

A Bond Polarizability Model for the C₆₀ Raman Spectrum

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Abstract. We have used a force-constant model to calculate all of the Raman- and infrared-active vibrational mode frequencies of C₆₀ within 3% of experimental values. Using the eigenvectors of the vibrations predicted by this model, we calculate the relative intensities of all of the Raman lines via a bond polarizability model. We compare the bond polarizabilities predicted by our model to those of single and double carbon-carbon bonds in hydrocarbons.

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One of the reasons that C_{60} “buckyballs” have received so much attention in the physics community, apart from leading when doped to high-temperature superconductivity, is the fact that they are one of the few examples in nature of icosahedral symmetry. This has changed the machinery of icosahedral group theory from a mere mathematical exercise into a useful tool for predictive theories. Beyond its applications for this new phase of carbon, the study of icosahedral symmetry has also been suggested as a cure for the common cold and AIDS.[1]

In this work, we take full advantage of the icosahedral symmetry of C_{60} to calculate its Raman and infrared vibrational frequencies and their shifts with pressure using a simple harmonic force-constant model of the carbon bonds. Using the eigenvectors of the same model, we predict the relative intensities of the 10 Raman lines by making a simple assumption about the bond polarizabilities. A basic question regarding the nature of buckyballs is whether the concept of “transferability” applies.[2] In other words, is a carbon-carbon bond in one material essentially the same as a carbon-carbon bond in other materials? Having obtained the polarizability constants of the single and double bonds in C_{60} from our fits to the Raman spectra, we can compare these to values already known for other carbon-based systems, including diamond and various hydrocarbons. We find that the values obtained for these constants in C_{60} deviate significantly from those found for the carbon bonds in other materials.

Calculation of the Vibrational Frequencies. Although *ab initio* molecular dynamics models of the vibrational spectrum of C_{60} have appeared,[3, 4] a force constant model of the vibrational frequencies has two advantages. First, the vibrational frequencies

can be fit to much higher accuracy using the force constants as parameters. Our model gives an average deviation of the predicted vibrational frequencies from the experimental Raman and infrared values of 1.5%, and no frequency has greater than 3% discrepancy with the experimental data, compared to discrepancies on the order of 10-20% in the *ab initio* models. Second, variation of the harmonic force constants in the model can give a better intuitive understanding of the dependence of various mode frequencies on certain bond changes.

We follow the formalism of Weeks and Harter[1] to block diagonalize the force constant matrix of C_{60} using icosahedral symmetry. Ref. [1], published before conclusive evidence of the existence of buckyballs had appeared, develops the representation formalism of the icosahedral group at length, including a prescription for the 1200 matrices of the 120 group operators in the 10 irreducible representations. We therefore present here only an overview of the procedure for diagonalization and how our model differs from theirs.

The model of Weeks and Harter employed four force constants to account for the following motions: nearest-neighbor stretching of the single bonds (p), nearest-neighbor stretching of the double bonds (h), bond bending in a pentagon (π), and bond bending in a hexagon (η). Variation of these parameters does not give a good fit to the experimental spectrum. In particular, the frequencies of the two A_g modes, which depend only on the two radial force constants, can not be simultaneously fit by variation of these two constants since the experimental values lie too close together in frequency— the two A_g frequencies have a minimum ratio of 3.52 in a model with only nearest-neighbor interactions.[5] Also, the $H_g(3)$ mode always appears much too low in frequency in this

model, while experimentally it is very close to the $H_g(4)$ frequency.

In analogy with the successful lattice dynamical model of Al-Jishi and Dresselhaus[6] for graphite, we include second-nearest-neighbor radial force constants and out-of-plane tangential force constants. This adds four more constants: second-nearest neighbor radial stretching across a pentagon ($p^{(2)}$), second-nearest neighbor radial stretching across a hexagon ($h^{(2)}$), out-of-plane bond bending of a single bond, relative to the tangent plane of the ball ($\pi^{(\perp)}$), and out-of-plane bond bending of a double bond, relative to the tangent plane of the ball ($\eta^{(\perp)}$). One can think of these last two as bending of the angle between a single or double bond and the dangling π bond on each atom.

