Theor Chem Acc (2009) 123:375–381
DOI 10.1007/s00214-009-0518-z

REGULAR ARTICLE

Calculations and assignments of endohedral helium-3 chemical shifts of open-cage fullerenes and higher fullerenes

Guan-Wu Wang · Ping Wu

Received: 22 November 2008 / Accepted: 17 January 2009 / Published online: 6 February 2009

Abstract The endohedral ^{3}He NMR chemical shifts of open-cage fullerene compounds and higher fullerenes ^{3}He@C$_n$ ($n = 82, 84, 86$) have been calculated at the GIAO-B3LYP/3-21G//AM1 level. The predicted ^{3}He NMR chemical shifts of open-cage fullerene compounds agree well with the experimental data. More importantly, the challenging peak assignments in the two ^{3}He NMR spectra of higher fullerenes have been successfully achieved by our computed endohedral ^{3}He chemical shifts in combination with experimental results.

Keywords Endohedral fullerenes · ^{3}He NMR · Density functional theory · Semiempirical

1 Introduction

Helium-3 NMR spectroscopy is a powerful tool for the structural assignments of fullerenes and their derivatives [1]. Each ^{3}He-encapsulated fullerene compound has a distinct ^{3}He NMR peak, while a nonfullerene chemical has no ^{3}He NMR peak. For higher fullerenes, an individual pure isomer was difficult to obtain due to its small amount in the arc-processed soot and the existence of other co-eluted isomer(s) during separation. Therefore, only the mixture of higher fullerenes was labeled with helium-3, and then subject to the ^{3}He NMR measurement. The ^{3}He NMR spectrum of a purified ^{3}He@C$_{84}$ fraction containing ^{3}He@C$_{76}$, ^{3}He@C$_{78}$ and ^{3}He@C$_{82}$ was reported in 1995 [2]. A few years later, the ^{3}He NMR spectrum of a mixture labeled with roughly 60% of C$_{84}$ isomers, 40% of C$_{76}$ and C$_{78}$ isomers, and small amount of other fullerenes such as C$_{82}$ and C$_{86}$ was recorded [3]. However, no assignment for the isomers of ^{3}He@C$_{82}$, ^{3}He@C$_{84}$ and ^{3}He@C$_{86}$ except for the D_2 isomer of ^{3}He@C$_{84}$ was made [2, 3].

At the same time, the calculation of ^{3}He NMR chemical shifts has become of increasing interest and importance in order to understand and assign the experimentally obtained ^{3}He NMR data. The ^{3}He NMR chemical shifts for ^{3}He@C$_n$ and their derivatives were theoretically studied at Hartree–Fock (HF), density functional theory (DFT) and semiempirical (MNDO) levels with gauge including atomic orbitals (GIAO) [4–14]. However, the deviations between the calculated and experimental ^{3}He NMR chemical shifts could be very large, e.g., for C$_{60}$ and C$_{70}$, depending on the calculation levels and optimized molecular structures [5, 7, 9, 14]. Endohedral ^{3}He NMR chemical shifts in higher fullerenes with 82–86 carbons were calculated at the levels of GIAO-SCF/tzp(He)/dz(C)//MNDO [7], GIAO-SCF/DZ//MNDO [9], GIAO-SCF/DZP//BP86/3-21G [9], GIAO-SCF/3-21G//B3LYP/6-31G* [13], GIAO-MNDO//B3LYP/6-31G* [14] and GIAO-MNDO//MNDO [14]. Unfortunately, these calculation data were not sufficient for quantitative prediction [13], and an unequivocal assignment of these close-lying peaks for C$_{84}$ isomers on the basis of the computations was not possible [9, 13]. Consequently, few of the ^{3}He NMR peaks for higher fullerenes above ^{3}He@C$_{82}$ have been assigned [9, 13], and the assignment for most of the ^{3}He NMR peaks still remains as a challenging task.

G.-W. Wang (✉) · P. Wu
Hefei National Laboratory for Physical Sciences at Microscale
and Department of Chemistry, University of Science
and Technology of China, 230026 Hefei, Anhui,
People's Republic of China
e-mail: gwang@ustc.edu.cn

G.-W. Wang
State Key Laboratory of Applied Organic Chemistry,
Lanzhou University, 730000 Lanzhou, Gansu,
People's Republic of China

Recently, we [15] calculated the ^{3}He NMR chemical shifts of ^{3}He@C$_n$ and their derivatives at the GIAO-B3LYP/3-21G and GIAO-HF/3-21G levels with AM1 and PM3 optimized structures. A good linear relationship between the computed and experimental ^{3}He NMR chemical shifts had been found. The calculated corrected ^{3}He NMR chemical shifts (δ_{corr}) matched the experimental data very well over a wide range of ^{3}He-encapsulated fullerene compounds. The GIAO-B3LYP/3-21G//AM1 method was one of most economical protocols and was applied to the assignments/reassignments of C_{76}, C_{78} isomers and bis-adducts of C_{60}. However, all of the examined ^{3}He-encapsulated fullerene compounds were closed-cage, and higher fullerenes beyond C_{78} have not been investigated. In continuation of our interest in ^{3}He NMR [15], in this paper we apply our developed GIAO-B3LYP/3-21G//AM1 method to open-cage fullerenes, and more importantly, we attempt to tackle the challenging assignments for the experimentally observed ^{3}He NMR peaks of ^{3}He@C$_{82}$, ^{3}He@C$_{84}$ and ^{3}He@C$_{86}$ isomers by our calculation method in combination with the previous experimental results.

