NMR spectra of icosahedral (I_h and I) fullerenes

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By analyzing the topological structures of the three types of icosahedral fullerenes: (1) $C_n(I_h, \; n = 60h^2, \; h = 1, 2, \ldots)$, (2) $C_n(I_h, \; n = 20h^2, \; h = 1, 2, \ldots)$ and (3) $C_n(I, \; n = 20(h^2 + hk + k^2), \; h > k, \; h, k = 1, 2, \ldots)$, we have obtained theoretically the ^{13}C NMR spectra with natural abundance for ^{13}C of all the icosahedral (I_h and I) fullerenes.

1. Introduction

NMR spectra, as well as the infrared and Raman spectra, have been widely used as a powerful tool for the determination of molecular structure. C_{60} was discovered in 1985 [8], and its structure was assumed to be of I_h symmetry [4,5,9]. This proposition has been confirmed by the observation of its NMR spectrum to be of only one line [1, 7,11], as all the sixty carbon atoms in C_{60} are equivalent with respect to the I_h group.

It has been pointed out that there are two types of the I_h fullerenes C_n: one being with $n = 60h^2$ ($h = 1, 2, \ldots$) and the other with $n = 20h^2$ ($h = 1, 2, \ldots$). C_{60}, C_{240}, C_{540}, etc. belong to the first type, while C_{20}, C_{80}, C_{180}, etc. belong to the second type. For the fullerenes C_n with I symmetry, the corresponding formula is $n = 20(h^2 + hk + k^2)$ with $h > k$ and h, k being the positive integers. There are 6 fivefold axes, 10 threefold axes, 15 twofold axes, so there are 60 elements in the I group. As shown in figure 1, an icosahedron can be divided into the 60 fundamental triangles, $PP_3P_2P_3'$ for the I fullerenes and the first type of the I_h fullerenes or P_3PP_2P' for the second type of the I_h fullerenes, corresponding to the 60 operations of the icosahedral rotation group. We have used the fundamental triangles to discuss the vibrational modes [10]; in this article, we shall derive the formulas for the ^{13}C NMR spectra with natural abundance for ^{13}C of all icosahedral (I_h and I) fullerenes.

Here we assume that many of the cages identified as of I or I_h symmetry should not be so in their ground-state-energy conformation, because of Jahn–Teller distortion. That is, frequently the considered cages are found to be open-shell at icosahedral symmetry so that they should distort, and if the distortion is "static", then the number
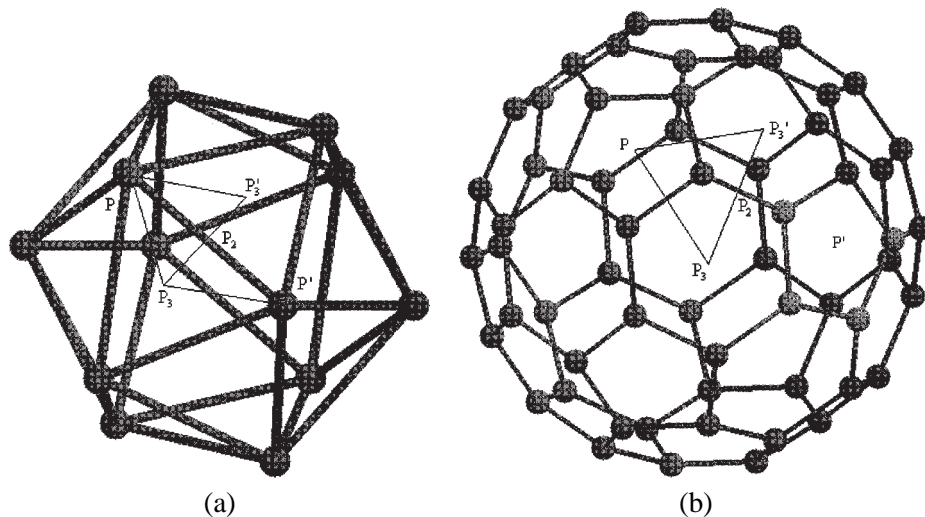
Figure 1. Icosahedrons of molecule (a) B_{12} and (b) C_{60} can be divided into the 60 fundamental triangles ($PP_3P_2P_3'$ or P_3PP_2P') corresponding to the 60 operations of the icosahedral rotation group.

of NMR lines would be greater than calculated, while if the distortion is "dynamic", then the number reported could take the proper value. There are a few theoretical papers [2,3,6] which have considered different questions concerning NMR spectra of fullerenes.

