Group theoretical analysis of vibrational modes and rovibronic levels of extended aromatic C_{48}N_{12} azafullerene

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Abstract

We have presented a group theoretical analysis of the vibrational normal modes and rovibronic levels of a novel extended aromatic C_{48}N_{12} azafullerene. We have also predicted the properties of the 3Au, 3Eg, and 3Eu excited states of C_{48}N_{12} that lie 1.9 eV above the 1Ag ground state, and that the 3Eg and 3Eu states would undergo Jahn–Teller distortion into chiral structures with no symmetry and an achiral structure with C_i symmetry. The correlation of the rovibronic and rotational levels and their relation to the parent I_h symmetry are presented through induced and subduced representations.

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1. Introduction

Ever since the discovery of buckminsterfullerene (C_{60}) [1–4] there has been increased interest in aromaticity of heteropolycyclics and in search of other buckyball analogs and other structures that exhibit icosahedral or dodecahedral structures that contain nitrogen and other atoms [5–19]. While there have been theoretical efforts suggesting such possibilities, it was not until a recent magnetron sputtering experiment that the synthesis of a cross-linked nanomaterial of carbon and nitrogen has been achieved [8]. This nanomaterial seems to contain C_{48}N_{12} as its core material. This has been confirmed by electron microscopy and electron energy loss spectroscopy (EELS). The related synthesis of solid buckydimier (C_{59}N)_{2} as well as a molecular species of the formula C_{60–2n}N_{2n} have been reported [11].

The concepts of aromaticity and extended aromaticity have been revisited by many investigators [16–22] due to their importance in both metallic and non-metallic clusters. In the context of extended aromaticity it has been shown using combinatorics, graph-theory and sextet polynomials [20–22] that extended aromatic systems can be formed by heterocyclic species, such as five-membered rings containing nitrogens fused with hexagons. In particular by using combinatorics [20] it can be shown that triphenylene exhibits eight canonical resonance structures due to the presence of fused rings and ‘kinks’ in the structure which result in a branched dual graph with four vertices for triphenylene. It has been shown by Herndon [20] that the numbers of Kekulé structures increase in a Fibonacci sequence as a function of the kinks in the catacondensed polycyclic benzenoid aromatics. Consequently, when a five-membered heterocycle with nitrogen comes together with the triphenylene structure, it is not surprising indeed to find that C_{48}N_{12} to be unusually stable.

Manaa and coworkers [12–15] have investigated C_{48}N_{12} and their analogs such as C_{48}B_{12} in a series of density functional level studies. Indeed Manaa et al. [13] have confirmed the existence of a very stable buckyball structure for C_{48}N_{12} exhibiting S_6 symmetry, and more stable than the previously computed isomer by Stafström et al. [9]. The structure that was found to be the
most stable by Manaa et al. [13] has one nitrogen per pentagon arranged in such a manner so as to minimize nitrogen repulsions and maximize extended aromaticity, as it is derived from triphenylene fused with five-membered heterocycle containing one nitrogen per ring. The resulting structure is a novel buckyball containing nitrogen atoms and exhibiting an overall $S_6$ symmetry. The structure has two triphenylene units fused with three pentagons, as shown in Fig. 1 as ‘cup’ and ‘cap’ of the ball, the remaining six nitrogen atoms are distributed among the equatorial pentagons so that each nitrogen is separated from the cup or cap nitrogen by one carbon atom, thus minimizing the nitrogen–nitrogen repulsion. By the use of DFT level of theory, Manaa et al. [13] have demonstrated that this isomer of $C_{48}N_{12}$ is 13.1 kcal/mol energetically more stable than the one reported earlier by Stafström et al. [9]. Moreover, Manaa et al. [13] have obtained the vibrational frequencies of all modes of $C_{48}N_{12}$ establishing the structure to be a true minimum. The current author [23–27] has been applying combinatorial methods to fullerenes. As shown by the current author [25] there are 233,227,974,475 possible combinatorial isomers for $C_{48}N_{12}$. Of course many of those isomers are not likely to be stable due to the fact that if two nitrogen atoms occur as neighbors there will be nitrogen–nitrogen repulsion, which would destabilize the structure. Hence, the ones that would overcome inherent repulsive interactions are those that would have nitrogens as far away as possible and also the ones that exhibit maximum canonical resonance structures and Clar’s aromatic sextets [21,22]. In particular it can be shown that there are 19 isomers of $C_{48}N_{12}$ that have $S_6$ or the isomorphic $C_{3h}$ symmetry using the mark version of Pólya’s theorem [28]. It is interesting to note that at least two stable isomers with potential minima separated by 13 kcal/mol have been computed thus far [9,10]. Since $C_{48}N_{12}$ is unusually stable and has been identified as the building block of a solid-state nanomaterial [8], it is clear that spectroscopic studies of laser-vaporized and supersonically cooled cluster of composition $C_{48}N_{12}$ are likely in the future. This is feasible with the supersonic expansion of the laser-vaporized solid film of the material. Indeed such spectroscopic studies would be quite exciting, and in anticipation of such studies, we have considered the complete rovibronic analysis, normal mode analysis and nuclear spin species and nuclear spin statistical weight analysis of the $C_{48}N_{12}$ dodecaazafulerene.

