Comparison of Bond Character in Hydrocarbons and Fullerenes

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Abstract

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.
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. [1] If the polarizability of the molecule does not change substantially during a particular vibration, then even if the scattering process is symmetry allowed, Raman signal will appear only very weakly for that phonon. The \textit{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 [2] showed that the bond polarizability model works well for carbon; more recent work has applied this model to hydrocarbons [3–5], and carbon in graphite and diamond solids [6]. 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
a next-nearest-neighbor force constant model with eight spring constants was used to reproduce the vibrational spectrum of the $C_{60}$ molecule, similar to the 20-spring-constant model used by Al-Jishi and Dresselhaus to model the vibration spectrum of graphite. The icosahedral symmetry of the $C_{60}$ 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 $C_{60}$ IR and Raman vibrational spectrum. Next, the phonon eigenvectors found from this fit were used in a five-parameter bond polarizability model in order to fit Raman intensities of $C_{60}$ reported early in the literature. At the time of those calculations, all the available Raman data were obtained with visible lasers, which turned out to have frequency near to the electronic resonance of the fullerenes. Ref. 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, use has been made of a four-parameter bond charge model to fit the vibrational spectrum of $C_{60}$ and $C_{70}$. 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. to Raman intensity data for $C_{60}$ taken far from resonance with a Nd:YAG laser. We find that a consistent picture arises from this comparison.

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

$$\tilde{\alpha} = \begin{bmatrix} \alpha_\perp + \alpha'_\perp \cdot d\ell \\ \alpha_\perp + \alpha'_\perp \cdot d\ell \\ \alpha_\parallel + \alpha'_\parallel \cdot d\ell \end{bmatrix}$$

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 $2\alpha_\perp + \alpha_\parallel \equiv P$, and its first derivative, and the anisotropic part, $\alpha_\parallel - \alpha_\perp \equiv Q$, 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 Raman lines. By symmetry, the two $A_g$ Raman lines of $C_{60}$ depend only on the two isotropic parameters $P_s$ and $P_d$ 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 $C_{60}$ to the Raman data are shown in Table 1. Table 2 shows the ratios of polarizability parameters obtained from this fit and from the bond-charge model [11]. Although the bond charge model in principle does not need a fit for the polarizability parameters, in practice the parameter $Q'/Q$ is not well determined by the fit to the vibration spectrum, because the anharmonic part of the interatomic Keating potential is not well known [13]. In order to best fit the $A_g$ line intensities, a value of $Q'/Q = 0.43 \AA = 0.3 r_0$ was used in the bond charge model of Ref. [11] (where the interatomic spacing in $C_{60}$ is $r_0 = 1.4 \AA$ [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.

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### Table 1. Raman Intensities

| Frequency | Relative Intensity | 5-parameter Fit Intensity |
|-----------|--------------------|--------------------------|
| 496       | 100                | 100                      |
| 1470      | 92                 | 92                       |
| **H<sub>g</sub> 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                       |

### Table 2. Bond Polarizability Parameters

| hydrocarbon data: [3,4] to Ref. [12] | Bond charge model fit: [11] |
|---------------------------------------|------------------------------|
| \(P_s'/Q_s'\)                        | 1.35                         |
| \(Q_s/Q_s'r_0\)                      | 0.41                         |
| \(Q_d/Q_s'\)                         | 1.13                         |
| \(P_d'/Q_s'\)                        | 2.81                         |
| \(Q_d/Q_s'r_0\)                      | 0.46                         |
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