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Quantum Chemical Calculation of the Ground State Geometry and Vibrational Frequencies for the C_{60}^+ Ion

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Quantum Chemical Calculation of the Ground State Geometry and Vibrational Frequencies for the C_{60}^+ Ion[#]

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Abstract

Theoretical calculations for the fullerene cation are important for several aspects. Jahn–Teller vibronic interactions are symmetry–allowed in this ion and the expectation is that such interactions lead to static geometrical effects. In addition it is interesting to study the change of the vibrational spectrum of C_{60} upon ionization. We have used semi–empirical AM1/UHF and PM3/UHF and density functional theoretical methods (B3LYP and LDA) to calculate the electronic ground state equilibrium geometry and vibrational frequencies for C_{60}^+. A small but significant reduction from icosahedral symmetry to D_{5d} obtained from DFT calculations without symmetry constraints supports the presence of static Jahn–Teller distortions. Structure optimizations constrained to D_{5d} and D_{3d} symmetry have also been carried out. The JT stabilization energy in the D_{5d} and D_{3d} structures is estimated according to two different methods. Vibrational frequencies calculated at B3LYP/6–31G level for the fullerene cation of D_{5d} geometry are reported and compared to literature values of neutral C_{60}.

Keywords. C_{60}^+; fullerene cation; density functional theory; molecular geometry; vibrations; Jahn–Teller effect.

Abbreviations and notations

DFT, density functional theory	AM1, PM3 (semi–empirical methods)
LDA, functional (local density approximation)	JT, (Jahn–Teller) effect
B3LYP, functional (Becke's 3 parameter functional with the Lee-Yang-Parr correlation functional)	HOMO, highest occupied molecular orbital

1 INTRODUCTION

Since the discovery and macroscopic preparation of fullerenes [1,2] research into the properties of C_{60} has been extensive. The corresponding properties of fullerene ions are, however, not known to the same extent as for the parent neutral fullerenes, due simply to the fact that ions need special experimental techniques for study. One particularly intriguing aspect of fullerene research is the search for their interstellar existence. This quest is handicapped since C_{60} does not have permanent

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[#] Dedicated to Professor Nenad Trinajstić on the occasion of the 65th birthday.
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electric dipole moment, thus no pure rotational transitions are available for its detection by radio astronomic techniques. Recent searches are directed to the positive ion C_{60}^+, as in the presence of cosmic ionizing radiation the fullerene cation is more likely to be found. Optical and infrared radio astronomy has lately been applied for this search but has not yet been successful [3,4,5]. These astronomical studies rely on laboratory matrix isolation spectra of the C_{60}^+ [6,7].

There have been a number of theoretical studies for the geometry and spectroscopy of the C_{60}^+ ion, by semi–empirical methods as well as by *ab initio* and DFT calculations [8–15]. In this work we used semi–empirical and DFT methods to study two particular aspects, the equilibrium molecular geometry and the vibrational frequencies of this ion. Our main purpose was to detect static Jahn–Teller effects at our computational level, and to study the extent of changes in the vibrational energy levels upon ionization. Our calculations are compared to previous studies of vibronic interactions in C_{60} and its ions [8–15]. Recent experimental evidence is available for dynamic JT effect in this fullerene cation [16].

2 MATERIALS AND METHODS

Ground state geometry calculations were carried out with the Gaussian 98 Windows (G98W) suite of programs [17] at the default (unrestricted) B3LYP/3–21G, B3LYP/6–31G and B3LYP/6–31G* density functional theory levels [18,19] assisted by semi–empirical level calculations (AM1/UHF and PM3/UHF levels [20,21]). Semi–empirical calculations were carried out using HyperChem version 5.1 Standard for Windows Molecular Modeling system (HyperCube Inc.). We have also used the LDA density functional as implemented in the CPMD program system [22].