2 Computational methods

All geometries were optimized at the AM1 semiempirical level [16], and the endohedral ^{3}He NMR chemical shifts were calculated at the GIAO (gauge including atomic orbitals [17])-B3LYP (Becke's [18] three-parameter hybrid-exchange functional and the correlation functional of Lee et al. [19]) level with the 3-21G basis set. The calculated endohedral ^{3}He NMR chemical shifts (δ_{calc}) for the ^{3}He located at the center of the fullerene cage at the GIAO-B3LYP/3-21G//AM1 level were given in ppm relative to the free ^{3}He (59.66 ppm). It should be noted that the magnetic field within a sphere of less than 1 Å diameter at the center of C_{60} was found to be very homogeneous [5], the δ_{calc} values were little affected for the displacement of ^{3}He out of the center. The corrected ^{3}He chemical shifts (δ_{corr}) were obtained from the correlation Eq. 1 [15]:

$$\delta_{corr} = -1.167 + 1.330\delta_{calc} \qquad (1)$$

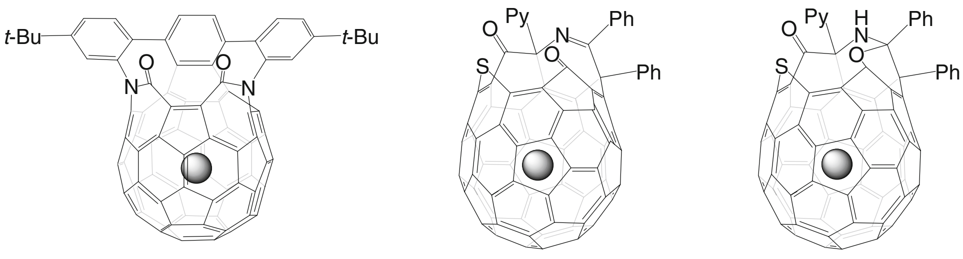
The correlation Eq. 1 was derived from the linear regression fitting of the calculated and experimental data for 27 ^{3}He-encapsulated fullerene compounds [15]. For the purpose of comparison, the δ_{calc} data for the three open-cage fullerene compounds (**1–3**) by the GIAO-B3LYP/3-21G//B3LYP/6-31G* method and then their δ_{corr} values by Eq. 1 were also computed. All optimized structures were verified as being minima except for the C_s ^{3}He@C$_{84}$:10 isomer by frequency calculations. All calculations were carried out with the help of GAUSSIAN 03 program package [20].

3 Results and discussion

3.1 Application to open-cage fullerene compounds

Previously, we had only included closed-cage fullerene compounds in the calculations of endohedral ^{3}He NMR chemical shifts. We wondered if our calculation method could be extended to open-cage fullerene compounds. The ^{3}He NMR chemical shifts of two ^{3}He-encapsulated open-cage fullerene compounds, i.e., compounds ^{3}He@**1** (Rubin's open-cage fullerene) [21] and ^{3}He@**2** (Komatsu's open-cage fullerene) [22] (Fig. 1), have been reported in the literature.

The δ_{calc}, δ_{corr} and experimental ^{3}He NMR chemical shifts (δ_{exp}) of compounds ^{3}He@**1** and ^{3}He@**2** at the GIAO-B3LYP/3-21G//AM1 and GIAO-B3LYP/3-21G//B3LYP/6-31G* levels are listed in Table 1. As seen from Table 1, the δ_{corr} values of compounds ^{3}He@**1** and ^{3}He@**2** at both GIAO-B3LYP/3-21G//AM1 and GIAO-B3LYP/3-21G//B3LYP/6-31G* levels agree well with their experimental data. Helium-4 rather than helium-3 was encapsulated in compound **3** (a modification of Komatsu's open-cage fullerene) [23], hence the endohedral ^{3}He NMR chemical shift was not available. It was reported that the ^{1}H NMR chemical shift of the encapsulated H_2 in compound H_2@**3** (−7.79 ppm [23]) was upfield shifted relative to that in compound H_2@**2** (−7.25 ppm [24]). Interestingly, the same trend is observed for the calculated δ_{corr} of compound



^{3}He@**1** ^{3}He@**2** ^{3}He@**3**

Fig. 1 Structures of ^{3}He-encapsulated open-cage fullerene compounds ^{3}He@**1–3**

Table 1 The δ_{calc}, δ_{corr} and δ_{exp} of compounds ^{3}He@**1–3**

Compound	δ_{calc} (ppm)[a]	δ_{corr} (ppm)[a]	δ_{calc} (ppm)[b]	δ_{corr} (ppm)[b]	δ_{exp} (ppm)
^{3}He@**1**	−6.07	−9.24	−5.81	−8.89	−10.10[c]
^{3}He@**2**	−8.35	−12.27	−8.31	−12.22	−11.86[d]
^{3}He@**3**	−8.54	−12.53	−8.82	−12.90	–

[a] Calculated at the GIAO-B3LYP/3-21G//AM1 level

[b] Calculated at the GIAO-B3LYP/3-21G//B3LYP/6-31G* level

[c] Experimental value from Ref. [21]

[d] Experimental value from Ref. [22]

^{3}He@**3** compared to that of compound ^{3}He@**2**, indicating that our computation method can be applied to open-cage fullerene compounds. Because the structural optimization at the AM1 level is much faster than that at the B3LYP/6-31G* level, and the optimized structures by both methods have insignificant influence on the δ_{corr} values, the GIAO-B3LYP/3-21G//AM1 method will be employed for the rest calculations of endohedral ^{3}He NMR chemical shifts.

