C\textsubscript{60}\textsuperscript{+} and B\textsubscript{80}\textsuperscript{+}: A Comparative Study of the Jahn-Teller Effect

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Abstract. The ground state wave function of the neutral icosahedral C\textsubscript{60} and B\textsubscript{80} belong to the totally symmetric representation, where the HOMOs are fivefold degenerate and form the basis of the \textit{H}\textsubscript{\textit{s}} representation of the \textit{Ih} point group. Hence both C\textsubscript{60}\textsuperscript{+} and B\textsubscript{80}\textsuperscript{+} are prone to a molecular distortion of the Jahn-Teller type. Density Functional Theory calculation is applied and revealed that a minimum energy configuration in \textit{D}_{5d} point group is obtained for C\textsubscript{60}\textsuperscript{+}; whereas a slight S\textsubscript{6} distortion of a \textit{D}_{3d} nuclear configuration is obtained for B\textsubscript{80}\textsuperscript{+}. Thus the vibronic coupling between the \textit{2}\textit{H}\textsubscript{\textit{s}} electronic states of both systems with the degenerate normal modes in the \textit{Ih} point group are analysed and presented here in a comparative point of view. Moreover, a simple and efficient procedure, which is fully non-empirical, based on the harmonic approximation, is presented in order to calculate the Jahn-Teller parameters and the first order vibronic coupling coefficient.

1. Introduction

The properties and the structure of non-planar boron allotrope were the subject of enormous work, [1-6] since the prediction of the existence of the boron buckyball B\textsubscript{80}. [7] The B\textsubscript{80} molecule is of significant interest due to the fact that B\textsubscript{80} and the analogue carbon buckyball C\textsubscript{60} are isoelectronic. The necessity to characterize the B\textsubscript{80} molecule also emerged from some physical properties, such as electrical conductivity [8] and hydrogen storage ability, [9] which appear to be superior comparing to those properties obtained in C\textsubscript{60}.

The distinguishing structural feature of the boron buckyball, as compared to the carbon buckyball, is the presence of twenty extra boron atoms, capping the twenty six-membered ring boron atoms of the buckyball (figure 1). Thus the neutral B\textsubscript{80}, like the case of the neutral C\textsubscript{60}, might exhibit the highest possible finite point group in nature, \textit{Ih}. Quite a number of theoretical investigations have been devoted to the structure of the neutral B\textsubscript{80} molecule. Although Szwacki and Tymczak [10] postulated the existence of B\textsubscript{80} with a nuclear configuration in the \textit{Ih} point group, using high level wave function theory calculation, Gopakumar et al., [11] together with Gunashinge et al., [12] predicted that this icosahedral
geometry is unstable leading to the formation of two stable structures in the $T_3$ point group, using Density Functional Theory (DFT) calculation. The corresponding descent in symmetry has been recently analysed by Muya et al., [13] and has been identified as the consequence of a weak pseudo-Jahn-Teller mechanism.

Figure 1. Structures of the neutral $B_{80}$ (a) and the neutral $C_{60}$ (b) in their icosahedral nuclear configurations.

Nevertheless, the structures of neutral $B_{80}$ and $C_{60}$ in their high symmetry point groups suppose that either the anionic or the cationic species are characterized by degenerate electronic states, giving rise to a Jahn-Teller instability. Moreover, this instability for the case of $B_{80}^+$ or $B_{80}^-$ will be superimposed on the pseudo-Jahn-Teller instability of the neutral species, leading to a complicated distortion mechanism, which has no counterpart in the case of $C_{60}^+$ or $C_{60}^-$. Hence the analysis of the structural distortion from the high symmetry arrangement to the global minimum of $B_{80}^+$ and $C_{60}^+$ presents a challenge because of the superposition of effect produced by many different normal modes. Herein, we report the analysis of the Jahn-Teller distortion, which is occurring in the icosahedral $B_{80}^+$ and compare the results of that we obtained for $C_{60}^+$. In order to tackle the multimode problem, the Intrinsic Distortion Path (IDP) model, [14] in which the distortion is represented as a linear combination of all totally symmetric normal modes of the low symmetry minimum energy configuration, is performed. Within this model, it is possible to directly separate the contribution of the different normal modes to the Jahn-Teller distortion, their energy contribution to the Jahn-Teller stabilization energy, and the forces at the high symmetry point, giving further insight into the first order vibronic coupling coefficient in both $B_{80}^+$ and $C_{60}^+$ Jahn-Teller effect.
2. Methodology

The DFT calculations reported in this work have been carried out using the Gaussian program package, Gaussian2009. [15] The Local Density Approximation (LDA) characterized by the Vosko-Wilk-Nussair (VWN) parametrization, [16] the Generalized Gradient Approximation (GGA) characterized by the Perdew-Burke-Ernzehof (PBE) functional, [17] and the Hybrid functional characterized by the B3LYP [18] parameterization were used for the analysis of the Adiabatical Potential Energy Surface (APES) of B₈₀⁺. The 6-31G(D) basis set was used to represent the boron and the carbon atoms. Analytical harmonic frequencies were calculated.