2. ^{13}C NMR spectra of $C_n(I_h,\ n = 60h^2)$

The circumsphere of a polyhedron $C_n(I_h,\ n = 60h^2)$ is made up of sixty patches which are equivalent with respect to the I group. We can take one of them as a representative patch, the structure of which reflects the whole topological characters of the corresponding fullerene $C_n(I_h,\ n = 60h^2)$. The patch is characterized by the presence of one fivefold axis OP, two threefold axes OP_3 and OP_3', and one twofold axis OP_2 on the boundaries, where O is the origin of the fullerene, furthermore, it has a symmetry plane σ defined by OP and OP_2 across the patch, as shown in figure 2.

Inside the patch, there are h^2 carbon atoms, which are symmetrically distributed from top to bottom about the symmetry plane σ in the manner according to the following distribution function:

$$D(h^2) = 1 + 1 + 2 + 2 + \cdots + (h - 1) + (h - 1) + h. \qquad (1)$$

In the patch, there are h carbon atoms on the symmetry plane σ and $h(h - 1)$ carbon atoms located symmetrically on the two sides of the plane. In totality, there are h different sets with 60 carbon atoms in each set lying on the symmetry planes, and $h(h - 1)/2$ different sets with 120 carbon atoms in each set not lying on any symmetry element of the I_h group. Therefore, the total number of NMR spectrum lines is $h + h(h - 1)/2$ for the icosahedral fullerenes $C_n(I_h,\ n = 60h^2)$.
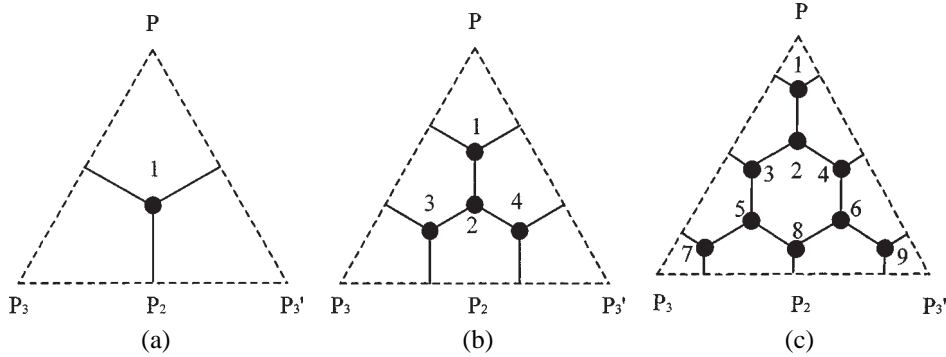
Figure 2. Patches of fullerenes $C_n(I_h, \ n = 60h^2)$. (a) $C_{60}(h = 1)$, (b) $C_{240}(h = 2)$, (c) $C_{540}(h = 3)$.
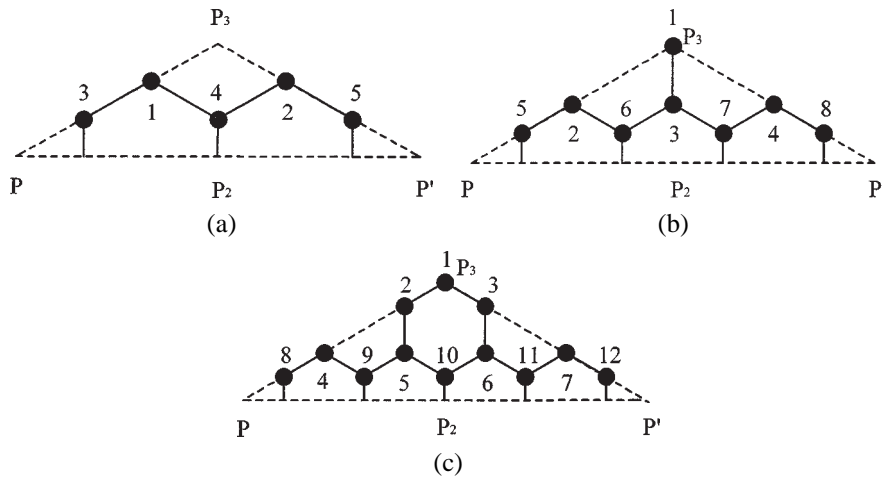