3.2 Structural assignment of ^{3}He@C_{82}

Nine isomers (2 × C_{3v}, C_{2v}, 3 × C_2, 3 × C_s) obey the isolated pentagon rule (IPR) for C_{82}. The ^{13}C NMR spectrum of a C_{82} isomeric mixture showed that the isomer with C_2 symmetry was the most abundant isomer while the isomers with C_{2v} and C_{3v} symmetries were minor, and at least three more isomers with C_2 and/or C_s symmetry might exist in very little amount [25]. Purified C_{82} containing only the isomer with C_2 symmetry was later achieved by Dunsch et al. [26, 27]. The major isomer with C_2 symmetry proved to be the isomer C_2 C_{82}:3 [28] (Fig. 1) by the ^{13}C NMR calculation of all nine IPR isomers of the C_{82} isomers [29].

The δ_{calc} and δ_{corr} data of all nine isomers of ^{3}He@C_{82} at the GIAO-B3LYP/3-21G//AM1 level along with the δ_{exp} value of ^{3}He@C_{82} are collected in Table 2.

Table 2 The δ_{calc}, δ_{corr} and δ_{exp} data of ^{3}He@C_{82} isomers

Species	δ_{calc} (ppm)	δ_{corr} (ppm)	δ_{exp} (ppm)
C_2 ^{3}He@C_{82}:1	−0.24	−1.49	
C_s ^{3}He@C_{82}:2	−7.22	−10.78	
C_2 ^{3}He C_{82}:3	−6.26	−9.50	−10.50[a]
C_s ^{3}He C_{82}:4	−6.45	−9.74	
C_2 ^{3}He@C_{82}:5	−2.39	−4.35	
C_s ^{3}He@C_{82}:6	2.56	2.23	
C_{3v} ^{3}He@C_{82}:7	13.20	16.40	
C_{3v} ^{3}He@C_{82}:8	18.52	23.46	
C_{2v} ^{3}He@C_{82}:9	7.41	8.69	

[a] δ_{exp} from Refs. [2, 3] after rounding off to two decimal

In the ^{3}He NMR spectrum reported in 1995, it was suggested that only the peaks at −10.50 and −11.12 ppm could be considered as C_{82} [2]. On the other hand, while the peak at −10.495 ppm was unassigned, the peak at −11.114 ppm was assigned as one of the ^{3}He@C_{84} isomers in the ^{3}He NMR spectrum presented in 2000 [3]. Therefore, the peak at −10.50 ppm should be ascribed to ^{3}He@C_{82}.

The assignment of the observed peak at −10.50 ppm cannot be made simply by comparison with the calculated corrected ^{3}He chemical shifts because some of the δ_{corr} values are very close and the calculation errors cannot be ignored [9, 13]. However, previous work demonstrated that the major C_{82} isomer was identified as a structure with C_2 symmetry [25–27]. The corrected ^{3}He chemical shifts of the three isomers with C_2 symmetry are −1.49, −9.50 and −4.35 ppm for C_2 ^{3}He@C_{82}:1, C_2 ^{3}He@C_{82}:3 and C_2 ^{3}He@C_{82}:5, respectively. The suggested minor isomers with C_{2v} and C_{3v} symmetries [25] have δ_{corr} values at 8.69, 16.40 and 23.46 ppm for C_{2v} ^{3}He@C_{82}:9, C_{3v} ^{3}He@C_{82}:7 and C_{3v} ^{3}He@C_{82}:8, respectively. Obviously, the peak at −10.50 ppm should be assigned as the C_2 ^{3}He@C_{82}:3 isomer.

3.3 Structural assignments of ^{3}He@C_{84} isomers

[84]Fullerene (C_{84}) is the third most abundant fullerene and has the richest experimentally observed isomers. Of the 24 IPR isomers (4 × D_2, 5 × C_2, 5 × C_s, 2 × D_{2d}, 4 × C_{2v}, C_1, D_{3d}, T_d, $D_{6\ h}$), at least ten isomers with D_2(IV) [30], D_{2d}(II) [30], D_{6h} [31], D_{3d} [31], D_{2d}(I) [32], D_2(II) [32], C_2 [32], C_s(a) [32], C_s(b) [32], C_2 [33] symmetries were isolated and characterized. The two major isomers were C_{84}:22 [28] and C_{84}:23 [28] with D_2 and D_{2d} symmetry, respectively [30]. Among the minor isomers, D_{2d} C_{84}:4 could be unambiguously assigned based on its ^{13}C NMR spectral data [32]. The previously temporarily assigned isomers D_2(II), C_2, C_s(a) and C_s(b) were identified as isomers C_{84}:5 C_{84}:11, C_{84}:16 and C_{84}:14, respectively [28], by comparison of the experimental and calculated ^{13}C NMR spectra of C_{84} isomers [34]. Similarly, the later found minor isomer with C_2 symmetry [33] should be tentatively assigned as the C_{84}:2 isomer by referring to the computation results of Sun and Kertesz [34].