At first we have used AM1 and PM3 converged geometries (obtained at unrestricted Hartree–Fock level) as initial geometry for B3LYP/3–21G level G98W structure optimizations. In these calculations no particular symmetry was enforced for C_{60}^+, so C_1 molecular point group was used. Geometry optimizations within the B3LYP method converged fully for both 3–21G and 6–31G basis set levels. In another approach we have used strict I_h, D_{3d} and D_{5d} structural parameters as a starting geometry for C_{60}^+, obtained from converged neutral fullerene (C_{60}) calculations. For these starting geometries the RHF/3–21G computational level for the I_h and D_{5d} symmetry and the AM1 level for the D_{3d} symmetry were used.[1] Geometry optimizations for the cation were carried out with the 6–31G basis set for D_{3d} and D_{5d} symmetries, and also with the 6–31G* basis set for D_{5d} symmetry. In addition vibrational frequencies were obtained for D_{5d} symmetry using the 6–31G basis set. We have not been able to achieve convergence in C_{60}^+ structural calculations using icosahedral symmetry, because the optimization cycles were oscillating.

For cases where we used no explicit starting symmetries, computed geometries and geometrical

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[1] These geometries were supplied by Dr. Stephan Irle at the Emory University, Atlanta, Georgia, U.S.A.

symmetries were analyzed by a 3D molecular geometry visualization software (SymApps, Version 1.0, SoftShell International Ltd.). This way point group symmetries were derived within various geometrical parameter tolerance limits to establish the extent of the resulting deviations from icosahedral (I_h) symmetry. Figure 1 below is a 3D rendition of the geometrical structure of the fullerene cation emphasizing five–fold symmetry.[2]

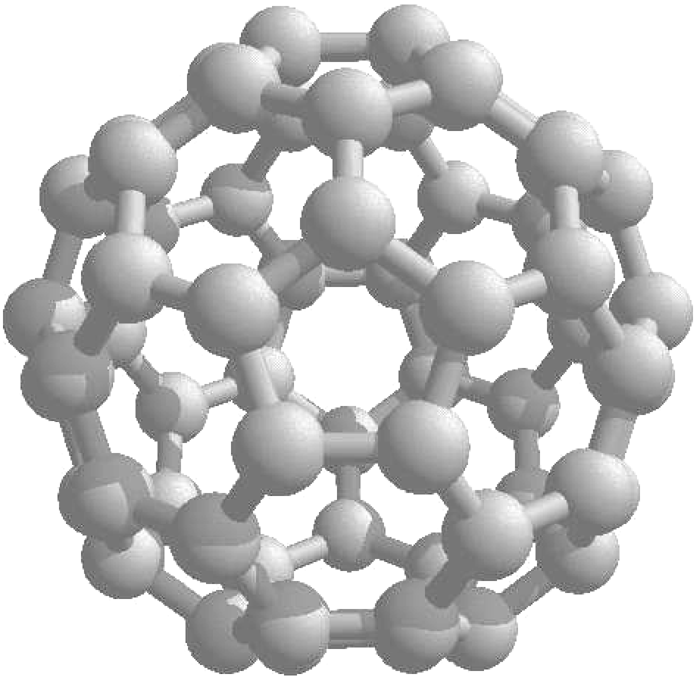

Figure 1. Three dimensional structure of C_{60}^+.

3 RESULTS AND DISCUSSION

3.1 Molecular geometry

All previous quantum chemical calculations on fullerene cation and anion structures have shown reduction from icosahedral symmetry of the parent fullerene molecule [8–15]. The removal of an electron from the HOMO orbital results in a five–fold degenerate ^2H_g ground state for the fullerene cation C_{60}^+ (h^9_u electronic configuration). The presence of electronic degeneracy leads to Jahn–Teller (JT) interactions with degenerate vibrational modes of H_g and G_g symmetry of C_{60}. As there are several possible distortions from icosahedral symmetry (D_{2h}, D_{3d} and D_{5d}) and since the energy differences among these are slight [10], one expects dynamical JT effects as well as a static one manifested in non–I_h equilibrium ground state symmetry. Dynamic JT effects leading to D_{3d} equilibrium symmetry for gas–phase C_{60}^+ ions have recently been confirmed by valence photoelectron spectroscopy [16].

