_1=\omega_2=\omega_3=\omega$; $\omega_\sigma=3\omega$), $[\alpha^2]^{0,0}$ will be small due to the optical frequency factor in the denominator of Eq. (5). However, that will not be so for other NLO processes such as the EOKE ($\omega_1=\omega$; $\omega_2=\omega_3=0$) and DFWM ($\omega_1=-\omega_2=\omega_3=\omega_\sigma=\omega$). In those instances the important terms may be found by invoking the infinite optical frequency approximation[21] $\omega\rightarrow\infty$. When that is done the NLO properties may be simply expressed in terms of the *static* square-bracket quantities. For the diagonal elements of γ^v and for the average values as well, we have.

$$\gamma^v(-\omega;\omega,0,0)_{\omega\rightarrow\infty}=\tfrac{1}{3}[\alpha^2]^{0,0}_{\omega=0}+\tfrac{1}{2}[\mu\beta]^{0,0}_{\omega=0}, \tag{6}$$

$$\gamma^v(-2\omega;\omega,\omega,0)_{\omega\rightarrow\infty}=\tfrac{1}{4}[\mu\beta]^{0,0}_{\omega=0}, \tag{7}$$

$$\gamma^v(-\omega;\omega,\omega,-\omega)_{\omega\rightarrow\infty}=\tfrac{2}{3}[\alpha^2]^{0,0}_{\omega=0}, \tag{8}$$

FWM is similar to DFWM except that $\omega_3=-\omega'$ (and $\omega_\sigma=2\omega-\omega'$), where the magnitude of $\omega-\omega'$ is of the order of a vibrational frequency. In that case we retain the same set of terms as in the $\omega\rightarrow\infty$ approximation of DFWM but there is no simple formula for γ^v like Eq. (8). Tests[22] of the infinite-frequency approximation show that it may be expected to give semiquantitative accuracy.

It follows from the symmetry of C_{60} that only the Raman active A_g and (fivefold degenerate) H_g vibrations can give rise to nonvanishing polarizability derivatives. For the A_g modes, the derivatives of the off-diagonal elements of the polarizability tensor are zero, while the derivatives of the diagonal elements are equal to one another. Hence, the average value of $[\alpha^2]^{0,0}$ associated with the average value of γ^v,

$$\overline{\gamma^v}=\sum_{\xi,\eta}^{x,y,z}(\gamma^v_{\xi\xi\eta\eta}+\gamma^v_{\xi\eta\xi\eta}+\gamma^v_{\xi\eta\eta\xi})/15, \tag{9}$$

is simply

$$\overline{[\alpha^2]}^{0,0}_{\omega=0}=\left(\frac{1}{3\omega_a^2}\right)\sum_{\xi}^{x,y,z}\left(\frac{\partial\alpha^e_{\xi\xi}}{\partial Q_a}\right)^2=\left(\frac{1}{\omega_a^2}\right)\left(\frac{\partial\alpha^e_{xx}}{\partial Q_a}\right)^2 \tag{10}$$

for each A_g vibration. The situation is a bit more complicated for the H_g vibrations. In that case, the (square of the) off-diagonal components of α are related to the (square of the) diagonal components by the sum rule:

$$\sum_{i=1}^{5}\sum_{\xi\neq\eta}^{x,y,z}\left(\frac{\partial\alpha^e_{\xi\eta}}{\partial Q_{ai}}\right)^2=\frac{3}{2}\sum_{i=1}^{5}\sum_{\xi}^{x,y,z}\left(\frac{\partial\alpha^e_{\xi\xi}}{\partial Q_{ai}}\right)^2, \tag{11}$$

where i varies from 1 to 5 for the fivefold-degenerate modes. For each one of these modes,

$$\sum_{\xi}^{x,y,z}\left(\frac{\partial\alpha^e_{\xi\xi}}{\partial Q_{ai}}\right)=0. \tag{12}$$

