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M. R. Manaa

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Enhanced Energetic Stability and Optical Activity of Symmetry-Reduced C₆₀

M. Riad Mana'a

University of California, Lawrence Livermore National Laboratory, Energetic Materials Center, P.O. Box 808, L-282, Livermore, California, 94551

Mana'al@llnl.gov

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Since its discovery in 1985,¹ the celebrated geodesic cage structure of the C₆₀ molecule has been recognized:² a truncated icosahedron in which all sixty vertices are equivalent and has the full I_h symmetry, making it thus far the most spherical of all known molecules. Inherent in this high symmetry is an intricate network of electron-phonon coupling, evident in phonon progressions and vibronic peak broadening,³ and resulting in structural distortions of neutral C₆₀ in the presence of solvent.⁴⁻⁶ Within the I_h symmetry group of this molecule, of the forty-six distinct vibrational frequencies only ten are Raman-active and four are IR-active (in the first order), while the remaining 32 modes are optically silent.⁷ Symmetry-reduced structures of C₆₀ would activate some of these silent modes, which could then be amenable to experimental verification such as in resonance Raman scattering.^{6, 8-9} Here, quantum chemical calculations within density functional theory establish for the first times (1) lower-symmetry, energetically more stable structures for C₆₀, the lowest of which is of D_{3d} symmetry, and with a new assignment of the ground state as the ¹A_g state, (2) the activation of some IR and Raman I_h silent modes: the IR H_u mode around 540 cm⁻¹ and G_u band at 1465 cm⁻¹, and the Raman G_g mode around 1530 cm⁻¹.

Several quantum chemical calculations at the density functional B3LYP and BPW91 levels,¹⁰⁻¹⁴ and using two different basis sets (Table 1) were performed for symmetry constrained structures of C₆₀: I_h, T_h, D_{5d}, D_{3d}, and S₆. Optimization within these symmetry constraints proved, consistently, the D_{3d} structure to be the lowest energy conformation at all levels of theory, being 0.8-0.9 kcal/mol lower than the I_h symmetry molecule, as listed in Table 1.

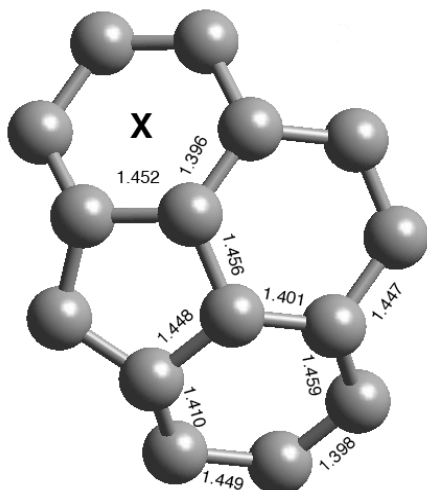


Figure 1. B3LYP/6-31G* optimized, symmetry – unique D_{3d} carbon-carbon bonds of C₆₀ (in Å). X denotes the C₃ axis of symmetry.

Table 1. Energetic of symmetry-constraints structures of C₆₀ at various levels of theory.

Method	Total Energy	Relative Energy ^a		
	I _h	D _{3d}	D _{5d}	S ₆
B3LYP/6-31G*	-2286.173080	-0.8	-0.6	-0.7
B3LYP/cc-pVDZ	-2286.314164	-0.9	-0.7	-0.7
BPW91/6-31G*	-2286.069710	-0.9	-0.7	-0.7

^a in Kcal/mol.