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[2] For the different computational models applied here the indication of the various bond lengths on the model are available from one of the authors (L.N.)

Near–IR spectra of the C_{60}^+ ion in glassy matrices [6,7] are in accord with the expected electronic transitions in the D_{5d} structure, but vibrational spectra reported so far for the cation have not yet been analyzed to the same extent as those for the parent molecule (see Chapter 11. for vibrational modes, and Chapter 12. for electronic structure in [23]). In our B3LYP DFT vibrational calculations the effect of ionization is further examined.

AM1/UHF and PM3/UHF structure optimizations by HyperChem led essentially to I_h geometries (so no JT distortions), and approximate heat of formation values for C_{60}^+. (The heat of formation for C_{60}^+ is obtained as the heat of formation for C_{60}: 672 kcal/mol [24] plus the first ionization energy of C_{60}: 7.6±0.2 eV [25], thus 847.3±4.6 kcal/mol.) From AM1/UHF and PM3/UHF calculations we obtained 1166.79 kcal/mol and 1017.59 kcal/mol, respectively. Dipole moment estimates were, however, grossly in error (relative to more accurate DFT calculations that yield a very small fraction of a Debye); 4.660 D and 3.723 D for the AM1 and PM3 calculations, respectively.

The C_{60} molecule has two different equilibrium bond lengths, gas–phase electron diffraction experimental values are 1.401(10) Å and 1.458(6) Å for the double and single bonds between the sp^2 hybrid carbon atoms, respectively [26]. Estimates from SCF/TZP *ab initio* calculations are 1.370 Å and 1.448 Å [27], and 1.403 Å and 1.461 Å for the double and single bonds, respectively, from density functional calculations, using the B–LYP functional at TZP level [28]. Our LDA calculations for neutral C_{60} yielded 1.387 Å and 1.441 Å for the two bond lengths.

In case of JT symmetry reduction to D_{2h}, D_{3d} and D_{5d} point group symmetries there are 15, 10 and 7 independent bond lengths (instead of 2 for I_h). The number of independent structural parameters corresponds to the number of totally symmetric normal modes in these geometries [29].

Table 1. Effective symmetries for different density functionals and levels for the C_{60}^+ ion

DFT Functional/Level	T value	effective symmetry
B3LYP/3–21G	0.025–0.145	D_{5d}
	0.185–0.285	I_h
B3LYP/6–31G	0.025	D_{2h}
	0.045–0.145	D_{5d}
	0.165–0.285	I_h
LDA	0.025–0.065	D_{2h}
	0.085–0.105	D_{5d}
	0.125–0.225	I_h
	>0.245	Exact I_h

For symmetry–unconstrained calculations the use of the SymApps software allowed us to estimate the deviations of the converged geometries from the icosahedral geometry of C_{60} both numerically (bond length values) and symmetry–wise (effective point group symmetries). In the use of SymApps a tolerance value (T) is applied to provide an error margin for point group calculations. The larger the values of T, the more coordinate distortions are allowed by the software to find an approximate symmetry. To find the effect of coordinate distortions multiple point groups were calculated for a range of T. This procedure yielded approximate D_{5d} geometries for B3LYP/3–21G and B3LYP/6–31G structures for low tolerance levels, while somewhat lesser symmetric geometry (close to D_{2h}) for the LDA structure. As a check an LDA calculation was carried out for the parent C_{60} molecule. This yielded exact I_h symmetry at and above a T value of 0.025.