Figure 3. Patches of fullerenes $C_n(I_h, \ n = 20h^2)$. (a) $C_{180}(h = 3m, \ m = 1)$, (b) $C_{320}(h = 3m+1, \ m = 1)$, (c) $C_{500}(h = 3m + 2, \ m = 1)$.

3. ^{13}C NMR spectra of $C_n(I_h, \ n = 20h^2)$

The representative patch of $C_n(I_h, \ n = 20h^2)$ is characterized by the presence of one threefold axis OP_3, two fivefold axes OP and OP', and one twofold axis OP_2 on the boundaries, furthermore, there is a symmetry plane σ' determined by OP_3 and OP_2, across the patch, as shown in figure 3.

In the patch, there are $h^2/3$ carbon atoms which are symmetrically distributed about the plane σ'. For those carbon atoms that are on both the boundary determined by OP_3 and OP and the other one by OP_3 and OP', we can only take the carbon atoms on one boundary to be in the patch. The distribution of carbon atoms about the symmetry plane σ' is according to the following three distribution functions, so we need to consider the three cases separately.

(a) ($h = 3m$, $m = 1, 2, \ldots$) The distribution function is shown below:

$$D\big((3m)^2/3\big) = (1 + 2) + (4 + 5) + \cdots + (3m - 2 + 3m - 1). \tag{2}$$

Because the plane defined by OP_3 and OP is equivalent to the plane σ' with respect to the threefold axis OP_3, it is also a symmetry plane. In the patch, there are $3m$ carbon atoms lying on the symmetry planes, and $3m(m - 1)$ carbon atoms located symmetrically on the two sides of the symmetry plane σ'. In the totality of the sixty equivalent patches, there are $3m$ different sets with 60 carbon atoms in each set lying on the symmetry planes, and $3m(m - 1)/2$ different sets each with 120 carbon atoms not lying on any symmetry element of the I_h group. Therefore, the number of NMR spectrum lines is equal to $3m + 3m(m - 1)/2$ for the fullerenes $C_n(I_h$, $n = 20h^2$, $h = 3m$).

(b) ($h = 3m + 1$, $m = 0, 1, 2, \ldots$) In this case, there are $(3m + 1)^2/3$ carbon atoms in the patch, and they are symmetrically located about the plane σ' in the manner according to the following distribution function:

$$D\big((3m + 1)^2/3\big) = 1/3 + (2 + 3) + (5 + 6) + \cdots + (3m - 1 + 3m), \tag{3}$$

where $1/3$ means one carbon atom located on the threefold axis OP_3; furthermore, there are $3m$ carbon atoms lying on the symmetry planes and $m(3m - 1)$ carbon atoms located symmetrically on the two sides of the plane σ'. Taking the sixty equivalent patches as a whole, we have one set of 20 carbon atoms on the threefold axes, $3m$ different sets with 60 carbon atoms in each set lying on the symmetry planes, and $m(3m - 1)/2$ different sets with 120 carbon atoms not lying on any symmetry element of the I_h group. Therefore, the number of NMR spectrum lines is equal to $3m + m(3m - 1)/2 + 1$ for the fullerenes $C_n(I_h$, $n = 20h^2$, $h = 3m + 1$).