To facilitate the understanding of our proposed model, we first outline a very basic part of the former achievements relevant to our analysis of the Jahn-Teller effect. Within the multideterminental approach, [19] we are able to evaluate the Jahn-Teller parameters (e.g. Jahn-Teller Energy) using direct DFT calculation. Then the approach has been successfully applied to a series of typical Jahn-Teller active molecules. [20-21] The approach itself can be found elsewhere, [19] and requires the DFT calculation of the high symmetry (HS) and low symmetry (LS) geometries and energies of the species. Although, the geometry and energy of the LS species can be found in a quite straightforward way, those corresponding to the HS species need further discussion. We always represented the geometry of the HS species as the structure exhibited in the so-called Average of Configuration (AOC) type of calculation. [19]

This procedure prevents us to consider the HS geometry as the geometry obtained for the neutral species and turns out to be the appropriate way to calculate the DFT Jahn-Teller energy. [19] [22]

Here, HS and LS denote the geometry obtained from the LDA calculation of the non-Jahn-Teller parent molecule, in this case the neutral species and the global minimum of the cationic species, respectively. It is noteworthy to point out that the choice of the neutral parent molecule as the HS structure does not bias our calculation since the Jahn-Teller parameters we are looking for, are extracted from the harmonic approximation without fitting to the DFT results.

The distortion vector is regarded as the difference between the mass-weighted Cartesian coordinate corresponding to the HS and the LS nuclear configurations, equation (1).

\[ \vec{R}_{JT} = \vec{R}_{HS} - \vec{R}_{LS} = \sum_{k=1}^{3N} w_{LS,k} \vec{Q}_{LS,k} \]  

(1)

where \( \vec{R}_{HS} \) and \( \vec{R}_{LS} \) are column vectors, which contain 3N elements (N being the total number of atoms in a molecule) of the mass-weighted Cartesian coordinates, corresponding to the optimized LDA geometry of the HS and the LS nuclear configurations, respectively.

Furthermore \( \vec{R}_{JT} \) can be represented in terms of the normal modes at the LS nuclear configuration, equation (1), where the weighting factor \( w_{LS,k} \) is a scalar, which represents the linear combination coefficient of the kth mass-weighted normal coordinate \( \vec{Q}_{LS,k} \) of the LS nuclear configuration obtained from the LDA frequency analysis. Since our approach deals with the first order Jahn-Teller distortion, only totally symmetric modes in the LS point group might have a non-zero \( w_{LS,k} \).

While the LS nuclear configuration is taken as reference point, within the harmonic approximation, the contribution to the stabilization energy in terms of the normal modes in the LS conformation is calculated in a simple analytical form, equation (2).
where $\lambda_{\text{LS},k}$ represents the eigenvalue of the Hessian obtained from the LDA frequency calculation on the LS global minimum energy. Therefore, using the same approach, the forces, which correspond to each normal mode through the distortion, can be obtained as:

$$E_{\text{LS},k} = \frac{1}{2} w_{\text{LS},k} \left| \vec{Q}_{\text{LS},k} \right|^2 \lambda_{\text{LS},k}$$  \(\text{(2)}\)

where $\lambda_{\text{LS},k}$ is a diagonal matrix with atomic masses in triplicate form as elements. $\vec{F}_{\text{LDOP}}$ can be projected in either LS or HS normal modes using the vector properties of the (3N-6) normal modes orthogonal basis.

Recently we proposed a simple and efficient approach for the determination of the Jahn-Teller parameters. [22] As the JT magnitude $q_{\text{HS,}k}$ and the forces $\vec{F}_{\text{HS,}k}$ are obtained in a straightforward way; the energy contributions to the Jahn-Teller stabilization energy of the normal modes in the HS nuclear configuration require a further refinement.