Combining Eqs. (9), (11), and (12), one obtains exactly the same result as in the first line of Eq. (10) except for an additional sum over the five degenerate modes. A similar analysis can be carried out for the $[\mu\beta]^{0,0}$ term. In this instance the triply degenerate infrared active F_{1u} modes are the only vibrations that can generate a dipole moment. As one might guess, the relation analogous to Eq. (10) is

$$\begin{aligned}\overline{[\mu\beta]}^{0,0}_{\omega=0}&=\left(\frac{1}{3\omega_a^2}\right)\sum_{i=1}^{3}\sum_{\xi}^{x,y,z}\left(\frac{\partial\mu^e_{\xi}}{\partial Q_{ai}}\right)\left(\frac{\partial\beta^e_{\xi\xi\xi}}{\partial Q_{ai}}\right)\\&=\left(\frac{1}{\omega_a^2}\right)\sum_{i=1}^{3}\left(\frac{\partial\mu^e_{x}}{\partial Q_{ai}}\right)\left(\frac{\partial\beta^e_{xxx}}{\partial Q_{ai}}\right).\end{aligned} \tag{13}$$

Because of the large number of vibrational degrees of freedom, computation of the normal coordinate derivatives for C_{60} that appear in $[\alpha^2]^{0,0}$ and $[\mu\beta]^{0,0}$ can be very computationally demanding even when symmetry is taken into account. In order to streamline the calculations we adopted a finite field (FF) procedure illustrated by the following identity:

TABLE I. Circular frequencies (in cm^{-1}) of C_{60} infrared-active modes and of Raman-active modes that dominate the vibrational hyperpolarizabilities.

		STO-3G	DFT (Ref. 19)	Expt. (Refs.)
ir	F_{1u}	561	527	527 (25, 26)
	F_{1u}	587	589	576 (25, 26)
	F_{1u}	1248	1218	1183 (25, 26)
	F_{1u}	1464	1462	1428 (25, 26)
Raman	H_g	269	259	270 (25, 27)
	A_g	495	494	493 (25, 27)
	A_g	1506	1504	1470 (25, 27)

TABLE II. Vibrational and electronic contributions to the polarizability and hyperpolarizability of C_{60}. The α (γ) values are given in atomic units (10^2 atomic units). (1 a.u. of $\alpha = 1.6488 \times 10^{-41}\ \mathrm{C^2\,m^2\,J^{-1}} = 0.1482\ \text{Å}^3$ and 1 a.u. of $\gamma = 6.2354\times 10^{-65}\ \mathrm{C^4\,m^4\,J^{-3}} = 7.0423\times 10^{-54}\ \mathrm{m^5\,V^{-2}} = 5.0367\times 10^{-40}$ esu.)

	STO-3G derivatives		6-31G derivatives	
	HF/STO-3G Hessian	DFT Hessian	HF/STO-3G Hessian	DFT Hessian
$\alpha^v(0;0)$	3.71	4.10	4.64	5.28
$\gamma^v(0;0,0,0)$	308	334	371	407
$\gamma^v(-\omega;\omega,0,0)$	104	112	124	137
$\gamma^v(-\omega;\omega,\omega,-\omega)$	204	220	245	267
$\gamma^v(-2\omega;\omega,\omega,0)$	0.5	1	1	2
$\alpha^e(0;0)$	315		428	
$\gamma^e(0;0,0,0)$	158		210	

$$\begin{aligned}\left(\frac{\partial \alpha_{xx}}{\partial \xi}\right)_0 &= \left[\frac{\partial}{\partial \xi}\left(-\frac{\partial^2 E(F_x)}{\partial F_x^2}\right)_{F_x=0}\right]_0\\ &= \left[\frac{\partial^2}{\partial F_x^2}\left(-\frac{\partial E(F_x)}{\partial \xi}\right)_0\right]_{F_x=0}\\ &= \left(\frac{\partial^2 \tau_\xi(F_x)}{\partial F_x^2}\right)_{F_x=0}. \end{aligned} \tag{14}$$