In this Letter, we consider the group theoretical correlation of the rotational levels, vibrational modes while the last section considers other features such as the induction and subduction of the representations in relation to the parent buckyball with $I_h$ symmetry and the Jahn–Teller effects in the excited states. Nuclear spin statistics [29,30] is considered in the ensuing paper [35].

2. Group theoretical analysis of rotational levels and vibrational modes of $C_{48}N_{12}$

Fig. 1 shows two different perspectives of the $C_{48}N_{12}$ isomer under consideration. The name of the isomer according to the IUPAC convention is $(8,13,18,23,26,29,32,35,38,40,45,50)$-dodecaaza$[60-S_6]$fullerene. This isomer has only an improper $S_6$ axis of symmetry or alternatively isomorphic $C_{3h}$ symmetry. The $S_6$ axis passes through the centers of the hexagons corresponding to the ‘cup’ and ‘cap’ of this structure. The $C_{48}N_{12}$ cluster is a near-spherical top with the orthogonal rotational constants of 0.08304, 0.08304 and 0.08221 GHz, respectively. First we obtain the group theoretical correlation of the rotational levels of $C_{48}N_{12}$ into the $S_6$ or equivalently the $C_{3h}$ point group. We have also used the subduced representation method to correlate the corresponding rotational levels of the parent buckyball in the $I_h$ symmetry group. Table 1 shows the correlation table of the rotational levels of $C_{48}N_{12}$ into the $S_6$ or equivalently the $C_{3h}$ point group. We have also used the subduced representation method to correlate the corresponding rotational levels of the parent buckyball in the $I_h$ symmetry group. Table 1 shows the correlation table of the rotational levels of $C_{48}N_{12}$ into the $S_6$ group together with the subduction chain from the $I_h$ group since $S_6$ is a subgroup of the $I_h$ group. As seen from Table 1, the rotational levels of $C_{48}N_{12}$ exhibit a cyclicity of three unlike the parent $I_h$ group that exhibits a period of 30 [26,31]. This implies that the correlation of the rotational levels with higher $K$ quantum numbers is readily obtained with the cyclicity of three. This is also due to the fact that only the $A_g$ and $E_g$ representations...
occur in the rotational representations of the $S_6$ group. In the ensuing Letter [35] we have obtained the nuclear spin statistical weights and spin species. The spin statistical weights are associated with the rotational or more generally the rovibronic levels.