The inclusion of the second-nearest-neighbor radial constants allows a good fit of the two A_g modes; the inclusion of the out-of-plane bond bending constants primarily affects the low- frequency H_g and T_{1u} modes which have a “dimpling” character, i.e. motion of atoms in opposite directions relative to the ball surface, in particular the $H_g(3)$ mode, as seen in the useful stereoscopic pictures of the modes in Ref. [1]. It turns out that the fit values of the out-of-plane bond bending constants are almost exactly the same as the in-plane bond bending constants.

Al-Jishi and Dresselhaus actually took into account interactions up to the fourth nearest neighbor, but we find that a model with only second-nearest neighbor interactions fits the ambient- pressure data adequately. In their model, the third-nearest neighbor interactions had an order of magnitude less strength than the first and second nearest neighbor interactions. We completely neglect interball interactions in this model.

Following Weeks and Harter, we use a four-point finite difference method to numeri-

cally calculate the second derivatives of the potential energy relative to in-plane (tangent to the ball surface) and out-of-plane motions of a carbon atom and its nearest and next-nearest neighbors. The 180×180 force matrix is then block diagonalized by icosahedral symmetry projection. The only blocks of interest to us are the five degenerate 8×8 H_g blocks and the 2×2 A_g block, which are Raman active, and the three degenerate 5×5 T_{1u} blocks, which are infrared active. The calculation of all the vibrational frequencies for a given choice of force constants therefore reduces to the diagonalization of three small matrices.

Fitting the experimental Raman and infrared data of Bethune et al.[7] (data reproduced within a percent or so by Refs. [8]-[12] and others), we find the values of the four pairs of force constants shown in Table 1. The bond-bending force constants are compared to the tangential force constants of Ref. [6] using a nearest-neighbor distance of 1.42 \AA for graphite, nearly the same as the nearest neighbor distance in C_{60} . The nearest-neighbor constants are also compared to the values for a first-order Keating model for diamond.[13, 14] As seen in this table, the values for the fullerene are comparable to those of graphite and diamond.

The predicted values of the vibrational frequencies are given in Table 2. For comparison, the best-fit predictions of a four-parameter bond-charge model[15] are given, as well as the best fit of a two-parameter Keating model,[13] which is the same as our model with $p=h$, $p^{(2)}=h^{(2)}=0$, and $\pi = \eta = \pi^{(\perp)} = \eta^{(\perp)}$. The bond-charge model gives nearly as good a fit as our model, although the physical pictures of the two models are quite different. One indication of the physical validity of our model is that it reproduces the

accidental degeneracy of the $H_g(7)$ and $T_{1u}(4)$ modes over a wide range of choices of force constant. Also, when we fit only the 10 Raman lines, and calculate the T_{1u} frequencies as a theoretical prediction, the values of the force constants found from the fit to the Raman data yield all four of the experimental infrared frequencies within 4%. Only slight adjustments of the parameters are necessary to obtain the fit of Table 1.

Our model indicates that the Bethune et al.[7] assignment of the lines is probably correct, although various authors have suggested a reassignment of the Raman lines.[10, 12] Leaving out the weak 1099 and 1250 cm^{-1} lines, assigned only tentatively as H_g modes by Bethune et al., creates a large gap in the H_g frequencies which the model wants to fill. Duclos et al.[12] observed several other Raman lines and reported no observation of the 273 cm^{-1} line in vacuum. The extra lines may be due to solid state interball interactions inhibited by oxygen; since the 273 cm^{-1} line appears quite strongly in other data, including in samples dissolved in liquid CS_2 [16], we feel there is good reason to take this as an internal mode of C_{60} . An interesting possibility involves reassignment of one high-frequency mode. Several workers have seen a weak line at 1625 cm^{-1} , e.g. Ref. [12] and Ref. [9]; it is also seen in the raw data of Bethune et al. One could interpret this as an H_g line and the 1428 cm^{-1} line as the forbidden infrared $T_{1u}(4)$ line, since several forbidden infrared lines appear in the Raman spectrum at low frequencies under certain conditions and the accidental degeneracy of these two modes within 1 cm^{-1} seems highly coincidental. The Bethune assignment is supported by several facts, however. When we use our model to fit the vibrational frequencies of this alternate line assignment, the best fit misses the 1575 cm^{-1} H_g line by 100 cm^{-1} , while as stated above our model fits all the