Even though the C_s ^{3}He@C_{84}:10 isomer could be optimized at the AM1 level, the frequency analysis had a convergence problem. Furthermore, the C_{84}:10 isomer was found to have an imaginary frequency at the PM3 and B3LYP/STO-3G levels [34]. Therefore, the calculation of its endohedral ^{3}He NMR chemical shift was not performed. The δ_{calc} and δ_{corr} values of all isomers of ^{3}He@C_{84} except for the ^{3}He@C_{84}:10 isomer at the GIAO-B3LYP/3-21G//AM1 level along with the δ_{exp} data of ^{3}He@C_{84} are listed in Table 3.

Table 3 The δ_{calc}, δ_{corr} and δ_{exp} data of ^{3}He@C$_{84}$ isomers

Species	δ_{calc} (ppm)	δ_{corr} (ppm)	δ_{exp} (ppm)
D_2 ^{3}He@C$_{84}$:1	−12.67	−18.01	
C_2 ^{3}He@C$_{84}$:2	−13.34	−18.90	
C_s ^{3}He@C$_{84}$:3	1.24	0.49	
D_{2d} ^{3}He@C$_{84}$:4	−17.68	−24.68	−24.35[a]
D_2 ^{3}He@C$_{84}$:5	−12.99	−18.45	
C_{2v} ^{3}He@C$_{84}$:6	−2.88	−5.00	
C_{2v} ^{3}He@C$_{84}$:7	−0.73	−2.14	
C_2 ^{3}He@C$_{84}$:8	−4.06	−6.56	
C_2 ^{3}He@C$_{84}$:9	4.21	4.43	
C_2 ^{3}He@C$_{84}$:11	−3.71	−6.10	−7.50[b]
C_1 ^{3}He@C$_{84}$:12	−2.37	−4.32	
C_2 ^{3}He@C$_{84}$:13	5.31	5.89	
C_s ^{3}He@C$_{84}$:14	−7.46	−11.09	−11.11[b]
C_s ^{3}He@C$_{84}$:15	−4.65	−7.35	
C_s ^{3}He@C$_{84}$:16	−5.65	−8.68	−9.61[b]
C_{2v} ^{3}He@C$_{84}$:17	0.58	−0.40	
C_{2v} ^{3}He@C$_{84}$:18	−6.21	−9.42	−10.01[b]
D_{3d} ^{3}He@C$_{84}$:19	−0.41	−1.72	
T_d ^{3}He@C$_{84}$:20	−8.44	−12.38	
D_2 ^{3}He@C$_{84}$:21	−1.41	−3.04	
D_2 ^{3}He@C$_{84}$:22	−5.14	−8.00	−8.96[b]
D_{2d} ^{3}He@C$_{84}$:23	−4.69	−7.40	−8.40[b]
D_{6h} ^{3}He@C$_{84}$:24	−8.72	−12.77	−13.05[b]

[a] δ_{exp} from Ref. [2]

[b] δ_{exp} from Ref. [3] after rounding off to two decimal

The highest peak among the C$_{84}$ isomers in both of the ^{3}He NMR spectra was tentatively assigned to the isomer with D_2 symmetry [2, 3]. Our calculations of all of the four isomers with D_2 symmetry show that only the δ_{corr} (−8.00 ppm) of ^{3}He@C$_{84}$:22 [28] is reasonably close to the experimentally observed −8.96 ppm. The assignment of the highest peak at −8.96 ppm as the D_2 ^{3}He@C$_{84}$:22 isomer is consistent with the previous conclusion that the D_2 C$_{84}$:22 isomer was the most abundant one among the C$_{84}$ isomers [30, 32].

Previously, the combined fractions for the C$_{84}$ isomers were separated again by HPLC on a Cosmosil *5PYE* column and the HPLC peak was cut into three fractions [35]. Taken the change trends of the relative ^{3}He NMR peak strengths in all three fractions into account, it could be concluded that the elution order of the isomers for the corresponding ^{3}He NMR peaks on the HPLC column was −13.05, −8.96, −8.40, −9.61, −7.50, −10.01 and −11.11 ppm [35]. Since the encapsulated ^{3}He atom is very small and has little interaction with the fullerene cages, it is expected that the ^{3}He-labeled fullerenes should have the same elution order as the unlabeled fullerenes. The empty C$_{84}$ isomers were separated by recycling HPLC technique, and the elution times on a *5PYE* column were C$_{84}$:19/C$_{84}$:24 < C$_{84}$:22 < C$_{84}$:23 < C$_{84}$:16 < C$_{84}$:11 < C$_{84}$:14 < C$_{84}$:4 < C$_{84}$:5 [30–32]. The δ_{corr} data for these identified C$_{84}$ isomers in the order of the increasing elution time on the *5PYE* column are −1.72/−12.77, −8.00, −7.40, −8.68, −6.10, −11.09, −24.68 and −18.45 ppm for ^{3}He@C$_{84}$:19/^{3}He@C$_{84}$:24, ^{3}He@C$_{84}$:22, He@C$_{84}$:23, ^{3}He@C$_{84}$:16, ^{3}He@C$_{84}$:11, ^{3}He@C$_{84}$:14, ^{3}He@C$_{84}$:4 and ^{3}He@C$_{84}$:5, respectively. The later isolated C$_{84}$ isomer with C_2 symmetry [33] is now tentatively assigned as C$_{84}$:2, and its δ_{corr} is −18.90 ppm. Thus, the ^{3}He NMR peaks at −13.05 [36], −8.96, −8.40, −9.61, −7.50 and −11.11 ppm can be safely assigned to ^{3}He@C$_{84}$:24, ^{3}He@C$_{84}$:22, ^{3}He@C$_{84}$:23, ^{3}He@C$_{84}$:16, ^{3}He@C$_{84}$:11 and ^{3}He@C$_{84}$:14, respectively. Note that the peak at −10.01 ppm is excluded as the ^{3}He@C$_{84}$:14 isomer because the experimentally observed ^{3}He NMR chemical shifts of these isomers are found to be more negative than their δ_{corr} values. The previous calculations at the B3LYP/6-31G* level of theory indicated that the energies of isomers C$_{84}$:1, C$_{84}$:2, C$_{84}$:3, C$_{84}$:7, C$_{84}$:8, C$_{84}$:9, C$_{84}$:10, C$_{84}$:13, C$_{84}$:17 and C$_{84}$:20 were at least 20 kcal/mol above that of the most stable isomers C$_{84}$:22 and C$_{84}$:23, and thus less likely existed in the higher fullerene mixture [34]. Therefore, the peak at −10.01 ppm is most probably due to the as-yet-not-isolated isomer C$_{84}$:18, of which the δ_{corr} is −9.42 ppm. This result implies that the next potentially isolated and characterized C$_{84}$ isomer might be the C_{2v} C$_{84}$:18 isomer.