Here ξ is a Cartesian displacement (from equilibrium) of a particular carbon atom, $E(F_x)$ is the energy in the presence of an applied field F_x, and $\tau_\xi(F_x)$ is the corresponding force. The advantage of Eq. (14) is that a complete set of Cartesian forces can be determined analytically for any F_x by means of the GAUSSIAN94 (Ref. 23) program. Then, using the transformation from Cartesian to normal coordinates given by Ref. 19 we can obtain the normal coordinates forces and finally differentiate numerically with respect to the field to find the desired electrical property derivatives. For satisfactory accuracy in the FF procedure it is necessary to (1) remove higher-order contaminants introduced by large field and (2) overcome the loss of significant figures when small fields are applied. The Romberg procedure[24] was adopted to deal with item (1); for item (2) a tight optimization threshold was chosen to minimize the residual zero-field forces and 12 significant figures were retained in the force calculations. We found that fields in the range $2^k F_0$ with $F_0 = 32\times 10^{-4}$ a.u. and $k = 0,1,2,3$ worked best in this context. From the value of the energy obtained in these same calculations we also found the static α^e and γ^e using the Romberg technique.

RESULTS

As noted above, the transformation from Cartesian to normal coordinates and the vibrational frequencies were taken from the DFT treatment of Giannozzi and Baroni.[19] For comparison purposes we also carried out a HF normal coordinate analysis. Because of computational limitations the latter was done in the STO-3G minimum Gaussian Slater-type Orbital basis. Table I lists the calculated and experimental frequencies of the four F_{1u} modes as well as the three particular Raman-active modes that dominate the $[\alpha^2]^{0,0}$ term. The Hartree-Fock frequencies have been uniformly scaled by the usual factor of $\sqrt{0.8}$ to account for the overly steep potential. Although the optimum bond lengths are somewhat different for the two calculations (for HF, 1.376 and 1.463 Å; for DFT, 1.393 and 1.446 Å) the relevant vibrational frequencies are in rather close agreement; the average magnitude of the difference is 11.5 cm^{-1}.

The required electrical property derivatives were obtained from Eq. (14) (and its analogs for μ_x, β_{xxx}) using the HF field-dependent Cartesian forces $\tau_\xi(F_x)$. Two different basis sets were employed, STO-3G and 6-31G, in order to get a ‘‘feeling’’ for the basis set error. For the same reason we also determined the transformation to normal coordinates and the vibrational frequencies from the two different Hessians—HF/STO-3G and DFT—discussed above. Our results for the vibrational polarizability and hyperpolarizabilities are reported in Table II along with the static electronic quantities. As anticipated, the larger basis set yields larger values for the vibrational and electronic properties. However, for the same Hessian, the basis set difference is only about 20% for $\gamma^v(0;0,0,0)$, $\gamma^v(-\omega;\omega,0,0)$, and $\gamma^v(-\omega;\omega,\omega,-\omega)$, whereas for most linear conjugated oligomers, the STO-3G versus 6-31G differences are much larger. Since further basis-set augmentations should have a lesser effect this gives a reasonable estimate of the basis-set error. Basis-set differences in the other listed vibrational properties—$\alpha^v(0;0)$ and $\gamma^v(-2\omega;\omega,\omega,0)$—are somewhat larger but in these cases it is clear that the vibrational contribution is negligible compared to the corresponding electronic term. Since $[\alpha^2]^{0,0} \gg [\mu\beta]^{0,0}$, the three vibrational properties of significance are almost exactly in the ratio 3:1:2 [cf. Eqs. (4), (6), and (8)]. For a given basis set, the difference between the two Hessians is less than 10% in each property. Thus, we feel that errors due to the normal coordinate transformation are probably small.