In Table 1 the various effective symmetries for the C_{60}^+ ion are given with the T value specified. Accepting D_{5d} geometry for the B3LYP calculations Table 2 contains the seven bond length values obtained from the different levels and functionals.

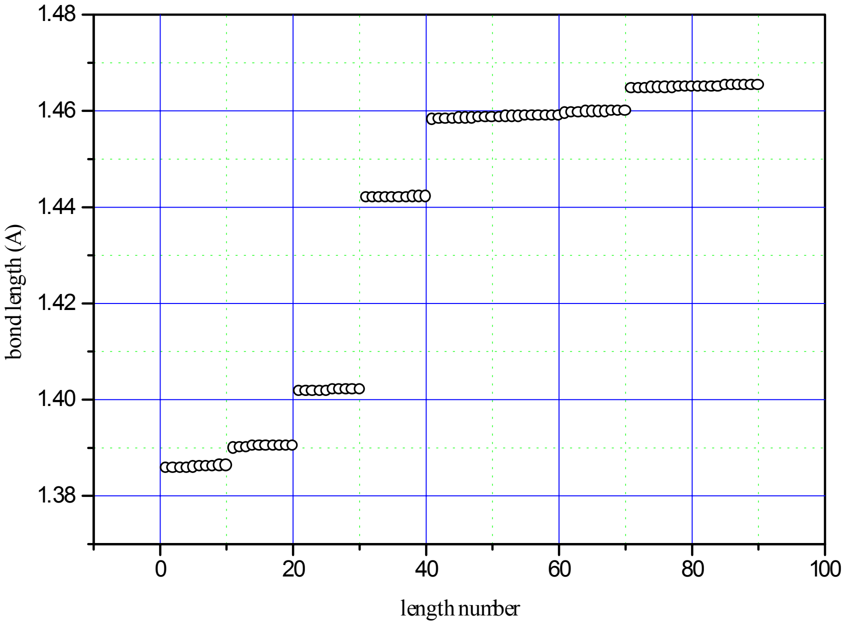

Figure 2. Distribution of bond length values for C_{60}^+ from symmetry unconstrained B3LYP/3–21G calculations.

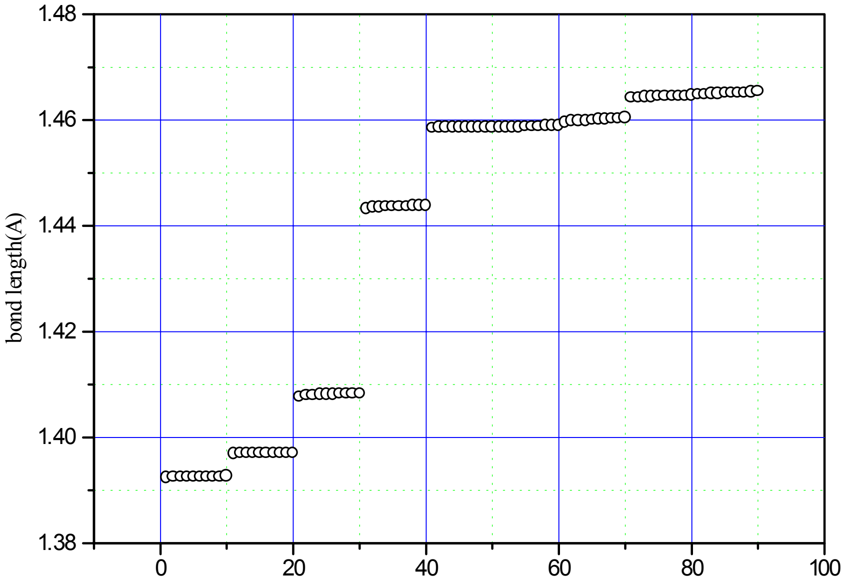

Figure 3. Distribution of bond length values for C_{60}^+ from symmetry unconstrained B3LYP/6–31G calculations.