Interestingly, a peak at −24.35 ppm was found in the earlier ^{3}He NMR spectrum [2]. This peak should be assigned to ^{3}He@C$_{84}$:4 because only the computed δ_{corr} (−24.68 ppm) of ^{3}He@C$_{84}$:4 is close to the experimental value and the C$_{84}$:4 isomer has been previously isolated and characterized [32].

3.4 Structural assignments of ^{3}He@C$_{86}$

There are 19 isomers (6 × C_1, 6 × C_2, 3 × C_s, 2 × C_{2v}, C_3, D_3) obeying the isolated pentagon rule for C$_{86}$. Two isomers with C_s and C_2 symmetries were separated and characterized by the ^{13}C NMR spectroscopic measurement [37]. The provisional assignments as C_s C$_{86}$:16 and C_2 C$_{86}$:17 [37] were confirmed by the ^{13}C NMR calculations by Sun and Kertesz [38].

The δ_{calc} and δ_{corr} data of all 19 isomers of ^{3}He@C$_{86}$ at the GIAO-B3LYP/3-21G//AM1 level along with the δ_{exp} values of ^{3}He@C$_{86}$ are collected in Table 4.

Previous B3LYP/6-31G calculations [38] showed that among the 19 isomers C_2 C$_{86}$:17 was the most stable isomer and C_s C$_{86}$:16 was less stable by only 6.58 kcal/mol. Both of them have a large HOMO–LUMO gap of at least

Table 4 The δ_{calc}, δ_{corr} and δ_{exp} data of ^{3}He@C_{86} isomers

Species	δ_{calc} (ppm)	δ_{corr} (ppm)	δ_{exp} (ppm)
C_1 ^{3}He@C_{86}:1	−16.02	−22.47	
C_2 ^{3}He@C_{86}:2	−17.97	−25.07	
C_2 ^{3}He@C_{86}:3	−14.59	−20.57	
C_2 ^{3}He@C_{86}:4	−2.21	−4.11	
C_1 ^{3}He@C_{86}:5	−7.49	−11.13	
C_2 ^{3}He@C_{86}:6	−8.32	−12.23	
C_1 ^{3}He@C_{86}:7	9.56	11.55	
C_s ^{3}He@C_{86}:8	9.28	11.17	
C_{2v} ^{3}He@C_{86}:9	17.35	21.91	
C_{2v} ^{3}He@C_{86}:10	−9.12	−13.29	
C_1 ^{3}He@C_{86}:11	−5.14	−8.00	
C_1 ^{3}He@C_{86}:12	−5.56	−8.56	
C_1 ^{3}He@C_{86}:13	−3.61	−5.97	
C_2 ^{3}He@C_{86}:14	−2.04	−3.88	
C_s ^{3}He@C_{86}:15	−0.83	−2.28	
C_s ^{3}He@C_{86}:16	−9.88	−14.31	−14.15[a]
C_2 ^{3}He@C_{86}:17	−6.43	−9.72	−10.58[a]
C_3 ^{3}He@C_{86}:18	−9.64	−13.99	
D_3 ^{3}He@C_{86}:19	−0.14	−1.36	