We have carried out the normal mode analysis of $C_{48}N_{12}$ by associating three orthogonal vectors on each atom, and studying their transformation properties. Since the $S_6$ group has a single generator, namely the $S_6$ operation, it does not leave any vector on all 60 atoms invariant. Consequently, it is straightforward to show that the 3N modes of $C_{48}N_{12}$ transform as

$$C_{180} = 30A_g + 30E_g + 30E_u.$$  

Since the three orthogonal rotations $R_z$ and $(R_x, R_y)$, transform as $A_g$ and $E_g$, representations of the $S_6$ point group, respectively, and the translations transform as the $A_u$ and $E_u$ representations, we have the normal modes of $C_{48}N_{12}$ as

$$\Gamma_e = 29(A_g + A_u + E_g + E_u).$$

Due to the presence of the inversion operation, complimentary IR and Raman selection rules hold for the $C_{48}N_{12}$ cluster and thus only $u$ modes are IR-active. Manaa et al. [13] have obtained the frequencies and intensities of the vibrational modes of $C_{48}N_{12}$ using the DFT/B3LYP level computations with a double-$\zeta$ 631G* basis set. Fig. 2 shows the computed IR spectrum of $C_{48}N_{12}$ that we have plotted from the B3LYP results of Manaa et al. [13]. Although the peak near 1300 cm$^{-1}$ seems to be the most intense in Fig. 2, this peak actually corresponds to multiple IR-allowed vibrational modes. The single most intense peak corresponds to the $A_u$ vibrational mode with a frequency of 1669.1 cm$^{-1}$ and an intensity of 242.9 km/mol. The peak near 1300 cm$^{-1}$ corresponds to an $A_u$ mode with a frequency of 1308.5 cm$^{-1}$ and another $E_u$ mode with a frequency of 1326.7 cm$^{-1}$ and another $E_u$ mode at 1292.5 cm$^{-1}$ with a component intensity of 61.9 km/mol.

The peak near 1425 cm$^{-1}$ corresponds to another $A_u$ vibrational mode with a computed intensity of 108.6 km/mol.

The vibrational modes with relatively strong IR intensities are depicted in Fig. 3. The $C_{48}N_{12}$ cluster is quite interesting in having multiply IR active modes occurring close to each other as with 2 $E_u$ modes with frequencies of 1292.5 and 1326.7 cm$^{-1}$, $E_u$ mode with a frequency of 1326.7 cm$^{-1}$ and another $E_u$ mode at 1292.5 cm$^{-1}$.

The peak near 1425 cm$^{-1}$ corresponds to another $A_u$ vibrational mode with a computed intensity of 108.6 km/mol.

Table 1
Correlation of rotational levels of $C_{48}N_{12}$ into the $S_6$ group and also induction into $I_h$ parent group

<table>
<thead>
<tr>
<th>$K$</th>
<th>$S_6$</th>
<th>$I_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$A_g$</td>
<td>$A_g$</td>
</tr>
<tr>
<td>1</td>
<td>$A_g + E_g$</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>2</td>
<td>$A_g + 2E_g$</td>
<td>$T_{2g}$</td>
</tr>
<tr>
<td>3</td>
<td>$3A_g + 2E_g$</td>
<td>$T_{2g} + G_g$</td>
</tr>
<tr>
<td>4</td>
<td>$3A_g + 3E_g$</td>
<td>$G_g + H_g$</td>
</tr>
<tr>
<td>5</td>
<td>$3A_g + 4E_g$</td>
<td>$T_{1g} + T_{2g} + H_g$</td>
</tr>
<tr>
<td>6</td>
<td>$5A_g + 4E_g$</td>
<td>$A_u + T_{1g} + G_g + H_g$</td>
</tr>
<tr>
<td>$n^*$</td>
<td>$2[n/3](A_g + E_g) + D^{(r)}$</td>
<td>$[n/3](A_g + 3T_{1g} + 3T_{2g} + 4G_g + 5H_g) + D^{(r)}$</td>
</tr>
</tbody>
</table>

*For $n > 3$, $[n/3]$ is the greatest integer contained in three and $r$ is the remainder obtained by dividing $n$ by 3 for the $S_6$ group and $[n/30]$ is the quotient obtained by diving 30 and $r$ is the corresponding remainder for the $I_h$ group.

