

## Comparison of bond character in hydrocarbons and fullerenes

D. W. Snoke

*Department of Physics and Astronomy, University of Pittsburgh, 3941 O'Hara Street, Pittsburgh, Pennsylvania 15260*

M. Cardona

*Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, 70506 Stuttgart, Germany*

S. Sanguinetti and G. Benedek

*Istituto Nazionale di Fisica della Materia—Dipartimento de Fisica dell'Università, Via Celoria 16, 20133 Milano, Italy*

(Received 31 January 1995; revised manuscript received 13 November 1995)

We present a comparison of the bond polarizabilities for carbon-carbon bonds in hydrocarbons and fullerenes, using two different models for the fullerene Raman spectrum and the results of Raman measurements on ethane and ethylene. We find that the polarizabilities for single bonds in fullerenes and hydrocarbons compare well, while the double bonds in fullerenes have greater polarizability than in ethylene. [S0163-1829(96)01920-0]

Countless experiments have used Raman spectroscopy to identify the vibrational spectrum of molecules. This use of Raman scattering inherently assumes (1) that the process (photon in  $\rightarrow$  photon out + phonon) is symmetry allowed, and (2) that the *change of the electric susceptibility* of the molecule, due to the particular molecular distortion associated with the phonon, is large enough to give an effect.<sup>1</sup> If the polarizability of the molecule does not change substantially during a particular vibration, then even if the scattering process is symmetry allowed, the Raman signal will appear only very weakly for that phonon. The *ab initio* estimation of these polarizability changes is difficult, however.

The "bond polarizability" model provides a greatly simplifying assumption. This model sets the polarizability of a molecule (or molecular solid) equal to the sum of polarizabilities of the individual bonds. Bonds are treated as independent clouds of electrons between the atoms, and the further simplifying assumption is made that the polarizability of these bonds depends only on their length and their total charge. Making this assumption, not only the Raman line frequencies can be fit to theory, but also the relative intensities.

This model has the benefit of providing a quantifiable measure of the basic characteristic of bonds. In what way can we say that a double bond between two carbon atoms in one molecule is similar to or different from a double bond of carbon atoms in a different molecule, or in a solid? How much do particulars of the electron distribution really affect the basic character of bonds? If we can use Raman intensities to measure the polarizabilities of the two bonds, and we find them nearly the same, we can justifiably say they have similar character.

The carbon-carbon bond, ubiquitous in biological systems, polymers, fuels, and composite materials, has received tremendous attention. Early work<sup>2</sup> showed that the bond polarizability model works well for carbon; more recent work has applied this model to hydrocarbons,<sup>3-5</sup> and carbon in graphite and diamond solids.<sup>6</sup> Following the discovery of carbon fullerenes, there has obviously been interest in

whether the carbon-carbon bonds in fullerenes have character similar to carbon-carbon bonds in other molecules.

Two previous works addressed this question using different approaches. In the first,<sup>7</sup> a next-nearest-neighbor force constant model with eight spring constants was used to reproduce the vibrational spectrum of the C<sub>60</sub> molecule, similar to the 20-spring-constant model used by Al-Jishi and Dresselhaus<sup>8</sup> to model the vibration spectrum of graphite. The icosahedral symmetry of the C<sub>60</sub> molecule was explicitly invoked in order to block diagonalize the force constant matrix, and force constants similar to those in diamond and graphite were found to give a good fit to the C<sub>60</sub> IR and Raman vibrational spectrum. Next, the phonon eigenvectors found from this fit were used in a five-parameter bond polarizability model<sup>7</sup> in order to fit Raman intensities of C<sub>60</sub> reported early in the literature.<sup>9</sup> At the time of those calculations, all the available Raman data were obtained with visible lasers, which turned out to have frequency near the electronic resonance of the fullerenes.<sup>10</sup> Reference 7 made a rough correction for the effect of this resonance, but the bond polarizabilities found from a fit of the Raman intensities did not compare well with those from hydrocarbons.

In a different approach,<sup>11</sup> a four-parameter bond charge model was used to fit the vibrational spectrum of C<sub>60</sub> and C<sub>70</sub>. Having obtained a successful fit to the vibration frequencies, this model automatically provides an estimate of the bond polarizabilities without additional fitting. This is because a bond charge model makes certain assumptions about how the charge of the bonds redistributes under distortion, which is exactly what gives a change in polarizability. No comparison to hydrocarbon polarizabilities was made at that time.

In this paper, we wish to directly compare these two models to the hydrocarbon data, using an updated fit of the model of Ref. 7 to Raman intensity data for C<sub>60</sub> taken far from resonance with a Nd:YAG (yttrium aluminum garnet) laser.<sup>12</sup> We find that a consistent picture arises from this comparison.

TABLE I. Raman intensities.

Frequency <sup>a</sup>	Relative intensity <sup>b</sup>	5-parameter fit intensity
<i>A<sub>g</sub></i> modes		
496	100	100
1470	92	92
<i>H<sub>g</sub></i> modes		
273	86	86
437	13	11
710	7	3
774	20	12
1099	11	16
1250	10	3
1428	6	5
1575	12	14

<sup>a</sup>References 9 and 12.<sup>b</sup>Reference 12.