[a] δ_{exp} from Ref. [3] after rounding off to two decimal

1.56 ev. However, other isomers have either too small HOMO–LUMO gap and/or relative energies higher than 20 kcal/mol, explaining well why only the C_s C_{86}:16 and C_2 C_{86}:17 isomers were stable and isolated. Thus, isomers except for C_s ^{3}He@C_{86}:16 and C_2 ^{3}He@C_{86}:17 should be discarded for the ^{3}He NMR peak assignment. The peak at −10.58 ppm labeled as C_{86} in the ^{3}He NMR spectrum can be confidently assigned as C_2 ^{3}He@C_{86}:17 according to our calculation. Interestingly, the calculated δ_{corr} (−14.31 ppm) of C_s ^{3}He@C_{86}:16 is nearly the same as the experimental value of −14.15 ppm, which was assigned as one of the C_{84} isomers [3]. The previous assignment was mainly based on the fact that the fraction at 36.6 min on a *PYE* column gave two ^{3}He NMR peaks at −10.59 and −14.15 ppm, which were determined as isomers of C_{86} and C_{84} by its mass spectrum [39]. However, the observed C_{84} in the mass spectrum could also arise from the fragmentation of C_{86} by loss of C_2. Hence, both of the two ^{3}He NMR peaks possibly came from isomers of C_{86}. Furthermore, the δ_{corr} values (−24.68 ppm for D_{2d} ^{3}He@C_{84}:4 and −18.45 ppm for D_2 ^{3}He@C_{84}:5) of the two isomers of C_{84} that co-eluted with C_{86} deviate far away from −14.15 ppm. Concluded from the above arguments, the peak at −14.15 ppm should be reassigned as the C_s ^{3}He@C_{86}:16 isomer.

Comparison of the two ^{3}He NMR spectra showed that five C_{84} isomers, that is, C_{84}:11, C_{84}:14, C_{84}:16, C_{84}:22 and C_{84}:23, existed in both cases. One small peak at −24.35 ppm due to C_{84}:4 was observed only in one ^{3}He NMR spectrum [2], while the two small peaks at −10.01 and −13.05 ppm for C_{84}:18 and C_{84}:24 could only be found in another ^{3}He NMR spectrum [3]. Thus, we believe that six C_{84} isomers were found in the spectrum reported in 1995 [2], while seven C_{84} isomers were observed in the ^{3}He NMR spectrum published in 2000 [3], not considering the doubly labeling species. The different distribution of

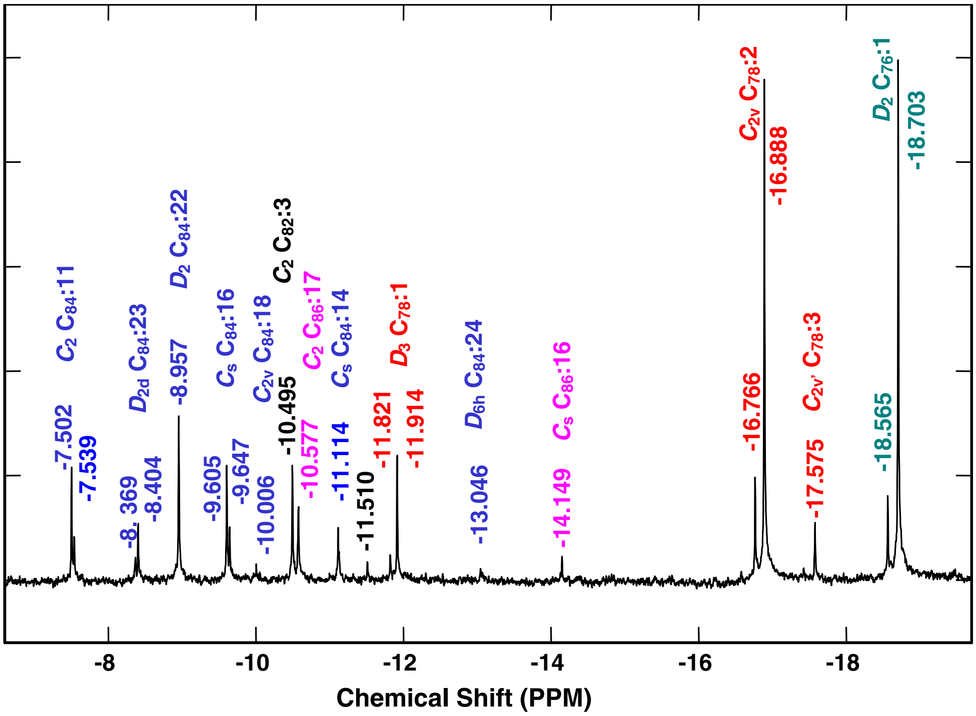
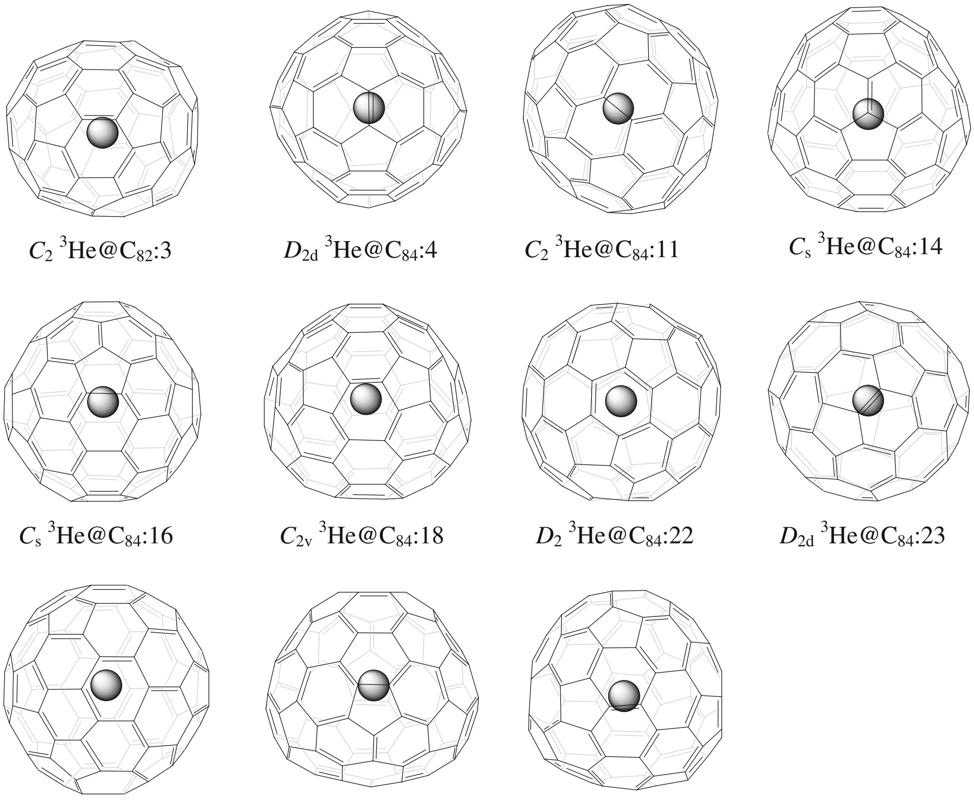