We presented in reference [22] that two sets of mass-weighted normal coordinates can be correlated as following:

$$Q_{\text{LS}} \cdot Q_{\text{HS}} = C$$  \(\text{(4)}\)

where $Q_{\text{LS}} = \left[ \vec{Q}_{\text{LS},1} \vec{Q}_{\text{LS},2} \ldots \vec{Q}_{\text{LS},3N-6} \right]$ and $Q_{\text{HS}} = \left[ \vec{Q}_{\text{HS},1} \vec{Q}_{\text{HS},2} \ldots \vec{Q}_{\text{HS},3N-6} \right]$ are matrices with 3N x (3N-6) elements, which contain the kth mass-weighted normal coordinates of the LS and HS nuclear configuration, respectively. $C$ is a (3N-6) x (3N-6) squared correlation matrix and the element $C_{ij}$ of the matrix $C$ gives the overlap between the two sets of normal coordinates.

Therefore the energy contribution of each HS normal mode to the Jahn-Teller stabilization energy can be easily obtained from equation (2) as:

$$E_{\text{HS},k} = \sum_{i=1}^{3N-6} \left( C_{ik} \right)^2 E_{\text{LS},i}$$  \(\text{(5)}\)

To summarize, using the scheme presented above, we can calculate:

1. The Jahn-Teller magnitude $q_{\text{HS,}k}$, considering:

$$\vec{R}_{\text{JT}} = \sum_{k=1}^{3N-6} v_k \vec{Q}_{\text{HS},k}$$  \(\text{(6)}\)

one can obtain the Jahn-Teller magnitude relative to the HS normal modes, in the present case, as:

$$q_{\text{HS,}k} = \left| v_k \vec{Q}_{\text{HS},k} \right| / \sqrt{m}$$  \(\text{(7)}\)
where \( m \) stands for the atomic mass of either boron atom or carbon atom, i.e., 11.0093 a.u. and 12.0000 a.u., respectively.

2. The energy contribution of each normal mode at the HS nuclear configuration \( E_{\text{HS},k} \) to the Jahn-Teller stabilization energy as given in equation (5). Therefore the Jahn-Teller stabilization energy is formulated as:

\[
E_{\text{JT}} = \sum_{k=1}^{3N-6} E_{\text{HS},k}
\]  

(8)

3. The forces \( F_{\text{HS},k} \), which exert each normal mode at the HS nuclear configuration to the distortion as:

\[
\vec{F}_{\text{DP}} = \sum_{k=1}^{3N-6} \left| F_{\text{HS},k} \right| \vec{Q}_{\text{HS},k}
\]  

(9)

3. Results and Discussion

**The ground state of \( \text{B}_{80}^+ \)**

We have analysed the APES of \( \text{B}_{80}^+ \) by means of DFT calculation, using the LDA, the GGA and the hybrid functional, table 1. Without going into much detail, because some of these results have been already published, [23] it can be seen from table 1, that according to the DFT calculations, the \( ^2\text{A}_u \) conformation in \( S_6 \) symmetry is the global minimum. This is confirmed by the absence of any imaginary frequency, while vibrational analysis was performed. In the other case, similar analysis of the APES of \( \text{C}_{60}^+ \) always predicted a global minimum in \( D_{5d} \) symmetry, [22] in agreement with several reported calculations. [24-25]

**Table 1.** Total electronic energies (Hartrees) of epikernels \( D_{5d}, D_{2d}, D_{3d} \) and \( S_6 \) of \( \text{B}_{80}^+ \) with three different DFT methods; relative energies to the global minimum are given in parenthesis (cm\(^{-1}\)), taken from reference [23].

| Symmetry | \( \Gamma_{\text{el}}^{\text{a}} \) | VWN/6-31G(D) | PBE/6-31G(D) | B3LYP/6-31G(D) | \# img. freq. (\( \Gamma_{\text{vib}} \))\(^{\text{b}} \) |
|----------|-------------------------------|--------------|--------------|----------------|----------------------------------|
| \( D_{5d} \) | \( ^2\text{A}_{1u} \) | -1974.37750 | -1984.80333 | -1987.31611 | 7 (e\(_{1g}\)+e\(_{2g}\)+e\(_{2u}\)+a\(_{2u}\)) |
|          |                               | (515.77)     | (602.50)     | (1095.62)     |                                  |
| \( D_{2d} \) | \( ^2\text{B}_{1u} \) | -1974.37928 | -1984.80492 | -1987.31956 | 3 (b\(_{1g}\)+b\(_{2g}\)+b\(_{3g}\)) |
|          |                               | (125.10)     | (392.86)     | (338.43)      |                                  |
| \( D_{3d} \) | \( ^2\text{A}_{1u} \) | -1974.37945 | -1984.80607 | -1987.32036 | 1 (a\(_{2g}\)) |
|          |                               | (87.79)      | (140.46)     | (162.85)      |                                  |
| \( S_6 \) | \( ^2\text{A}_u \) | -1974.37985 | -1984.80671 | -1987.32110 | 0 (-) |
|          |                               | (0.00)       | (0.00)       | (0.00)        |                                  |