From Table II we see that the static vibrational hyperpolarizability is about twice as large as its electronic counterpart. For our best calculation (HF/6-31G electrical properties and DFT Hessian) the ratio is 1.94. The ratio for the vibrational DFWM with respect to $\gamma^e(0;0,0,0)$ is $\frac{2}{3}$ as large or 1.26, for EOKE the latter figure is reduced by 50% to 0.64, and for FWM we present a plot (see Fig. 1) of this ratio versus $\omega-\omega'$ with $\omega-\omega'$ lying between the vibrational resonances at 494 and 1504 cm^{-1}. In general, the above results are not very sensitive to basis set—they vary by about

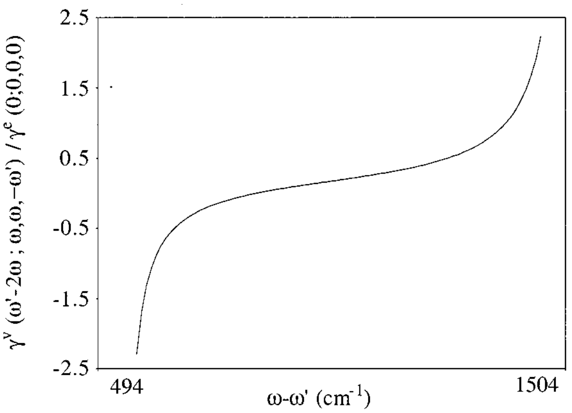

FIG. 1. Ratio for the vibrational FWM with respect to $\gamma^e(0;0,0,0)$ between the vibrational resonances at 494 and 1504 cm^{-1}.

TABLE III. Computed values of $(\partial\mu_x/\partial Q_a)^2$ (in 10^{-6} a.u.) for infrared-active modes and $(\partial\alpha_{xx}/\partial Q_a)^2$ (in 10^{-3} a.u.) for Raman-active modes of C_{60}. In the latter case, only the three modes that dominate the vibrational hyperpolarizabilities are included. For degenerate vibrations (all except 494- and 1504-cm^{-1} Raman modes) the values listed is the sum over degenerate set.

		ω (cm^{-1})	STO-3G derivatives	6-31G derivatives
STO-3G Hessian	ir	561	20	21
		587	0.5	6
		1248	14	6
		1464	7	14
	Raman	269	6	8
		495	17	14
		1506	80	99
DFT Hessian	ir	527	19	23
		589	1	5
		1217	15	7
		1462	6	12
	Raman	259	5	9
		494	20	17
		1504	77	96

10% from STO-3G to 6-31G. A similar statement applies to the difference between values determined using the DFT and HF/STO-3G Hessians. This indicates that the ratios are better determined than either the static γ^e or γ^v by itself, as is typical.

The results we have obtained for the static electronic properties can be compared to earlier studies. As far as α^e is concerned, our value of 428 a.u. is consistent with other computational methods: 417 a.u. [HF/3-21G (Ref. 28)], 441 a.u. [random-phase approximation/6-31G* (Ref. 29)], 524 a.u. [local density approximation (Ref. 9)], and 549 a.u. [incomplete neglect of differential overlap (INDO) (Ref. 8)]. Indeed, the fairly close agreement between all HF calculations beyond a minimum basis set is encouraging. Experimental values, deduced primarily from measurements of the dielectric constant in thin films[30] or fullerite crystals[31] range between 540 and 608 a.u. Recently, Antoine *et al.*[32] measured 517 ± 54 a.u. for the isolated molecule. For the polarizability, the static vibrational term has been derived from both ir (2.5 a.u.) and high-resolution electron-energy loss (8.4 a.u.) experiments.[33] Our best result is just about halfway between these two measurements.

In the case of $\gamma^e(0;0,0,0)$ previous calculations are either of the semiempirical[8–12] variety or DFT.[9,14–16] Except for the semiempirical sum-over-states treatments[10,13] the computed values fall in the range $(31-87)\times10^3$ a.u. We would expect our HF/6-31G result of 21×10^3 a.u. to increase somewhat using a larger basis and, if the linear polyenes are a guide, electron correlation would lead to a further enhancement. Thus, the consistency between the several different methods is reasonable if not quantitative. The best DFT treatment to date,[16] based on the asymptotically correct LB94 potential, gives 65×10^3 a.u. for the static limit. Recently, Geng and Wright[7] have reviewed the experimental situation, noting several difficulties in earlier work that they circumvent. Although earlier measurements[3–6] of γ gave much larger values, they obtained an upper bound of 410×10^3 a.u. in a FWM experiment. Thus, experiment is now beginning to approach theory, particularly if one takes into account the vibrational contribution. There is always the possibility that frequency dispersion would play an important role in the electronic NLO properties, but the semiempirical INDO–time-dependent HF[14] and DFT[16] studies that examined this question have found otherwise.