(c) ($h = 3m + 2$, $m = 0, 1, 2, \ldots$) In this case, the $(3m + 2)^2/3$ carbon atoms in the patch are symmetrically located about the plane σ' in the manner according to the following distribution function:

$$D\big((3m + 2)^2/3\big) = (1/3 + 1) + (3 + 4) + (6 + 7) + \cdots + (3m + 3m + 1). \tag{4}$$

In each patch, there are $1/3$ carbon atom located on the threefold axis OP_3, $(3m + 1)$ carbon atoms lying on the symmetry planes, and $m(3m + 1)$ carbon atoms located symmetrically on the two sides of the plane σ'. Taking the sixty equivalent patches as a whole, we have one set of 20 carbon atoms located on the threefold axes, $(3m + 1)$ different sets with 60 carbon atoms in each set lying on the symmetry planes, and $m(3m + 1)/2$ different sets with 120 carbon atoms in each set not lying on any symmetry element of I_h group. Therefore, the number of NMR spectrum lines is equal to $(3m + 1) + m(3m + 1)/2 + 1$ for the fullerenes $C_n(I_h$, $n = 20h^2$, $h = 3m + 2$).

Table 1

NMR spectra of icosahedral (I$_h$ and I) fullerenes. For many of the fullerenes, there should be Jahn–Teller distortion. If the distortion is "dynamic", the number of NMR lines are as reported here, if the distortion is "static", the number of the ^{13}C lines would be larger than the reported value.

Type	NMR spectra
C$_n$(I$_h$, $n = 60h^2$)	$h(h-1)/2 + h(\sigma)$
C$_n$(I$_h$, $n = 20h^2$)	
$\quad h = 3m$	$3m(m-1)/2 + 3m(\sigma)$
$\quad h = 3m + 1$	$m(3m-1)/2 + 3m(\sigma) + 1(C_3)$
$\quad h = 3m + 2$	$m(3m+1)/2 + (3m+1)(\sigma) + 1(C_3)$
C$_n$(I, $n = 20(h^2 + hk + k^2)$, $h > k$)	
$\quad h - k = 3m$	$k^2 + 3mk + 3m^2$
$\quad h - k = 3m + 1$	$[k^2 + (3m+1)k + 3m^2 + 2m] + 1(C_3)$
$\quad h - k = 3m + 2$	$[k^2 + (3m+2)k + 3m^2 + 4m + 1] + 1(C_3)$

4. ^{13}C NMR spectra of C$_n$(I, $n = 20(h^2 + hk + k^2)$, $h > k$)

The fullerenes with I symmetry can be divided into three cases:

$$\text{(a) } h - k = 3m, \ n = 60(k^2 + 3mk + 3m^2); \tag{5}$$

$$\text{(b) } h - k = 3m + 1, \ n = 60[k^2 + (3m+1)k + 3m^2 + 2m] + 20; \tag{6}$$

$$\text{(c) } h - k = 3m + 2, \ n = 60[k^2 + (3m+2)k + 3m^2 + 4m + 1] + 20. \tag{7}$$

For case (a), there are $k^2 + 3mk + 3m^2$ different sets with 60 carbon atoms in each set, so the number of NMR spectrum lines is equal to $k^2 + 3km + 3m^2$.

For case (b), there are $k^2 + (3m+1)k + 3m^2 + 2m$ different sets with 60 carbon atoms in each set, furthermore, there is one set of 20 carbon atoms lying on the threefold axes. Therefore, the number of NMR spectrum lines is equal to $[k^2 + (3m+1)k + 3m^2 + 2m] + 1$.

For case (c), similar to case (b), the number of NMR spectrum lines is equal to $[k^2 + (3m+2)k + 3m^2 + 4m + 1] + 1$, where the last number 1 is due to the presence of 20 carbon atoms located on the threefold axes.

In summary, the above results are listed in table 1.

Acknowledgement

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