\(^{\text{a}}\) Electronic state

\(^{\text{b}}\) number of imaginary frequencies obtained from the DFT frequency calculation and their symmetry in parenthesis.
The $D_{5d}$, $D_{2h}$ and $D_{3d}$ epikernel symmetries of B$_{80}^+$ exhibit imaginary frequencies (table 1), which indicate a further instability of the parent geometry. The choice of the LS point group of the Jahn-Teller distortion is mostly based on the epikernel principle, [26] which states that extremum point on the APES are more favourable to maximal epikernels than to the lower ranking ones. It is noteworthy to highlight that at least, the icosahedral B$_{80}^+$ distorts in a trigonal route, unless the icosahedral C$_{60}^+$ prefers a pentagonal distortion. Nevertheless, the $D_{3d}$ structure of B$_{80}^+$ is characterized by a single imaginary frequency of $a_2g$ symmetry. This mode, which is anti-symmetric with respect to the twofold axes and the dihedral symmetry planes, reduces the $D_{3d}$ geometry to the $S_6$ point group. This difference between the ground state symmetry of C$_{60}^+$ and B$_{80}^+$ is then attributed to the presence of persistent pseudo-Jahn-Teller forces, present in the neutral B$_{80}$. [23]

The hybrid functional B3LYP overestimates the relative energies, whereas the GGA and LDA functionals give a relatively reasonable range of energy.