Figures 2, 3 and 4 illustrate the differences among bond lengths obtained at the two different levels of B3LYP calculations and from the LDA approach. The abscissa of these Figures (length number) enumerates the 90 bond lengths as ordered according to their value. From the B3LYP calculations (Figures 2 and 3) it is evident that there are two single bond lengths that are only slightly different, this probably is the reason for the uncertainty of establishing a unique geometrical symmetry by the SymApps software. From the LDA level calculations no distinct bond length groups were obtained (see Figure 4) in accordance with the resultant symmetry being lower than for B3LYP calculations.

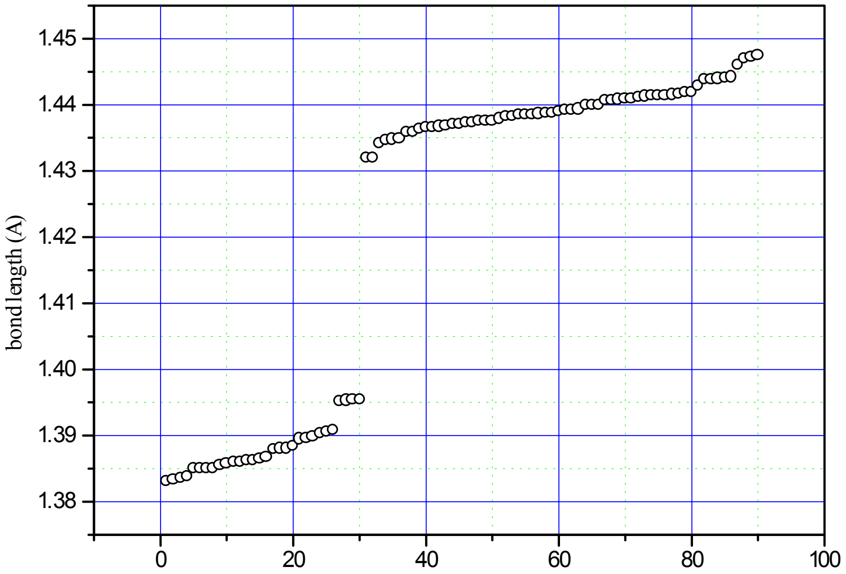

Figure 4. Distribution of bond length values for C_{60}^+ from symmetry unconstrained LDA calculations.

Table 2. Bond lengths for C_{60}^+ from symmetry unconstrained B3LYP DFT calculations

Bond length type	B3LYP/3–21G	B3LYP/6–31G
double	1.386	1.393
double	1.390	1.397
double	1.402	1.408
single	1.442	1.444
single	1.459	1.459
single	1.460	1.460
single	1.465	1.465

Table 2 summarizes the seven groups of 90 individual bond length values obtained from symmetry unconstrained calculations. The changes from previously reported B–LYP/TZP calculations for C_{60} [28] are less than 0.02 Å for the double bonds and less than 0.01 Å for the single bonds. This is, however, a comparison between neutral C_{60} and its cation, and our computational level differs from that in [28]. Previous theoretical calculations for the JT effect for electronic excitations in C_{60} came up with a maximum distortion of 0.02 Å [14].

It is noticeable from Table 2 that enlarging the basis for the B3LYP calculations results in a lengthening of the double bonds, while single bonds are not affected. In other words, the larger basis leads to a smaller difference between single and double bonds.