In addition to α^v, the dipole derivatives (squared) also determine infrared intensities, and similarly, the polarizability derivatives (squared) determine Raman intensities. It is of interest to compare our values for these properties (given in Table III) with spectroscopic measurements and other calculations. As expected, the results we obtain are more sensitive to the basis set used in determining the field-dependent forces than to the method employed in computing the Hessian. This is most notably true for the infrared-active modes. For the Raman-active modes—only those three modes that play an important role in the vibrational second hyperpolarizability (and are also the most intense) are included—the computed values are more robust. In either case the comparisons below will be made with respect to our best calculations carried out using 6-31G derivatives and the DFT Hessian.

In order to relate to experiment for the Raman effect we consider a nonresonant Stokes measurement of backscattered light. In that case the intensity I_S is given by[25]

$$I_S \approx (1+n_a)\frac{(\omega_i-\omega_a)^4}{\omega_a}\left(\frac{\partial\alpha^e_{xx}}{\partial Q_a}\right)^2, \tag{15}$$

where ω_i is the frequency of the incident light and $n_a=[\exp(\hbar\omega_a/k_BT)-1]^{-1}$ is the thermal average occupation number of mode a. Different observations of I_S at the same incident frequency turn out to be quite similar, but the results depend strongly on ω_i because of the resonance effects that occur when the photon energy begins to approach the band gap. Thus, we include in Table IV just the longest wavelength measurements[38,39] at 1064 nm, which still may reflect some resonant scattering. The agreement between both sets of experimental results and our calculations is very reasonable considering the experimental and theoretical uncertain-

TABLE IV. Comparison between various experimental and theoretical relative Raman and ir intensities. The circular frequencies are experimental values.

ω (cm^{-1})	This work	Ref. 19	Ref. 34	Ref. 39	Ref. 33	Ref. 35	Ref. 36	Ref. 37
				Raman				
270	122	122	103	93				
493	94	121	109	109				
1470	100	100	100	100				
				Infrared				
527	100	100	100		100	100	100	100
576	22	63	37		34	29	35	58
1183	30	36	23		29	29	187	141
1428	53	57	24		33	143	435	213

ties. Two other theoretical calculations have been reported. One of them is the DFT treatment of Giannozzi and Baroni[19] mentioned earlier. Despite our initial trepidations their values agree quite well with us and, by the same token, with experiment. The other is based on an empirical bond polarizability model[41] that has two versions. If hydrocarbon parameters are used substantial deviations from experiment are found. In contrast, when the five required parameters are obtained by fitting observed relative intensities for the ten Raman fundamentals of C_{60} the agreement becomes quite good.

In infrared spectroscopy one usually measures the integrated absorption coefficient C_{abs} which, for C_{60} is proportional to[40]

$$C_{\mathrm{abs}} \approx \left(\frac{\partial \mu_x^e}{\partial Q_a} \right)^2 . \tag{16}$$

As seen in Table IV the measurements of Chase, Herron, and Holler[39] (presented in Ref. 33) are similar to those of Meilunas *et al.*[34] (assuming that the latter reports C_{abs} rather than peak intensity, or equivalently, that the linewidths do not significantly vary). On the other hand, the values of C_{abs} given by Krätschmer, Fostiropoulos, and Huffman[35] are qualitatively different from those of the other two experimental groups. This is undoubtedly due, in part, to varying experimental conditions. Our best values are most nearly in accord with Ref. 33. There are significant differences; however, they must be considered against the fact that our calculations are not converged with respect to increasing the basis set and that electron correlation is not taken into account. The DFT values,[19] which in some form include correlation, differ somewhat further from Gensterblum *et al.*,[33] particularly for the (DFT) 589-cm^{-1} mode. The two semiempirical calculations[36,37] done earlier on yield intensity patterns that resemble neither the experimental observations nor the later *ab initio* treatments.