**Multimode Jahn-Teller effect of B$_{80}^+$**

B$_{80}^+$ and C$_{60}^+$ have a $^3H_u$ electronic ground state in their icosahedral nuclear configurations, $I_h$ point group. Nine electrons (one hole) fill the fivefold degenerate HOMO. Hence B$_{80}^+$ and C$_{60}^+$ are Jahn-Teller active molecules and are subjected to a lowering of the symmetry of their nuclear configuration. According to the DFT analysis of the ground state of both cations, the descent in symmetry goes to $S_6$ and $D_{5d}$, respectively for the case of B$_{80}^+$ and C$_{60}^+$. In $D_{5d}$ point group, the electronic state splits into $^2A_{1u}$, $^2E_{1u}$ and $^2E_{2u}$, while $^2A_h$ and two times $^2E_h$ are obtained in the $S_6$ point group. B$_{80}$ in $I_h$ symmetry has 234 vibrational modes, where seven among them were calculated with an imaginary frequency forming the basis of $g_g$ and $t_{2u}$ representation. There are three $a_g$, four $t_{1u}$, five $t_{2g}$, eight $g_g$ and eleven $h_g$ vibrational modes, which at least one component of the degenerate modes becomes totally symmetric under the descent in symmetry to $S_6$ (except the case of $g_g$ modes, where two components become totally symmetric). Thus in the $S_6$ point group, there are thirty-nine totally symmetric normal modes, which can mix and contribute to our analysis of the Jahn-Teller distortion. Out of the thirty-nine totally symmetric normal modes in $S_6$ point group, with our model, we are able to identify the two most important vibrations with respect to the Jahn-Teller distortion. These particular vibrations are illustrated in figure 2, mainly correspond to the first $g_g$ vibration in the $I_h$ configuration of B$_{80}^+$, which has an imaginary frequency and contribute almost 86% to the Jahn-Teller distortion. C$_{60}$ in $I_h$ nuclear configuration has 174 vibrational modes, where only one component of each of the eight $h_g$ modes becomes totally symmetric under the descent in symmetry to $D_{5d}$, together with the two icosahedral $a_h$ modes. Therefore, there are ten totally symmetric normal modes in $D_{5d}$ point group, which contribute to the distortion of the $I_h$ C$_{60}^+$. Out of those ten totally symmetric normal modes, the distortion is mainly due to the lowest frequency ones, which is a part of the squashing $h_g$ modes of $I_h$ C$_{60}$. [22]
In order to complete the study of the Jahn-Teller distortion in \( B_{80}^+ \) and \( C_{60}^+ \), we calculated the Jahn-Teller magnitude \( q_{HS,k} \), the Jahn-Teller energy \( E_{HS,k} \) and the forces \( F_{HS,k} \), according to the equations (7), (5) and (9), respectively. The results of the calculations using the original formulation of the harmonic approximation are tabulated in table 2 and table 3, respectively, for \( B_{80}^+ \) and \( C_{60}^+ \) Jahn-Teller problems. According to the group theory prediction, the destabilization of the \( ^2H_u \) degenerate state of \( B_{80}^+ \) and \( C_{60}^+ \) involves the distortion force representative of \( g_{ag} \) and \( h_{ag} \) normal modes (\( H_u \otimes H_u = \{t_{1g} \oplus t_{2g} \oplus g_{u} \} \oplus \{a_{g} \oplus g_{u} \oplus 2 \, h_{g} \} \)). This is reproduced in table 2 and table 3, since the \( t_{1g} \) and \( t_{2g} \) normal modes of the \( I_h \) \( B_{80}^+ \) participate in a relatively weak contribution (table 2), either to the Jahn-Teller distortion or to the energy stabilization. Thus the calculated forces to those normal modes are almost negligible. However, the Jahn-Teller radius of the distortion of the \( I_h \) \( B_{80}^+ \) (0.406 Å) is 2.7 times larger than the radius corresponding to the distortion of the geometry of the \( I_h \) \( C_{60}^+ \) (0.151 Å). Then we have used the distortion vector \( \vec{R}_{JTE} \) of \( B_{80}^+ \) to separate the eighty boron atoms in two different fragments. The first fragment grouped the sixty boron atoms that form the buckyball, while the second fragment consisted to the remaining 20 boron caps. Therefore 18% (i.e. 0.173 Å) of the distortion is occurring on this first group of boron atoms, while 82% (i.e. 0.367 Å) of the distortion is due to the twenty boron caps. Thus the relaxation of the geometry of \( B_{80}^+ \) takes place mainly at the twenty boron caps and turns out to be a complex combination of Jahn-Teller and pseudo-Jahn-Teller mechanisms. A detailed analysis of these results will be found elsewhere. [23] Moreover, the Jahn-Teller stabilization energy of \( B_{80}^+ \) (1289 cm\(^{-1}\)) is 2.3 times higher than that obtained for the stabilization of \( C_{60}^+ \) (575 cm\(^{-1}\)), while the total force corresponding to the \( B_{80}^+ \) problem is found two times weaker in comparison to the total force corresponding to the \( C_{60}^+ \) problem (table 2 and table 3).
Table 2. Analysis of 1st order Jahn-Teller distortion of the \( I_6 B_{80}^+ \): The Jahn-Teller magnitude \( q_{HS,k} \) [Å], the stabilization energy \( E_{HS,k} \) [cm\(^{-1}\)] and the forces \( F_{HS,k} \) [mdyne].

| Mode     | \( q_{HS,k} \) | \( E_{HS,k} \) | \( F_{HS,k} \) |
|----------|----------------|----------------|----------------|
| \( a_g \) #01 | 0.102         | 98             | 0.073          |
| \( a_g \) #02 | 0.073         | 53             | 0.061          |
| \( a_g \) #03 | 0.007         | 2              | 0.043          |
| \( t_{1g} \) #01 | 0.002         | 0              | 0.006          |
| \( t_{1g} \) #02 | 0.002         | 0              | 0.005          |
| \( t_{1g} \) #03 | 0.000         | 0              | 0.001          |
| \( t_{1g} \) #04 | 0.001         | 0              | 0.003          |
| \( t_{2g} \) #01 | 0.001         | 1              | 0.002          |
| \( t_{2g} \) #02 | 0.001         | 0              | 0.004          |
| \( t_{2g} \) #03 | 0.000         | 0              | 0.004          |
| \( t_{2g} \) #04 | 0.001         | 1              | 0.002          |
| \( t_{2g} \) #05 | 0.000         | 0              | 0.003          |
| \( \text{img}^b \ g_g \) #01 | 0.379         | 489            | 0.090          |
| \( g_g \) #02 | 0.052         | 40             | 0.032          |
| \( g_g \) #03 | 0.003         | 1              | 0.004          |
| \( g_g \) #04 | 0.010         | 1              | 0.011          |
| \( g_g \) #05 | 0.005         | 2              | 0.014          |
| \( g_g \) #06 | 0.002         | 24             | 0.068          |
| \( g_g \) #07 | 0.007         | 9              | 0.065          |
| \( g_g \) #08 | 0.005         | 8              | 0.039          |
| \( h_g \) #01 | 0.025         | 358            | 0.017          |
| \( h_g \) #02 | 0.001         | 63             | 0.010          |
| \( h_g \) #03 | 0.033         | 64             | 0.015          |
| \( h_g \) #04 | 0.017         | 16             | 0.032          |
| \( h_g \) #05 | 0.004         | 17             | 0.041          |
| \( h_g \) #06 | 0.001         | 2              | 0.012          |
| \( h_g \) #07 | 0.005         | 8              | 0.035          |
| \( h_g \) #08 | 0.012         | 6              | 0.033          |
| \( h_g \) #09 | 0.001         | 6              | 0.036          |
| \( h_g \) #10 | 0.007         | 18             | 0.071          |
| \( h_g \) #11 | 0.002         | 1              | 0.014          |
| Total      | 0.406         | 1289           | 0.208          |