Fig. 2 The ^{3}He NMR spectrum of a ^{3}He@C_n mixture with structural assignments



C_2 ^{3}He@C$_{82}$:3 D_{2d} ^{3}He@C$_{84}$:4 C_2 ^{3}He@C$_{84}$:11 C_s ^{3}He@C$_{84}$:14

C_s ^{3}He@C$_{84}$:16 C_{2v} ^{3}He@C$_{84}$:18 D_2 ^{3}He@C$_{84}$:22 D_{2d} ^{3}He@C$_{84}$:23

D_{6h} ^{3}He@C$_{84}$:24 C_s ^{3}He@C$_{86}$:16 C_2 ^{3}He@C$_{86}$:17

Fig. 3 The structures of the assigned ^{3}He@C$_{82}$, ^{3}He@C$_{84}$, ^{3}He@C$_{86}$ isomers

C$_{84}$ isomers in the two ^{3}He NMR spectra was due to the different sample sources, which might be prepared under different conditions.

The ^{3}He NMR spectrum published in 2000 with structural assignments for the isomers of C$_{82}$, C$_{84}$, C$_{86}$ as well as C$_{76}$ and C$_{78}$ [40] is shown in Fig. 2. The corresponding structures for the assigned higher fullerenes ^{3}He@C$_n$ ($n = 82, 84, 86$) are given in Fig. 3.

4 Conclusion

The endohedral ^{3}He NMR chemical shifts of open-cage fullerene compounds and higher fullerenes ^{3}He@C$_n$ ($n = 82, 84, 86$) have been calculated at the GIAO-B3LYP/3-21G//AM1 level. Our developed method can be successfully applied to the calculation and prediction of endohedral ^{3}He chemical shifts for open-cage fullerene derivatives. More importantly, the combination of our GIAO-B3LYP/3-21G//AM1 method with the previous experimental results allows us to tackle the challenging ^{3}He NMR peak assignments of ^{3}He@C$_{82}$, ^{3}He@C$_{84}$ and ^{3}He@C$_{86}$ in the two reported ^{3}He NMR spectra. It is expected that the calculated ^{3}He NMR chemical shifts will continue to play an important role in the structural assignments of fullerene compounds.

Acknowledgments The authors are grateful for the financial support from National Natural Science Foundation of China (Nos. 20621061 and 20772117).

References

1. Saunders M, Cross RJ, Jiménez-Vázquez HA, Shimshi R, Khong A (1996) Science 271:1693. doi:10.1126/science.271.5256.1693
2. Saunders M, Jiménez-Vázquez HA, Cross RJ, Billups WE, Gesenberg C, Gonzalez A, Luo W, Haddon RC, Diederich F, Herrmann A (1995) J Am Chem Soc 117:9305. doi:10.1021/ja00141a023
3. Wang GW, Saunders M, Khong A, Cross RJ (2000) J Am Chem Soc 122:3216. doi:10.1021/ja994270x
4. Cioslowski J (1994) J Am Chem Soc 116:3619. doi:10.1021/ja00087a066
5. Bühl M, Thiel W, Jiao H, Schleyer Pv R, Saunders M, Anet FAL (1994) J Am Chem Soc 116:6005. doi:10.1021/ja00092a076
6. Cioslowski J (1994) Chem Phys Lett 227:361. doi:10.1016/0009-2614(94)00844-2
7. Bühl M, Thiel W (1995) Chem Phys Lett 233:585. doi:10.1016/0009-2614(94)01459-9
8. Bühl M, Thiel W, Schneider U (1995) J Am Chem Soc 117:4623. doi:10.1021/ja00121a019
9. Bühl M, Cv Wüllen (1995) Chem Phys Lett 247:63. doi:10.1016/0009-2614(95)01193-6
10. Bühl M, Patchkovskii S, Thiel W (1997) Chem Phys Lett 275:14. doi:10.1016/S0009-2614(97)00733-1
11. Bühl M (1998) Chem Eur J 4:734. doi:10.1002/(SICI)1521-3765(19980416)4:4<734::AID-CHEM734>3.0.CO;2-C

