C_{60}^+の ^{13}C 置換体 ：回転スペクトルの予測

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^{13}C-substituted C_{60}^+: Predictions of the rotational spectra

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1. Introduction

On the basis of laboratory spectra using mass-selected He-tagging spectroscopy, Maier and coworkers recently [1] reported that two diffuse interstellar bands can be assigned to the C_{60}^+ ion. Stimulated by their work we consider the possibility of high resolution spectroscopy of C_{60}^+. The C_{60}^+ ion is spherical and rotational transitions are therefore not expected. However, if one carbon atom is substituted by ^{13}C the centre of mass will no longer coincide with the centre of charge and we expect a sizable dipole moment and thus the possibility of rotational spectroscopy in the MW region. We denote singly substituted species as 13^1C_{60}. Because C_{60} is composed of 60 carbon atoms the number density of 13^1C_{60} in natural abundance is comparable with that of the normal species. It is therefore worth predicting the rotational spectrum of $13^1C_{60}^+$.

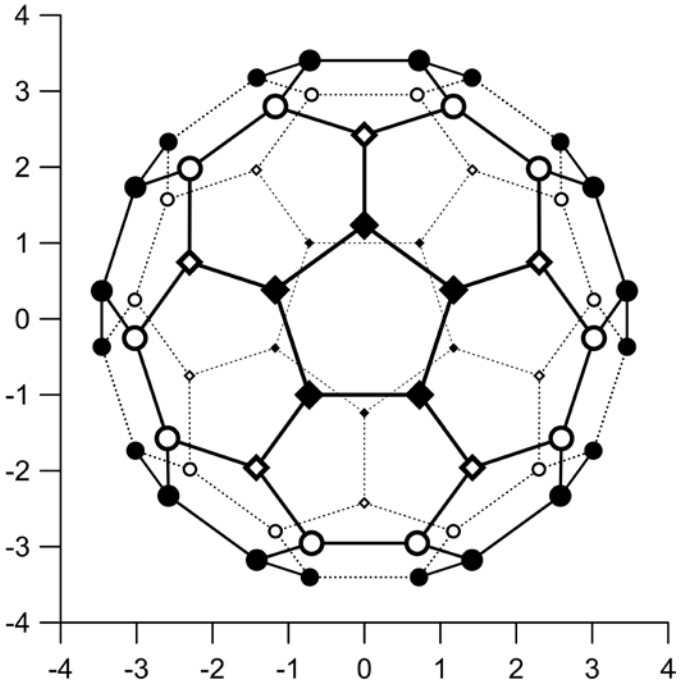

Figure 1. View of C_{60}^+ along a C_5 axis. Scales in Å. “Axial” atoms are shown by solid diamonds (◆), “satellite” atoms by open diamonds (◇), “ring” atoms by open circles (○), and “equatorial” atoms by solid circles (●).

2. The rotational constants and the dipole-moment of $13^1C_{60}^+$: *I_h Model*

Due to the very large number of electrons in this system it is reasonable to assume that the structure of the C_{60}^+ ion (Fig.1) is not very different from that of neutral C_{60} of I_h symmetry. Because the positions of each carbon atom are equivalent in this assumption, the $13^1C_{60}^+$ ion is a prolate symmetric-top. The predicted rotational constants are A=82.98 MHz and B=82.81 MHz. From the shift of the center-of-mass due to the isotope substitution the dipole moment can easily be calculated to be 0.006 D.

3. The rotational constants and the dipole-moment of $13^1C_{60}^+$: *D_{5d} Model*

In 1990 Ceulemans and Fowler [2] pointed out that the structure of the C_{60}^+ ion may be distorted by the Jahn-Teller effect. In fact the matrix isolation spectra of C_{60}^+ by Kern *et al.* [3] indicate that in its ground electronic state the ion is of D_{5d} symmetry. By calculating the

structure using Density Function Theory (DFT) with the B3LYP functional we found that the locations of the 60 carbon atoms can be classified into four categories by their distance, *R*, from the center of mass. These categories are illustrated in Fig. 1. The 10 atoms of the two pentagons containing the C_5-axis have the largest value of *R*. We denote these as "axial" atoms and pentagons. In Fig. 1 the axial-atoms are show by solid diamonds. The 10 atoms directly connected to the axial-pentagons have the second largest value of *R*. We denote these as "satellite" atoms and they are shown by the open diamonds. The 20 atoms of the satellite hexagons which belong to neither "axis" nor "satellite" sets are of medium *R* and we denote them "ring" atoms and show them by open circles. Finally, the remaining 20 atoms have the shortest *R* and are shown by the solid circles in Fig. 1. Due to their locations we denote these as "equatorial" atoms.

The singly substituted ions, $13^1C_{60}^+$, can therefore be classified into four categories depending on which class of atom is substituted. Furthermore, $13^1C_{60}^+$ is an asymmetric-top either without symmetry, *i.e.* of C_1-symmetry (chiral), or of C_s-symmetry with a symmetry plane passing through the substituted carbon atom.

The predicted rotational constants, symmetry, and dipole-moments for singly substituted C_{60}^+ are given in Table 1.

Table 1: Rotational constants predicted for $13^1C_{60}^+$ (Model D_{5d}) by DFT (B3LYP) for each radius category of the substituted carbon†

category	axis	satellite	ring	equator
symmetry	C_s	C_s	C_1	C_1
Number	10	10	20	20
R/Å	3.57	3.56	3.55	3.53
A/MHz	84.2	84.1	84.1	84.1
B/MHz	83.1	83.2	83.2	83.3
C/MHz	83.1	83.1	83.1	83.1
μ_a/D	0.005	0.004	0.003	0.001
μ_b/D	0.002	0.003	0.004	0.005
μ_c/D	0‡	0‡	0.000	0.000

† The dipole moments are predicted from the shift of the center-of-mass due to isotopic substitution.

‡ Vanish by symmetry.

References

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[3] B. Kern, D. Strelnikov, P. Weis, A. Böttcher, M.M. Kappes, *J. Phys. Chem.* **117** (2013) 8251–8255.