Manaa et al. [13] have obtained the frequencies and intensities of the vibrational modes of $C_{48}N_{12}$ using the DFT/B3LYP level computations with a double-$\zeta$ 631G* basis set. Fig. 2 shows the computed IR spectrum of $C_{48}N_{12}$ that we have plotted from the B3LYP results of Manaa et al. [13]. Although the peak near 1300 cm$^{-1}$ seems to be the most intense in Fig. 2, this peak actually corresponds to multiple IR-allowed vibrational modes. The single most intense peak corresponds to the $A_u$ vibrational mode with a frequency of 1669.1 cm$^{-1}$ and an intensity of 242.9 km/mol. The peak near 1300 cm$^{-1}$ corresponds to an $A_u$ mode with a frequency of 1308.5 cm$^{-1}$, $E_u$ mode with a frequency of 1326.7 cm$^{-1}$ and another $E_u$ mode at 1292.5 cm$^{-1}$.
Au mode at 1308.5 cm\(^{-1}\) and the Eu mode 1326.7 cm\(^{-1}\) both involve C–N bond vibrations. Thus the peaks near 1308–1327 cm\(^{-1}\), which are attributable to these modes, would be the most characteristic feature of the C\(_{48}\)N\(_{12}\) cluster that would aid in identifying the cluster.

3. Rovibronic levels and Jahn–Teller effects in the excited states of C\(_{48}\)N\(_{12}\)

The rovibronic levels of C\(_{48}\)N\(_{12}\) are obtained as direct products of the rotational, vibrational and electronic levels. Since the ground state of C\(_{48}\)N\(_{12}\) is of 1\(\text{Ag}\) symmetry, this causes no additional complication from the electronic state. The nuclear spin statistical weight of each rovibronic level is obtained by stipulating that the overall symmetry of the total wavefunction, which is a direct product of the rovibronic function and nuclear spin function must be totally symmetric (1\(\text{Ag}\)) since 14\(\text{N}\) nuclei are bosons. This is the case for the C\(_{48}\)N\(_{12}\) cluster, and the total nuclear spin statistical weights are obtained \([35]\) as 88,725, 88,476, 177,360, and 176,880 for the 1\(\text{Ag}\), 1\(\text{Au}\), 1\(\text{Eg}\), and 1\(\text{Eu}\) levels, respectively. If the cluster is of the composition 13\(\text{C}_{48}\)N\(_{12}\) then the overall wavefunction must be antisymmetric since the 13\(\text{C}\) nuclei are fermions; in this case the overall nuclear spin species are inverted relative to \(g\) and \(u\) symmetries. We \([34]\) have computed the energetics of the excited states of C\(_{48}\)N\(_{12}\) using effective core potentials combined with a triple-\(\zeta\) + polarization (3s3p1d) basis sets and DFT/B3LYP level. The HOMO–LUMO gap of C\(_{48}\)N\(_{12}\) is 2.74 eV at the DFT level, where the first LUMO is of 1\(\text{Au}\) symmetry. However, there is a low-lying second LUMO of 1\(\text{Eg}\) symmetry at 2.97 eV and third one of 1\(\text{Eu}\) symmetry at 3.00 eV. At the DFT-ECP-(3s3p1d) level the first excited state, 3\(\text{Au}\) is found to be at 1.91 eV above the 1\(\text{Ag}\) ground state. This energy gap is much lower than the HOMO–LUMO gap as expected for the triplet state, which is stabilized by the spin exchange energy. Since the first LUMO is close in energy to the second and third LUMOs, the 3\(\text{Eg}\) and 3\(\text{Eu}\) states are both competitors for the 3\(\text{Au}\) excited state of C\(_{48}\)N\(_{12}\). The 3\(\text{Eg}\) and 3\(\text{Eu}\) states would be subjected to the Jahn–Teller effect through the \(E \otimes \varepsilon\) vibronic coupling. This should distort the excited state structure from the S\(_6\) group to two possible structures: a chiral structure that has no symmetry at all and an achiral structure with only an inversion operation. This follows from the fact that only possible non-trivial subgroups of the S\(_6\) group are the C\(_3\) group and the C\(_i\) group. A structure with C\(_3\) symmetry and with E representation would undergo further Jahn–Teller distortion becoming a structure with the C\(_i\) symmetry. It seems that the excited states arising from 3\(\text{Eg}\) and 3\(\text{Eu}\) electronic states would exhibit dynamic pseudo Jahn–Teller motion if the barrier to pseudo rotation were to be particularly small. This would be

\[
D^\text{a1} \otimes D^\text{a2} = D^{(s_1+s_2)} \oplus D^{(s_1+s_2-1)} \oplus \ldots D^{(s_1-s_2)}.
\]

This results in a larger number of spin multiplets than those shown in Table 2 of \([35]\). However, the ratios of the overall nuclear spin statistical weights vary approximately as the dimensions of the representations, thus making the parity difference negligible for this case. Hence, the differences in the spin populations and fine structures are more readily seen for the naturally occurring C\(_{48}\)N\(_{12}\) for the high spin multiplets.