Figure 1 shows the optimized unique bonds of the lowest energy D_{3d} symmetric C₆₀ at the B3LYP/6-31G* level of computation. Within this symmetry, there are 10 unique carbon-carbon bonds. Optimization of the I_h structure at the same level yields 1.454 and 1.396 Å for the two unique C-C bonds, to be compared with neutron scattering average values of 1.391 and 1.455 Å.¹⁵ Note that the diffraction results are averages for three sets of values comprising of fifteen measured bonds. The D_{3d} optimized structure has four short bonds in the range 1.396-1.410 Å, and six long bonds within the range 1.447-1.459 Å. These values illustrate only small distortions from the I_h structure, consistent with the slight energy change reported in Table 1. The C₆₀ molecule transitions from a spherical top form in the I_h symmetry to a prolate symmetric top form in the D_{3d} symmetry structure. This symmetry lowering produces a slight, anisotropic change in the quadrupole moment from σ = -324.09 (Debye-Å) in I_h symmetry, to σ_{xx} = σ_{yy} = -324.09, σ_{zz} = -324.15 in the D_{3d} structure. It should be noted that a change in the quadrupole moment has been predicted by Gallagher et al. in order to account for their observed solvatochromism shifts of C₆₀.¹⁶

The energetic of four symmetry-reduced structures at various level of treatment are listed in Table 1, excluding the T_h symmetry structure, which was energetically identical to the I_h conformation. All three structures of D_{3d}, D_{5d}, and S₆ are almost degenerate and lower in energy than the I_h structure by as much as 0.9 Kcal/mol (49 meV) for the D_{3d} structure. Reorganization among these various symmetry structures can thus occur easily through tunneling or due to external perturbations such as solvent environment. It is interesting to note that similar D_{3d} and D_{5d} lower energy structures; Jahn-Teller distortions in the

C_{60} anion radical have been predicted.¹⁷ Transitions between neutral and anionic C_{60} , both of which are now geometrically of D_{3d} symmetry, is very favorable according to the Franck-Condon principle. Further, with the full vibrational structure of I_h , D_{3d} , and D_{5d} symmetry calculated, the D_{3d} structure has the largest zero-point energy of 235.3 kcal/mol, compared with 234.7 kcal/mol for the I_h structure at the B3LYP/6-31G* level.

A consequence of symmetry lowering is the splitting of electronic molecular energy levels. The highest occupied state of C_{60} in I_h symmetry is the completely occupied, five-fold degenerate h_u state, while the lowest unoccupied state is the three-fold degenerate t_{1u} state. The energy band gap between the HOMO and LUMO states is calculated to be 2.76 eV at the B3LYP/6-31G* level. In D_{3d} symmetry, the h_u state splits into one a_{2u} and two doubly degenerate e_u states, separated by 24 cm^{-1} . The t_{1u} LUMO state splits into a_{2u} and e_u , with the a_{2u} level being 18 cm^{-1} lower in energy at this level of calculation. The HOMO-LUMO separation is then an e_u - e_u gap in D_{3d} symmetry, equal to that of the I_h symmetry. The level splitting in this symmetry causes both the HOMO and LUMO to be shifted higher in energy by an almost similar magnitude.

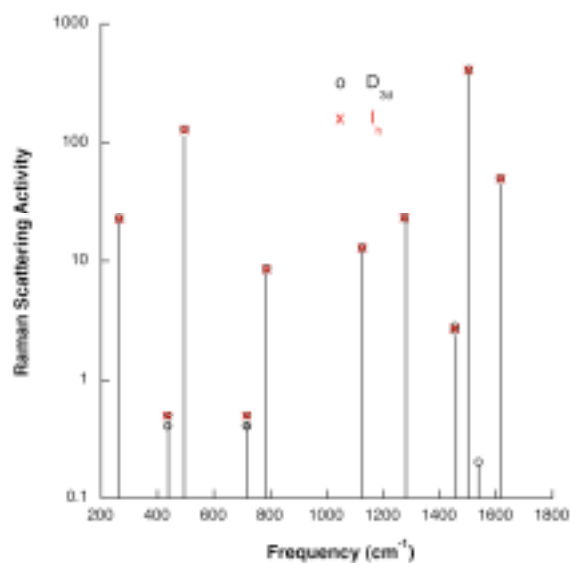


Figure 2. Calculated Raman scattering activities (in $\text{\AA}^4/\text{a.m.u.}$) of D_{3d} and I_h symmetry structures of C_{60} .