Finally, it is of interest to identify the vibrational modes that make the most significant contribution to $[\mu^2]^{0,0}$ and $[\alpha^2]^{0,0}$, which determine the vibrational polarizability and hyperpolarizability, respectively. These are reported in Table V for the calculation done using the HF/6-31G electrical property derivatives and the DFT Hessian. In contrast with linear π-conjugated chains (polyenes, polyynes, polydiacetylenes) two low-frequency (below 500 cm^{-1}) vibrations, known as *squashing* $H_g(1)$ and *breathing* $A_g(1)$ are the largest contributors to $[\alpha^2]^{0,0}$. Together they give 71% of the total value. Another 16% originates from the *pentagonal pinch* $A_g(2)$ mode, and all remaining Raman-active vibrations contribute less than 3% apiece. As far as $[\mu^2]^{0,0}$ is concerned, two vibrations in the 500–600-cm^{-1} frequency range contribute over 90% of the total.

CONCLUSIONS

We have demonstrated that Raman-active vibrations can make a major contribution to NLO properties of C_{60}—particularly the EOKE, DFWM, and FWM. Initial calculations based on the double harmonic and infinite optical frequency approximations predict a ratio of 1.26 for $\gamma^v(-\omega;\omega,\omega,-\omega)/\gamma^e(0;0,0,0)$ and 0.64 for $\gamma^v(-\omega;\omega,0,0)/\gamma^e(0;0,0,0)$. The corresponding ratio for FWM depends upon the splitting of the degeneracy, i.e., $\omega-\omega'$ (see Fig. 1). Based on a comparison with relativistic HF (RHF) STO-3G properties and/or RHF/STO-3G normal modes, as well as past experience, we judge that the ratios are more accurately determined than either the numerator or denominator separately. Our results for C_{60} are similar to those calculated previously for the linear polyenes[42] with regard to their magnitude and the unimportance of infrared-active vibrations. However, for C_{60} the vibrational effect is somewhat larger while the modes that contribute the most occur at much lower frequency.

The treatment presented here omits a number of factors

TABLE V. Contributions of individual modes to the static α^v (in a.u.) and γ^v (in 100 a.u.) of C_{60}. In the case of γ^v only the most important vibrations are included. The percent of the total is given in parentheses.

ω (cm^{-1})		Type of cage deformation	$\alpha^v(0;0)$	$\gamma^v(0;0,0,0)$
259	H_g	Radial		184 (46%)
494	A_g	Breathing		101 (25%)
527	F_{1u}	Radial	4.06 (77%)	
589	F_{1u}	Radial	0.70 (14%)	
1217	F_{1u}	Tangential	0.23 (4%)	
1462	F_{1u}	Tangential	0.28 (5%)	
1504	A_g	Tangential		62 (16%)

including mechanical and electrical anharmonicity as well as the effect of correlation on electrical properties. A recent study[43] shows that anharmonicity does not significantly affect NR in planar π-conjugated oligomers but can be significant for EOKE in the nonplanar case. The situation for C_{60} is difficult to predict except to say that very extensive computations would be required. Similarly, it is not known to what extent correlation will have a differential influence on the vibrational versus the electronic hyperpolarizability. If it can be established that the DFT electrical properties are reliable for C_{60}, then it would be practical to investigate this point. We also note that neither zero-point vibrational averaging nor solvent effects have been examined here.

The experimental situation for C_{60} is at least as unsettled as the theoretical results but the vibrational contribution appears to bring experiment and theory closer. We have established that the vibrational contribution must be considered in making comparisons of the two and have provided an estimate for the ratio of the vibrational versus electronic terms.

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