lines in the Bethune assignment within 3% and reproduces naturally the $H_g(7)$ and $T_{1u}(4)$ near-degeneracy in the Bethune assignment, supporting the view that this coincidence is real. Experimentally, the 1428 cm^{-1} line appears strongly under a wide variety of conditions. The fact that the $H_g(7)$ line and the $T_{1u}(4)$ line have very different shifts with pressure,[9, 17] so that the degeneracy does not remain, confirms the assumption of accidental degeneracy.

Calculation of the Raman Line Intensities. Using the fitted parameters and frequencies of Tables 1 and 2 for the vibrational modes, we can obtain the eigenvectors of the vibrational motion of the atoms and use the first-order theory of Raman scattering to calculate the relative intensities of the Raman lines.

The relative first-order Stokes Raman line intensities far from resonance are given by[18]

$$\frac{d\sigma_s}{d\Omega} \propto \omega_S^4 \left| \hat{e}_S \cdot \frac{\partial \tilde{\chi}}{\partial \xi} \cdot \hat{e}_L \right|^2 (1+n)/\omega \quad (1)$$

where $\tilde{\chi}$ is the susceptibility matrix, \hat{e}_L and \hat{e}_S are the unit vectors in the directions of the incident and scattered radiation, respectively, and ξ represents the amplitude of the eigenvector with eigenfrequency ω . The Bose-Einstein $(1+n)$ factor gives a correction for the low-frequency modes at room temperature.

In molecular substances the ansatz is well established that the total susceptibility is just the sum of the individual polarizabilities of the bonds, normalized to the volume, i.e. $\tilde{\chi} = \Sigma \tilde{\alpha}$; for example, Ref. [19] demonstrates this for carbon. One can make in addition the “bond polarizability” hypothesis, that the polarizability of each bond is simply a function of bond length ℓ . Ref. [20] showed that this assumption works well for a fit

to the first- and second-order Raman spectra and the elasto-optic constants of diamond; it works less well for crystalline Si and Ge, a fact which is attributed to the greater metallicity of these materials.

Making this assumption, the polarizability matrix of each bond is then simply

$$\tilde{\alpha} = \begin{vmatrix} \alpha_{\perp} + \alpha'_{\perp} \cdot d\ell & & \\ & \alpha_{\perp} + \alpha'_{\perp} \cdot d\ell & \\ & & \alpha_{\parallel} + \alpha'_{\parallel} \cdot d\ell \end{vmatrix} \quad (2)$$

where the z axis is along the bond. This matrix can be calculated in an absolute coordinate system for each of the 90 bonds in the buckyball (60 single bonds and 30 double bonds) by simple three-dimensional rotation of the matrices given the vector of the bond direction in the absolute coordinate system.

We find the eigenvectors for the ten Raman modes from the 2×2 A_g matrix and the 8×8 H_g matrix used in our force constant model during the diagonalization process and then use the icosahedral projection recipe of Weeks and Harter in reverse to find the position of each of the 60 atoms in the ball in absolute x,y, and z coordinates for some small displacement $d\xi$ along the eigenvector. The change of each bond length and direction is calculated, and the derivative $\partial\tilde{\alpha}/\partial\xi$ is found by a two-point difference method.

Once the matrix $\partial\tilde{\alpha}/\partial\xi$ is calculated for each bond in an absolute reference frame, these are summed to give the total matrix $\tilde{\chi}$. The relative intensities I_{xx} for $\hat{e}_L \parallel \hat{e}_S$ are found for each eigenfrequency via Eq. (1), averaging over all 4π radians of possible incident direction. In principle we could also find calculate the intensity I_{xy} for $\hat{e}_L \perp \hat{e}_S$ for each mode, but the H_g modes all have a depolarization ratio I_{xy}/I_{xx} of 0.75 by symmetry,

while the totally-symmetric A_g modes all have zero depolarization. In fact, depolarization ratios substantially less than 0.75, for the H_g modes are seen experimentally[7], on the order of 0.3, while slightly nonzero depolarization is seen for the A_g Raman lines, on the order of 0.1. We can understand this as arising from small deviations from perfect H_g and A_g symmetry of the modes; deviations of the order ϵ will give deviations from the theoretical depolarization ratio linear with ϵ in the case of the H_g modes and proportional to ϵ^2 in the case of A_g modes, since I_{xy} is at a minimum. Our calculations which assume perfect symmetry always give the exact theoretical result of the depolarization ratio for the mode symmetry, however.