The rovibronic levels of the excited electronic states of C\(_{48}\)N\(_{12}\) seem to be quite interesting as some of the excited states of C\(_{48}\)N\(_{12}\) are predicted here to undergo the Jahn–Teller distortion. The Jahn–Teller distortion in larger clusters is quite interesting as can be seen from the reviews of Bersuker \([32,33]\). While the ground state of C\(_{48}\)N\(_{12}\) is unambiguously the 1\(\text{Ag}\) closed-shell state, the excited states appear to be interesting. We \([34]\) have computed the energetics of the excited states of C\(_{48}\)N\(_{12}\) using effective core potentials combined with a triple-\(\zeta\) + polarization (3s3p1d) basis sets and DFT/B3LYP level. The HOMO–LUMO gap of C\(_{48}\)N\(_{12}\) is 2.74 eV at the DFT level, where the first LUMO is of 1\(\text{Au}\) symmetry. However, there is a low-lying second LUMO of 1\(\text{Eg}\) symmetry at 2.97 eV and third one of 1\(\text{Eu}\) symmetry at 3.00 eV. At the DFT-ECP-(3s3p1d) level the first excited state, 3\(\text{Au}\) is found to be at 1.91 eV above the 1\(\text{Ag}\) ground state. This energy gap is much lower than the HOMO–LUMO gap as expected for the triplet state, which is stabilized by the spin exchange energy. Since the first LUMO is close in energy to the second and third LUMOs, the 3\(\text{Eg}\) and 3\(\text{Eu}\) states are both competitors for the 3\(\text{Au}\) excited state of C\(_{48}\)N\(_{12}\). The 3\(\text{Eg}\) and 3\(\text{Eu}\) states would be subjected to the Jahn–Teller effect through the \(E \otimes \varepsilon\) vibronic coupling. This should distort the excited state structure from the S\(_6\) group to two possible structures: a chiral structure that has no symmetry at all and an achiral structure with only an inversion operation. This follows from the fact that only possible non-trivial subgroups of the S\(_6\) group are the C\(_3\) group and the C\(_i\) group. A structure with C\(_3\) symmetry and with E representation would undergo further Jahn–Teller distortion becoming a structure with the C\(_i\) symmetry. It seems that the excited states arising from 3\(\text{Eg}\) and 3\(\text{Eu}\) electronic states would exhibit dynamic pseudo Jahn–Teller motion if the barrier to pseudo rotation were to be particularly small. This would be
particularly interesting as the undistorted structure is achiral while two of the distorted structures are predicted to be chiral. It remains to be seen if the Jahn–Teller effect in the excited state would be inversion conserving or if it totally destroys the inversion symmetry.

We have provided in Table 3 the subduction and induction chains for the relation between the parent buckyball and the C_{48}N_{12} cluster. The subduction chain is from higher I_h group symmetry to the lower S_6 point group symmetry. This chain is useful to correlate the rovibronic levels of C_{60} to C_{48}N_{12}. For example, the T_{1g} rovibronic level of C_{60} splits into A_g + E_g + T_{2g} + G_g + 2H_g due to the lowering of symmetry from I_h to S_6. Likewise the H_2 level of C_{60} splits into A_g and two E_g levels. The induction chain is obtained by using the concept of induced representation, that is, when an irreducible representation of S_6 is induced into I_h according to the Clifford algebra it becomes reducible in the I_h group and splits into irreducible representations. For example, as can be seen from Table 3, the totally symmetric A_1 irreducible representation of the S_6 point group becomes A_g + T_{1g} + T_{2g} + 2G_g + H_g in the I_h group.

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