Table 3. Bond lengths for C_{60}^+ from symmetry constrained B3LYP DFT calculations (Å)

Bond Length type	B3LYP/6–31G (D_{5d})	B3LYP/6–31G* (D_{5d})	B3LYP/6–31G (D_{3d})
double	1.393	1.391	1.390
double	1.398	1.395	1.398
double	1.408	1.406	1.401
double	–	–	1.403
single	1.444	1.437	1.454
single	1.458	1.452	1.455
single	1.460	1.454	1.458
single	1.464	1.458	1.458
single	–	–	1.458
single	–	–	1.464

In Table 3, symmetry constrained geometrical parameters are given in the indicated bases for the D_{5d} and D_{3d} symmetries. For D_{5d} there are three distinct double bonds, and four distinct single ones, for D_{3d} there are four distinct double bonds and six distinct single ones. Because we use only three decimals for the bond lengths in the Tables, three single bonds appear to have the same value for the D_{3d} geometry; they would all be different using four decimal places. Extending the 6–31G basis set to include d functions (6–31G*) results in a slight contraction of all bond lengths. The bond lengths calculated with this polarized basis constitute our highest level DFT results and when the averages over single (1.450 Å) and double (1.397 Å) bonds are compared to the gas–phase electron diffraction structure for neutral C_{60} [26] (single bond length: 1.458(6) Å, double bond length: 1.401(10) Å), a very small contraction of the molecule is seen to be predicted upon ionization.

3.2 Vibrational Modes

Removal of a single electron from the 240 valence electrons in C_{60} should not greatly affect the values of the force constants for the various internal displacement coordinates, thus one expects only small frequency changes [7]. However JT effects lower geometrical symmetry, thus the degeneracy of the vibrational levels is affected. Symmetry correlations among the irreducible representations for the I_h and D_{5d} groups allow us to derive the infrared and Raman active modes in D_{5d} C_{60}^+ from the IR and Raman modes and the so–called silent modes (non–electric–dipole active modes) of parent C_{60}.

Such a correlation table is found in [23] (see: Table 4.15 there). C_{60} has four IR active F_{1u} modes, and ten Raman active modes (two A_g modes and eight H_g modes). Each F_{1u} mode splits to a non–degenerate A_{2u} and a doubly degenerate E_{1u} mode in D_{5d}, A_g modes correlate to A_{1g} modes in D_{5d}, and each five–fold degenerate H_g mode splits to a non–degenerate A_{1g} mode and to a pair of doubly degenerate modes E_{1g} and E_{2g} in D_{5d}. This is also seen from the character table of the D_{5d} point group (see e.g. [30]); the IR active modes belong to representations A_{2u} and E_{1u}, while Raman active modes to representations A_{1g}, E_{1g} and E_{2g}. Thus the dipole active modes of C_{60} will result in eight IR active modes (four A_{1u} and four E_{1u}), and 26 Raman active modes (ten A_{1g}, plus eight E_{1g} and eight E_{2g} modes) in C_{60}^+ according to D_{5d} symmetry. The 14 dipole active modes in C_{60} lead to altogether 34 dipole active modes in C_{60}^+ of D_{5d} symmetry. Symmetry correlations show, however, that IR and Raman active modes of the cation derive also from the silent modes of the parent fullerene so there are more than 34 dipole active modes in the cation.

Naturally such symmetry considerations do not lead to the prediction of the appearance of the IR spectrum of C_{60}^+ as no intensity considerations are involved in group theory. Nonetheless one would expect infrared active modes of the ion to appear around the frequency of infrared modes of C_{60}.

In Cartesian coordinates C_{60} has 174 genuine intramolecular modes that are grouped into degenerate sets according to the I_h group representation [23, Eq. 11.1]. Modes of symmetry A are non–degenerate, F modes are three–fold, G modes are four–fold and H modes are five–fold degenerate:

$$\Gamma_{vib}=2A_g + 1A_u + 3F_{1g} + 4F_{1u} + 4F_{2g} + 5F_{2u} + 6G_g + 6G_u + 8H_g + 7H_u \qquad (1)$$

Thus there are 46 vibrational normal modes in icosahedral symmetry. In Figure 5 a comparison is given for two different assignments of the experimental frequencies of neutral fullerene C_{60}, taken from [31] and [32]. Each normal mode frequency is repeated according to the degeneracy number according to Eq. (1) in order to be comparable to our results. The comparison demonstrates the differences that still exist in the assignment of silent modes. This is particularly evident in the region 600 – 1000 cm^{-1}.