The calculated Raman scattering activities of for the I_h and D_{3d} symmetry structures at the B3LYP/6-31G* level is shown in Figure 2. In I_h symmetry, two A_g and eight H_g fundamental vibrational modes are Raman active, altogether with combination and overtone modes have been experimentally assigned for the solid phase.¹⁸ The calculated and measured frequencies are in good agreement. In D_{3d} symmetry, the H_g mode correlates with one A_{1g} and two E_g modes. The calculated Raman activities show very small splitting of the active modes: the lowest frequency H_g mode at 265 cm^{-1} splits into two modes at 266 and 267 cm^{-1} . Similar splitting for all other active modes at 434, 715, 786, 1125, 1275, 1453, and 1616 cm^{-1} , with a frequency shift of at most 3 cm^{-1} is calculated for the D_{3d} symmetry structure. Similar results have been obtained for the calculated Raman activities of the D_{5d} structure, for which the H_g mode splits into the A_{1g} , E_{1g} and E_{2g} modes. For this structure, the only active modes in the

region of up to 500 cm^{-1} are determined at 266, 436, and 497 cm^{-1} . Thus, it is concluded that a recent claim attributing the appearance of a resonance Raman band at 281 cm^{-1} is primarily due to distortion to either D_{3d} or D_{5d} structures of C_{60} in solution is precluded.⁶

The Raman spectrum of D_{3d} C_{60} in figure 2 shows a weak band at 1539 cm^{-1} . This is due to the activation of otherwise silent mode, and of A_{1g} character. Two much weaker E_g modes also appear at 1538 cm^{-1} . Experimentally, a silent G_g band at 1525 cm^{-1} has been assigned in I_h symmetry. In D_{3d} symmetry, this mode should correlate with the A_{1g} , A_{2g} , and E_g modes, of which only the A_{1g} and E_g are Raman active. The appearance of this band in a region significantly removed from other fundamentals should, therefore, be a Raman signature for the existence of this structure and could be discerned in high-resolution Raman spectroscopy of C_{60} in the gas-phase. The existence of two H_g overtones in the same region, however, could prove its identification a challenging task indeed.¹⁸

The four IR-active T_{1u} modes in the I_h symmetry are calculated at the B3LYP/6-31G* level to have frequencies of 532, 587, 1212, and 1459 cm^{-1} . These also compare well with the experimental measurements of 527, 576, 1183, and 1430 cm^{-1} .¹⁹ The small distortions into D_{3d} symmetry shift these frequencies to higher values of an utmost 5 cm^{-1} . Two weak bands are activated: one with frequencies of 541, 543 cm^{-1} , and a weaker still band at 1465 cm^{-1} . The first could be attributed to the I_h H_u silent mode at the experimentally assigned 563 band, while the second emanate from the silent G_u band, appearing with a frequency of 1446 cm^{-1} .¹⁹ Previous assignments of weak IR modes, specifically in the high frequency region, as due to combination modes caused by anharmonicity may well in fact be originated from a geometrical change of C_{60} to the lower D_{3d} symmetry.²⁰

The present work shows that small distortions from the perfectly spherical C_{60} to lower symmetries are energetically feasible. Activations of otherwise silent IR and Raman modes may perhaps require the assignments of previously identified combinations modes as fundamentals in the new, lowest energy D_{3d} symmetry structure.

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Abstract:

Quantum chemical calculations within density functional theory establish that small distortions from the perfectly spherical I_h symmetry of C_{60} to lower symmetries are energetically feasible. A D_{3d} symmetry structure proved to be the lowest energy structure, almost 0.9 kcal/mol lower than the I_h symmetry structure. Activations of otherwise I_h symmetrical silent modes, the IR G_u band at 1465 cm^{-1} , and the Raman G_g mode around 1530 cm^{-1} may require the assignments of previously identified combinations modes as fundamentals in the new symmetry structure. A recent experimental observation that attribute the appearance of a resonance Raman band at 281 cm^{-1} as primarily due to distortion to either D_{3d} or D_{5d} structures of C_{60} in solution is discounted.

