Comment on "Large Infrared Nonlinear Optical Response of C_{60}"

In a recent Letter, Blau *et al.* [1] measured the nonlinear optical response of C_{60} molecules using degenerate four wave mixing at 1.064 μm. From the observed diffraction efficiency, they infer that the hyperpolarizability of the C_{60} molecule is $|\gamma| = (1.5 \pm 0.3) \times 10^{-42}$ $m^5 V^{-2}$. They present a simple model of delocalized electrons on a spherical surface, from which they calculate a γ which is in agreement with the foregoing number. From this agreement, they conclude that the nonlinear optical response of C_{60} is described by this delocalized electron model. We point out that there are large numerical errors in determining their experimental and theoretical values for γ and that the theory used is seriously wrong for reasons we will explain.

From the diffraction efficiency of the laser induced grating, Blau *et al.* [1] infer a $|\chi^{(3)}|^2$ ($\chi^{(3)}$ is the third-order optical susceptibility), which they plot in their Fig. 2 as a function of C_{60} dissolved in benzene. At low concentrations, this inferred $|\chi^{(3)}|^2$ depends linearly on the C_{60} concentration with an increase of about 25% at a concentration of 100 mg/L. At higher concentrations, this increase levels off, which they ascribe to aggregation. Our direct analysis of the data in the linear regime yields a hyperpolarizability of $|\gamma| = 1.3 \times 10^{-45}$ $m^5 V^{-2}$, which is about 10^3 smaller than the value presented in Ref. [1].

Blau *et al.* [1] present a model of this nonlinear optical response that assumes that the electrons are delocalized on a spherical shell. They predict that the value of the hyperpolarizability is given by Eq. (3), which is derived using the theory of Ref. [2]. Our evaluation of their Eq. (3) yields $|\gamma| = 2 \times 10^{-49}$ $m^5 V^{-2}$ which is about 8×10^6 smaller than the calculated value of Ref. [1] and it is also 7×10^3 smaller than our value inferred from the experimental data. In evaluating this number, we have used the definition of γ in esu units from Eq. (4) of Ref. [2] and in mks units from Eqs. (1) and (2) of Ref. [1]. We have also used $N = 30$ to be the number of levels with electron pairs in evaluating Eq. (3) to be in agreement with Ref. [2]. (This increased our γ by 32 as opposed to using $N = 60$ as suggested in Ref. [1].)

Furthermore, Eq. (3) cannot correctly describe the hyperpolarizability of a spherical shell for the following reasons. Blau *et al.* [1] claim that this equation is derived by an extension to three dimensions of the one-dimensional electron gas confined in box [2]. Equation (3) is identical to the one-dimensional result of Ref. [2], except for a redefinition of L to be the circumference and a to be the thickness of the spherical shell of delocalized π electrons rather than the one-dimensional width and the Bohr radius a_0. This redefinition transfers the Bohr radius, which is a constant of nature, to a shell thickness which is a variable for this problem. The correct analysis of the three-dimensional problem must also contain the constants m,e,h (or some suitable combination such as a_0), unless a specific potential is introduced which connects these constants with a. In addition, the problem of three-dimensional spherical shell differs from the one-dimensional box by the inclusion of the repulsive centrifugal barrier, which leads to eigenfunctions that are spherical Bessel functions as opposed to trigonometric functions. There must also be different statistics due to the additional quantum numbers l and m.

In summary, our direct analysis of the data yields a value of γ which is about 10^3 less than the value presented in Ref. [1]. Also, the conclusion of Ref. [1] that this nonlinearity is due to complete electron delocalization on a spherical shell is not proven.

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R. J. Knize and J. P. Partanen
Departments of Physics and Electrical Engineering
University of Southern California
Los Angeles, California 90089-0484

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