In the bond polarizability model, the polarizability of each bond is written as

$$\bar{\alpha} = \begin{pmatrix} \alpha_{\perp} + \alpha'_{\perp} d\ell & & \\ & \alpha_{\perp} + \alpha'_{\perp} d\ell & \\ & & \alpha_{\parallel} + \alpha'_{\parallel} d\ell \end{pmatrix}, \quad (1)$$

where the  $z$  axis is along the bond, and  $d\ell$  is the change in length of the bond. This leads to four parameters for each bond, namely, the isotropic part  $2\alpha_{\perp} + \alpha_{\parallel} \equiv \mathcal{P}$ , and its first derivative, and the anisotropic part,  $\alpha_{\parallel} - \alpha_{\perp} \equiv \mathcal{Q}$ , and its first derivative. [In theory,  $\alpha_{\perp}$  could have different values along the  $x$  (in-plane) and  $y$  (out-of-plane) directions, but the data do not warrant such a distinction here.] Because the constant isotropic part just contributes to the overall dielectric constant, this leaves three parameters that contribute to the Raman intensities. Since the single and double bonds can have different character, six parameters should actually be used. Usually, however, the absolute intensities of the Raman lines are not measured, and therefore the absolute values of these parameters cannot be determined. This leads to five ratios among the parameters for the relative intensities of the Ra-

TABLE II. Bond polarizability parameters.

	Hydrocarbon data <sup>a</sup>	Ref. 7 model fit to Ref. 12 data	Bond charge model <sup>b</sup>
$\mathcal{P}'_s/\mathcal{Q}'_s$	1.35	1.31	1.56
$\mathcal{Q}'_s/\mathcal{Q}'_s r_0$	0.41	0.34	0.31
$\mathcal{Q}'_d/\mathcal{Q}'_s$	1.13	2.92	2.96
$\mathcal{P}'_d/\mathcal{Q}'_s$	2.81	4.97	4.68
$\mathcal{Q}'_d/\mathcal{Q}'_s r_0$	0.46	0.98	0.93

<sup>a</sup>References 3 and 4.<sup>b</sup>Reference 11.

man lines. By symmetry, the two  $A_g$  Raman lines of  $C_{60}$  depend only on the two isotropic parameters  $\mathcal{P}_s$  and  $\mathcal{P}_d$  for the single and double bonds, respectively, and the eight  $H_g$  symmetry lines depend only on the other four parameters.

The results of the fit of the model of Ref. 7 to the off-resonant Raman data for  $C_{60}$  (Ref. 12) to the Raman data are shown in Table I. Table II shows the ratios of polarizability parameters obtained from this fit and from the bond-charge model.<sup>11</sup> Although the bond charge model in principle does not need a fit for the polarizability parameters, in practice the parameter  $\mathcal{Q}'/\mathcal{Q}$  is not well determined by the fit to the vibration spectrum, because the anharmonic part of the interatomic Keating potential is not well known.<sup>13</sup> In order to best fit the  $A_g$  line intensities, a value of  $\mathcal{Q}'/\mathcal{Q}=0.43 \text{ \AA}=0.3r_0$  was used in the bond charge model of Ref. 11 [where the interatomic spacing in  $C_{60}$  is  $r_0=1.4 \text{ \AA}$  (Ref. 14)].

As seen in this table, the parameters obtained in these two very different ways agree remarkably well. These are compared to the experimental values from ethane ( $CH_6$ , with one single carbon-carbon bond) and ethylene ( $CH_4$ , with one double carbon-carbon bond). This comparison indicates that in both of these models the polarizability of the double bonds in  $C_{60}$  is about twice that of the double bond in ethylene. The bond charge model suggests that this result has a physical basis in the way the charge on the double bonds redistributes.

We thank J. Menéndez, S. Montero, and G. Onida for helpful discussions. We acknowledge partial financial support from Italian Consiglio Nazionale delle Ricerche through project "Crescita, caratterizzazione e proprietà di strutture fullereniche."

<sup>1</sup>See, e.g., M. Cardona, in *Light Scattering in Solids II*, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982).<sup>2</sup>A.A. Maradudin and E. Burstein, *Phys. Rev.* **164**, 1081 (1967).<sup>3</sup>J. Martin and S. Montero, *J. Chem. Phys.* **80**, 4610 (1984).<sup>4</sup>M.F. Oruna, A. del Olmo, C. Domingo, and S. Montero, *J. Mol. Struct.* **142**, 201 (1986).<sup>5</sup>J.M. Fernandez-Sanchez and S. Montero, *J. Chem. Phys.* **90**, 2909 (1989).<sup>6</sup>S. Go, H. Bilz, and M. Cardona, *Phys. Rev. Lett.* **34**, 580 (1975).<sup>7</sup>D.W. Snoke and M. Cardona, *Solid State Commun.* **87**, 121 (1993).<sup>8</sup>R. Al-Jishi and G. Dresselhaus, *Phys. Rev. B* **26**, 4514 (1982).<sup>9</sup>D.S. Bethune *et al.*, *Chem. Phys. Lett.* **179**, 181 (1991).<sup>10</sup>K. Sinha *et al.*, *Chem. Phys. Lett.* **186**, 287 (1991).<sup>11</sup>S. Sanguinetti, G. Benedek, M. Righetti, and G. Onida, *Phys. Rev. B* **50**, 6743 (1994).<sup>12</sup>B. Chase, N. Herron, and E. Holler, *J. Chem. Phys.* **96**, 4262 (1992).<sup>13</sup>E. Anastassakis, A. Cantarero, and M. Cardona, *Phys. Rev. B* **41**, 7529 (1990).<sup>14</sup>T. Shibusya and M. Yoshitani, *Chem. Phys. Lett.* **137**, 13 (1987).