12. Bühl M, Kaupp M, Malkina OL, Malkin VG (1999) J Comput Chem 20:91. doi:10.1002/(SICI)1096-987X(19990115)20:1<91::AID-JCC10>3.0.CO;2-C
13. Chen Z, Cioslowski J, Rao N, Moncrieff D, Bühl M, Hirsch A, Thiel W (2001) Theor Chem Acc 106:364. doi:10.1007/s002140100283
14. Chen Z, Thiel W (2003) Chem Phys Lett 367:15. doi:10.1016/S0009-2614(02)01660-3
15. Wang GW, Zhang XH, Zhan H, Guo QX, Wu YD (2003) J Org Chem 68:6732. doi:10.1021/jo0341259
16. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) J Am Chem Soc 107:3902. doi:10.1021/ja00299a024
17. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251. doi:10.1021/ja00179a005
18. Becke AD (1993) J Chem Phys 98:5648. doi:10.1063/1.464913
19. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785. doi:10.1103/PhysRevB.37.785
20. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador, P Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, Revision B.03, Gaussian Inc., Pittsburgh
21. Rubin Y, Jarrosson T, Wang GW, Bartberger MD, Houk KN, Schick G, Saunders M, Cross RJ (2001) Angew Chem Int Ed 40:1543. doi:10.1002/1521-3773(20010417)40:8<1543::AID-ANIE1543>3.0.CO;2-6
22. Stanisky CM, Cross RJ, Saunders M, Murata M, Murata Y, Komatsu K (2005) J Am Chem Soc 127:299. doi:10.1021/ja045328x
23. Chuang SC, Murata Y, Murata M, Komatsu K (2007) Chem Commun (Camb) 1751. doi:10.1039/b702589k
24. Murata Y, Murata M, Komatsu K (2003) J Am Chem Soc 125:7152. doi:10.1021/ja0354162
25. Kikuchi K, Nakahara N, Wakabayashi T, Suzuki S, Shiromaru H, Miyake Y, Saito K, Ikemoto I, Kainosho M, Achiba Y (1992) Nature 357:142. doi:10.1038/357142a0
26. Zalibera M, Rapta P, Dunsch L (2007) Electrochem Commun 9:2843. doi:10.1016/j.elecom.2007.10.012
27. Zalibera M, Popov AA, Kalbac M, Rapta P, Dunsch L (2008) Chem Eur J 14:9960. doi:10.1002/chem.200800591
28. For the numbering of the fullerene isomers, see: Fowler PW, Manolopoulos DE (1995) An Atlas of Fullerenes, Oxford University Press, New York
29. Sun G, Kertesz M (2001) J Phys Chem A 105:5468. doi:10.1021/jp004544z
30. Dennis TJS, Kai T, Tomiyama T, Shinohara H (1998) Chem Commun (Camb) 619. doi:10.1039/a708025e
31. Tagmatarchis N, Avent AG, Prassides K, Dennis TJS, Shinohara H (1999) Chem Commun (Camb) 1023. doi:10.1039/a901709g
32. Dennis TJS, Kai T, Asato K, Tomiyama T, Shinohara H, Yoshida T, Kobayashi Y, Ishiwatari H, Miyake Y, Kikuchi K, Achiba Y (1999) J Phys Chem A 103:8747. doi:10.1021/jp9925132
33. Tagmatarchis N, Okada K, Tomiyama T, Yoshida T, Kobayashi Y, Shinohara H (2001) Chem Commun (Camb) 1366. doi:10.1039/b103679n
34. Sun G, Kertesz M (2001) J Phys Chem A 105:5212. doi:10.1021/jp0108418
35. See Ref. [10] in Ref. [2] of this paper, the details were not reported at that time
36. In the Ref. [3], the peak at -13.05 ppm was tentatively assigned to C_{82} because it was present only in the first fraction of the cut three fractions and C_{82} was known to be eluted earlier than the main isomers of C_{84}. However, the minor isomers C_{84}:19 and C_{84}:24 were also eluted before the main isomers C_{84}:22 and C_{84}:23 [31]. The calculated δ_{corr} (-12.77 ppm) of $^{3}He@C_{84}$:24 nicely matches the observed value. In contrast, the δ_{corr} (-9.50 ppm) of $^{3}He@C_{82}$:3 (the most stable isomer of $^{3}He@C_{82}$) is far away from -13.05 ppm. The above statements lead us to reassign the peak at -13.05 ppm as $^{3}He@C_{84}$:24
37. Miyake Y, Minami T, Kikuchi K, Kainosho M, Achiba Y (2000) Mol Cryst Liq Cryst (Phila Pa) 340:553. doi:10.1080/10587250008025524
38. Sun G, Kertesz M (2002) Chem Phys 276:107. doi:10.1016/S0301-0104(01)00576-6
39. See Ref. [9] in Ref. [3] of this paper
40. Our previous work [15] showed that the peak at $-11.91/-11.92$ ppm was assigned as the D_3 $^{3}He@C_{78}$:1. Even though the previous calculation results by us [15] and Chen et al. [13] supported the original assignment of peak at -16.77 ppm as $C_{2v'}$ $^{3}He@C_{78}$:3 [2], this peak was reassigned as the doubly labeled C_{2v} $^{3}He_2@C_{78}$:2 [3]. The peak located at -17.58 ppm should be assigned to $C_{2v'}$ $^{3}He@C_{78}$:3, in accord with the result reported by Sternfeld et al. [41]
41. Sternfeld T, Saunders M, Cross RJ, Rabinovitz M (2003) Angew Chem Int Ed 42:3136. doi:10.1002/anie.200351429