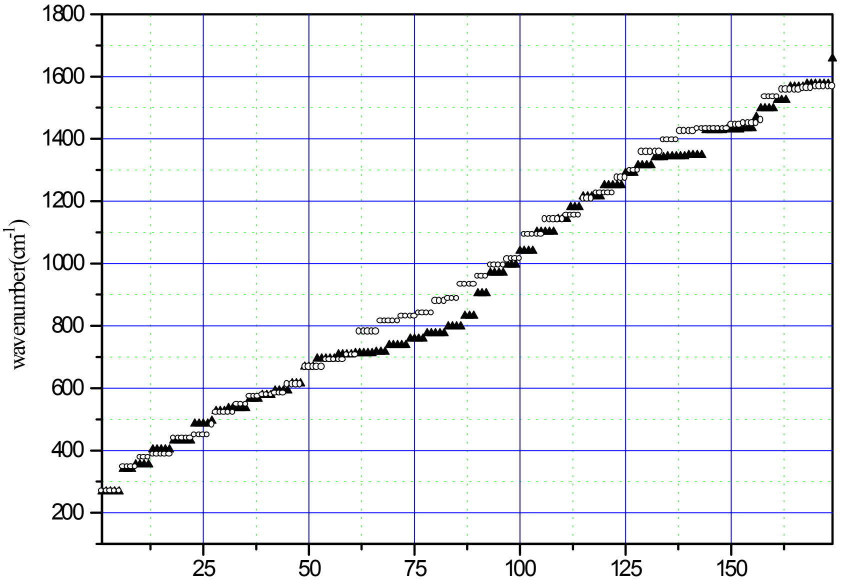

Figure 5. Vibrational mode assignments for neutral C_{60} from [31] (circles) and [32] (triangles).

In our present DFT calculations the results are given in non–symmetrized Cartesian coordinates thus we have 174 vibrational frequencies. Figure 6 contains the vibrational frequencies for the C_{60}^+ cation from D_{5d} B3LYP/6–31G calculations, as compared to the experimental values from [32]. We note that no empirical scaling factors were applied in these frequency calculations. To facilitate comparison the experimental values are represented by a thin solid line, while the calculated frequencies are given as open circles.

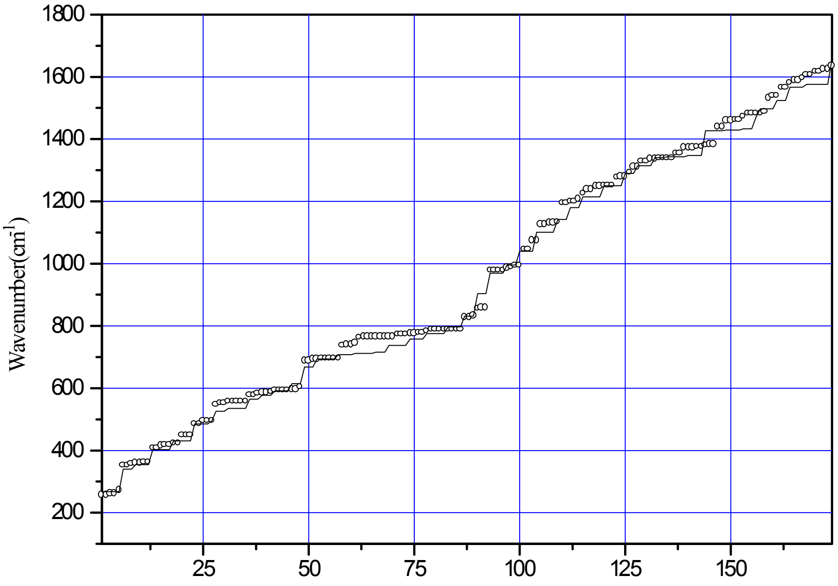

Figure 6. Comparison of experimental C_{60} and calculated C_{60}^+ vibrational frequencies.