*1 mdyne represents \( 10^{-8} \) N

*img stands for imaginary
Table 3. Analysis of the 1st order Jahn-Teller distortion of the $I_h\ C_{60}^+$: The Jahn-Teller magnitude $q_{HS,k}$ [Å], the stabilization energy $E_{HS,k}$ [cm$^{-1}$] and the forces $F_{HS,k}$ [mdyne].

| Mode   | $q_{HS,k}$ | $E_{HS,k}$ | $F_{HS,k}$ |
|--------|------------|------------|------------|
| a$_g$ #01 | 0.004      | 0          | 0.010      |
| a$_g$ #02 | 0.006      | 30         | 0.103      |
| h$_g$ #01 | 0.143      | 246        | 0.069      |
| h$_g$ #02 | 0.036      | 39         | 0.046      |
| h$_g$ #03 | 0.001      | 0          | 0.003      |
| h$_g$ #04 | 0.021      | 50         | 0.087      |
| h$_g$ #05 | 0.002      | 2          | 0.012      |
| h$_g$ #06 | 0.010      | 23         | 0.122      |
| h$_g$ #07 | 0.016      | 100        | 0.253      |
| h$_g$ #08 | 0.014      | 86         | 0.263      |
| Total   | 0.151      | 575        | 0.416      |

$^a$ 1 mdyne represents 10$^{-8}$ N

The calculated forces of the normal modes of HS nuclear configurations give an information about the linear vibronic coupling coefficient in $B_{80}^+$ and $C_{60}^+$ problems. Considering the forces obtained for the distortion of the $I_h\ C_{60}^+$, the two hardest anti-squashing h$_g$ #07 and h$_g$ #08 modes have the largest vibronic coupling coefficient, as previously determined by other theoretical studies. [22, 24] Although, the squashing h$_g$ #01 mode has a smaller force, its contribution to the Jahn-Teller energy is the most important. For the case of $B_{80}^+$, the coupling is found stronger among the g$_g$ modes than the h$_g$ modes, although the energy stabilizations by h$_g$ and g$_g$ modes are almost similar.

4. Conclusion

In this paper, our general approach to analyse the multimode Jahn-Teller distortion is applied to study the Jahn-Teller effect of the cationic form of the icosahedral boron and carbon buckyball ($C_{60}^+$ and $B_{80}^+$). It is shown how a simple model based on harmonic approximation can be successfully applied in order to determine the Jahn-Teller parameters, i.e. the Jahn-Teller magnitude, the Jahn-Teller energy and the forces at the HS reference point. The origin of our approach states that the Jahn-Teller distortion may be expressed as a linear combination of all totally symmetric normal modes in the LS global minimum energy conformation. This specific formulation based on the Hessian of the LS structure has several advantages. The LS structure is true minima on the APES and the potential energy expression has a simple analytical form in the harmonic approximation. Therefore while the Jahn-Teller magnitude and the forces are obtained in a straightforward way, due to the vector properties of the normal modes, the Jahn-Teller stabilization energy with respect to the HS normal modes can be obtained using the correlation matrix between the normal modes in the HS and LS nuclear configurations.

Hence we presented here the static part of the multimode problem in $B_{80}^+$ and compared the results to that obtained for $C_{60}^+$. The ground state geometry of $B_{80}^+$ distorts slightly from the $D_{5d}$ to the $S_6$ symmetry, while the ground state geometry of $C_{60}^+$ has a $D_{5d}$ symmetry. Thus these two inorganic cations present the only two possible solutions of the solving of the standard Jahn-Teller problem corresponding to the quintet $H\otimes(g\oplus2h)$ Jahn-Teller instability. [27]
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