Our model for the intensities of the Raman lines has six parameters: the first derivatives of the perpendicular and parallel polarizabilities of the single and double bonds, $\alpha'_\perp(s)$, $\alpha'_\parallel(s)$, $\alpha'_\perp(d)$, and $\alpha'_\parallel(d)$, and the differences of the absolute polarizabilities, $(\alpha_\parallel(s) - \alpha_\perp(s))$ and $(\alpha_\parallel(d) - \alpha_\perp(d))$ for the single and double bonds, respectively, which come into play because of the changes in orientation of the bonds during the vibrations. Since we are calculating only relative intensities, however, the fit is really a five parameter search since an overall multiplicative constant for the parameters can be chosen arbitrarily— the absolute values of the constants can only be calculated given an additional constraint, for instance a measurement of the dielectric constant versus the volume of a buckyball, $2\alpha'_\perp(s) + \alpha'_\parallel(s) + 2\alpha'_\perp(d) + \alpha'_\parallel(d)$. The H_g intensities are multiplied by five relative to the A_g intensities to take into account the fivefold degeneracy of these modes. A slight correction is also made for the effect of the broad resonance around 2.4 eV;[16] the resonance is assumed to enhance the intensities by simple linear factor of $(1 + A\omega)$, which gives a

factor of two increase of intensity over the phonon frequency range. This correction leads to at most a 20% change in the polarizability constants.

In Table 3 we show a fit of the Raman intensity data of Bethune et al. [7], corrected to give a total integrated intensity of each line taking into account the varying linewidths; Table 4 gives the resulting values of the polarizability parameters. (The overall multiplicative constant for the polarizability parameters is chosen to give equal values of the second fit parameter, the trace of the first-derivative polarizability matrix for the single bonds.) The isotropic A_g modes depend only on the traces of the first derivative polarizability matrix of the single and double bonds, $2\alpha'_{\perp}(s)+\alpha'_{\parallel}(s)$ and $2\alpha'_{\perp}(d)+\alpha'_{\parallel}(d)$; the H_g modes depend only on the depolarizing terms, $\alpha'_{\parallel}(s)-\alpha'_{\perp}(s)$, $\alpha'_{\parallel}(d)-\alpha'_{\perp}(d)$, $\alpha_{\parallel}(s) - \alpha_{\perp}(s)$, and $\alpha_{\parallel}(d) - \alpha_{\perp}(d)$. As seen in Table 3, a good fit can be obtained for the experimental Raman intensities.

Table 4 compares the fit polarizabilities to values from Raman-scattering studies of the single and double bonds in hydrocarbons.[2, 21] The values for single bonds from hydrocarbons have been shown to agree with the bond polarizabilities found for diamond,[20] using a reasonable local-field correction.[2] The numbers shown for the double bond of carbon come from ethylene,[21] which has only double carbon-carbon bonds; Ref. [21] also shows that the in-plane and out-of-plane values of α'_{\perp} in ethylene are nearly the same, as assumed here for C_{60} .

As seen in this table, the fit values for the carbon bonds in C_{60} are only roughly comparable to those for hydrocarbon bonds. The most significant discrepancy is the fact that the one-parameter fit to the two A_g lines implies a ratio of $(2\alpha'_{\perp}(s)+\alpha'_{\parallel}(s))/(2\alpha'_{\perp}(d)$

$+\alpha'_{\parallel}(\text{d})$) of around 0.2, whereas for the Montero data the ratio is closer to 0.5. This seems to imply that the character of the carbon-carbon bonds in C_{60} deviates substantially from the character of bonds in hydrocarbons. This is not entirely surprising, since the absolute polarizability of C_{60} is known to be much larger than that of hydrocarbons, as evidenced by the fact that in mixtures of C_{60} and hydrocarbons only the Raman lines of C_{60} appear.[22, 23] Apparently the presence of dangling π orbitals substantially affects the total polarizability.