The vibrational frequencies calculated at the B3LYP/6–31G level are fairly close to the experimental ones in [32], the frequency differences caused by ionization are small on the scale of Figure 6. Removal of a single electron from C_{60} thus brings about small changes in vibrational level energies. This change appears to be the largest in mode numbers between 50 and 75, and around 160 (*i.e.* in the wave number range 700 and 800 cm^{-1}, and near 1450 cm^{-1}). At low frequencies vibrations are predominantly radial modes (*i.e.* the carbon atoms are moving radially outward or inward relative to the fullerene surface) (for vibrational mode pictures, see *e.g.* [33]), and near 1450 cm^{-1} the so–called pentagonal pinch fivefold degenerate Raman mode is found (this mode involves mainly tangential vibrational amplitudes [23, Figure 11.2]). Based on our calculations the effect of removing one electron from C_{60} fullerene appears to have the largest effect on these vibrations.

4 CONCLUSIONS

In the present work, in symmetry unconstrained calculations we obtained symmetry lowering in the electronic ground state from icosahedral to D_{5d} point group symmetry that we attribute to Jahn–Teller effects in this highly symmetric ion. This geometrical effect was clearest in our DFT B3LYP level calculations, while semi–empirical AM1 and PM3 approaches did not reveal such a symmetry reduction. When the initial symmetry in structure optimization was constrained to D_{5d} and D_{3d} the calculations converged thus showing that such geometries correspond to minima on the potential energy hyper surface, in accordance to previous work [10,11]. On the other hand it has not been possible to obtain converged geometries when icosahedral symmetry constraint was applied to the fullerene cation.[3]

In the absence of a converged single point energy value for icosahedral C_{60}^+, in order to estimate the stabilization energy gained in relaxing the geometry of neutral C_{60} to that of D_{5d} and D_{3d} C_{60}^+, we have followed two different routes. In the first method the optimized geometry of neutral C_{60} was obtained at B3LYP/6–31G level, starting from an RHF/3–21G structure. The SCF energy was –2285.58984755 E_h. Upon comparing this value to the final SCF energy for C_{60}^+, calculated also at B3LYP/6–31G level, at constrained D_{5d} symmetry (–2285.31627601 E_h), an increase of 60042 cm^{-1} is obtained for the cation energy. Using the gas phase first ionization energy of C_{60} (7.61 ± 0.02 eV = 61378.76±161.31 cm^{-1}) for correcting the previous value, a stabilization energy 1337 ±161 cm^{-1} resulted for the D_{5d} structure.

In the second approach the single point energy of C_{60}^+ was calculated using B3LYP/6–31G level at the converged icosahedral structure of neutral C_{60}. The SCF single point energy was then obtained as –2285.29203551 E_h. This, in turn, led to the D_{5d} stabilization energy of the cation as 5320.2 cm^{-1}. Previous estimate for this stabilization energy was 8.1 kcal/mol = 2833 cm^{-1} [10].

The difference between the SCF energies for converged structures of C_{60}^+ in D_{5d} and D_{3d} symmetry was 0.001561 E_h = 342.5 cm^{-1}, the D_{5d} ion structure lies at a deeper potential surface position.

The vibrational effect of forming the C_{60}^+ cation showed up in our D_{5d} symmetry B3LYP/6–31G calculations as small changes in normal mode frequencies of $C_{60,}$ and was mainly revealed between 700 and 800 cm^{-1}, and near 1450 cm^{-1}.

We plan to pursue higher level quantum chemical calculations to study the vibrational and electronic spectra of C_{60}^+ and static and dynamic JT effects manifested in them.

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[3] We are planning more sophisticated calculations on this problem in cooperation with Dr. Stephan Irle at Emory University, Atlanta, Georgia, U.S.A.

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