Conclusion. Bermejo et al.[2] showed that the polarizability of the single bonds of diamond is transferable to the polarizability of the single carbon-carbon bonds in saturated hydrocarbons. Our work indicates that the polarizability constants of the single and double bonds of C_{60} are not perfectly transferable. Using a bond polarizability model we can obtain a good fit of the Raman intensity data, but values of the single and double bond polarizabilities which deviate from literature values for carbon bonds in hydrocarbons by up to a factor of three. The force constants obtained in fitting the vibrational frequencies similarly have values of the same order of magnitude as those for carbon-carbon bonds in other materials, but have deviations of up to a factor of two.

We have been able to reproduce all of the main features of the Raman spectra of C_{60} using simple models of the carbon-carbon bonds and taking advantage of the icosahedral symmetry of the ball. A basically consistent picture of the vibrational spectrum is obtained which indicates that the common mode assignment[7] is correct.

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Table 1. Force Constants

radial force constants (in 10^5 dyne/cm):

	this work	graphite, Ref. [6]	diamond, Ref. [14]
p	3.66	3.13	3.20
h	4.12		
$p^{(2)}$	0.66	1.21	
$h^{(2)}$	0.47		

bond bending force constants (in 10^5 dyne/cm):

	this work	graphite, Ref. [6]	diamond, Ref.[14]
π	0.62	1.33	1.09
η	0.28		
$\pi^{(\perp)}$	0.54	0.43	1.09
$\eta^{(\perp)}$	0.30		

Table 2. Raman and Infrared Frequencies

Assignment	Expt., Ref. [7]	8-parameter fit	4-parameter bond-charge model Ref.[15]	Keating model, $\beta/\alpha=0.2$
A _g (1)	496	483	496	402
A _g (2)	1470	1450	1435	1446
H _g (1)	273	270	265	257
H _g (2)	437	450	408	466
H _g (3)	710	700	726	661
H _g (4)	774	775	786	684
H _g (5)	1099	1112	1149	1043
H _g (6)	1250	1225	1207	1257
H _g (7)	1428	1443	1433	1517
H _g (8)	1575	1570	1651	1669
T _{1u} (1)	527	518	527	510
T _{1u} (2)	577	599	586	576
T _{1u} (3)	1183	1193	1177	1172
T _{1u} (4)	1428	1442	1423	1478
average relative error:		1.5%	2.2%	5.5%

Table 3. Raman Intensities from the Bond Polarizability Model

Frequency Ref. [7]	Integrated Intensity Ref. [7]	5-parameter Fit Intensity
A _g modes:		
496	42.7	43.0
1470	100.	100.
H _g modes:		
273	20.4	23.0
437	9.1	9.0
710	8.5	9.8
774	13.3	11.4
1099	2.3	1.5
1250	2.3	2.0
1428	20.7	18.0
1575	18.8	20.7

Table 4. Polarizability Constants

single bonds:	Fit values	Ref.[2] values
$(\alpha'_{\parallel} - \alpha'_{\perp})/r_0^2$	1.2 ± 0.1	1.8 ± 0.3
$(2\alpha'_{\perp} + \alpha'_{\parallel})/r_0^2$	1.7 ± 0.2	1.7 ± 0.4
$(\alpha_{\parallel} - \alpha_{\perp})/r_0^3$	0.5 ± 0.05	1.2 ± 0.2
double bonds:	Fit values	Ref. [21] values
$(\alpha'_{\parallel} - \alpha'_{\perp})/r_0^2$	1.5 ± 0.1	6.5 ± 0.7
$(2\alpha'_{\perp} + \alpha'_{\parallel})/r_0^2$	3.2 ± 0.1	7.8 ± 1.0
$(\alpha_{\parallel} - \alpha_{\perp})/r_0^3$	0.6 ± 0.05	0 ± 0.2