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Computed Structures of Two Known Yb@C$_{74}$ Isomers

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Six isomers of Yb@C$_{74}$ are considered, namely one cage with isolated pentagons, three isomers with a pentagon−pentagon junction, two structures with one pentagon−pentagon pair, and one heptagon. The computations based on the Gibbs energy point out the endohedral derived from the only C$_{74}$ cage with the isolated pentagons and from a cage with one pentagon−pentagon junction as the major and minor observed isomer, respectively. Temperatures giving the best agreement with the experimental production ratio are evaluated.

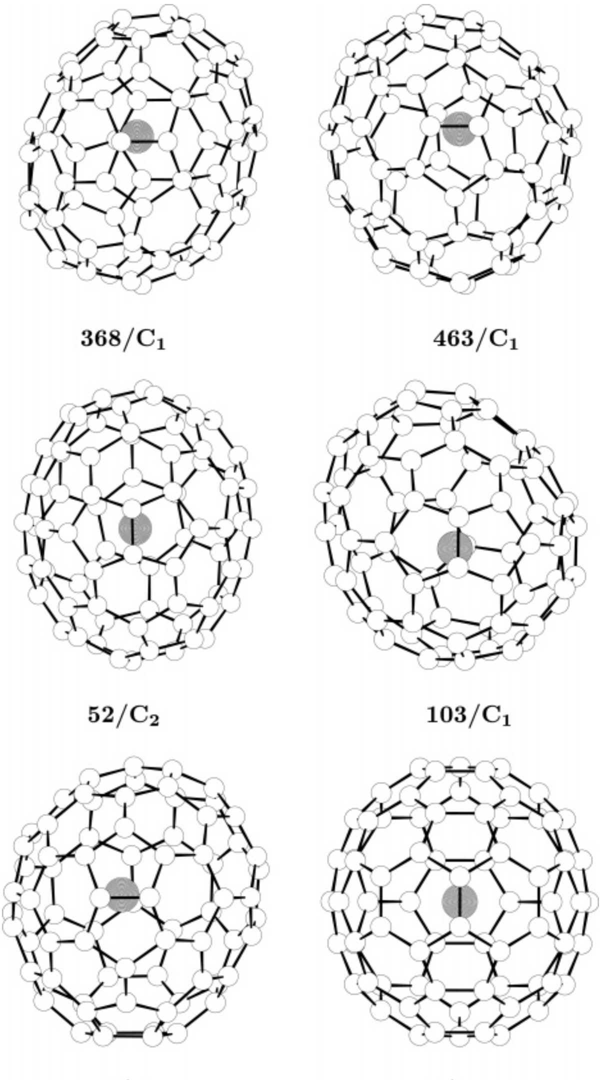
1. Introduction

Recently, Xu et al.[1] isolated two isomers of an ytterbium containing metallofullerene, namely Yb@C$_{74}$, and even found their production ratio as 100:3. It is the first such isomerism finding in the C$_{74}$ endohedral family, though single species have been known like Ca@C$_{74}$,[2,3] Sr@C$_{74}$,[4] Ba@C$_{74}$,[5] La@C$_{74}$,[6−9] Eu@C$_{74}$,[10] Sc$_2$@C$_{74}$,[11] or Er$_3$@C$_{74}$.[12] This isomerism finding is particularly interesting as there is just one[13] C$_{74}$ cage that obeys the isolated pentagon rule (IPR), namely of D_{3h} symmetry. The cage was experimentally confirmed in Ca@C$_{74}$,[2] Ba@C$_{74}$,[4] and La@C$_{74}$.[8] Clearly enough, with Yb@C$_{74}$ a non-IPR cage should be involved (as it is the case in the Ca@C$_{72}$ system[14]). Interestingly enough, empty C$_{74}$ and C$_{72}$ species could not be isolated yet, perhaps owing to solubility problems.[2,15−17]

This experimental finding is obviously of computational interest. Some computations on metallofullerenes based on C$_{74}$ are available, especially for Ca@C$_{74}$ with considerations of selected non-IPR cages.[2,16,18,19] In fact, the non-IPR encapsulations are not significant with Ca@C$_{74}$, in contrast to Ca@C$_{72}$.[20,21] Thus, the present paper reports computations on the Yb@C$_{74}$ system in order to clarify the structures of its two known isomers. To respect high temperatures in fullerene/metallofullerene preparations, the Gibbs energy should be used[22,23] in relative stability considerations rather than the mere potential energy terms, and the approach is also followed in this computational study.

2. Calculations

The computations treat a set of six Yb@C$_{74}$ isomers, using the carbon cages investigated with Ca@C$_{74}$, namely the three structures selected from dianion energetics,[2,18] and three additional cages with non-negligible populations as empty C$_{74}$ cages.[24,25] In the computations[18,24] the cages have been labeled by some code numbers that are also used here, combined with the symmetry of the complexes: 1/C_{2v}, 4/C_1, 52/C_2, 103/C_1, 368/C_1, and 463/C_1. The 1/C_{2v} endohedral is the species derived from the unique C$_{74}$ IPR structure. The previously considered[16] two non-IPR C$_{74}$ cages are now labeled by 4/C_1 and 103/C_1. A pair of connected pentagons is also present in the 52/C_2 structure.


368/C_1 463/C_1

52/C_2 103/C_1

4/C_1 1/C_{2v}

Figure 1. B3LYP/3-21G∼CEP-4G optimized structures of Yb@C$_{74}$ isomers.

The remaining two species, 368/C_1 and 463/C_1, contain a pentagon/pentagon pair and one heptagon. The optimized structures are depicted in Figure 1 (note that the cages are

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TABLE 1: Yb@C_{74} Relative Potential Energies $\Delta E_{pot,rel}$ (kcal/mol) Computed in the B3LYP Optimized Geometries[a]

species	CEP-4G[a]	3-21G∼CEP-4G[b]	6-31G*∼CEP-4G[b]	SDD[b,c]	6-31G*∼SDD[b,c]	6-311G*∼SDD[b,c]
368/C_1	43.03	47.36	49.10	48.54	48.24	47.87
463/C_1	36.21	41.36	43.94	43.75	43.35	43.00
52/C_2	22.51	27.00	30.88	29.92	30.25	30.30
103/C_1	8.55	12.80	17.15	16.87	16.98	16.99
4/C_1	7.38	10.78	13.68	12.99	13.14	13.30
1/C_{2v}	0.0	0.0	0.0	0.0	0.0	0.0
species					6-31G*∼SDD[c,d]	
103/C_1					16.89	
4/C_1					13.01	
1/C_{2v}					0.0	

[a] Computed in the geometries optimized at the B3LYP/CEP-4G level. [b] Computed in the geometries optimized at the B3LYP/3-21G∼CEP-4G level (see Figure 1). [c] SDD basis set.[32,33] [d] The structures optimized at the B3LYP/6-31G*∼SDD level.

TABLE 2: Mulliken Charge on Yb, Ionization Potential, Electron Affinity, and Lowest Triplet and Singlet Electronic Excited State for the Three Most Stable Isomers[a] of Yb@C_{74}

species	Mulliken charge on Yb	IP 3-21G	IP 6-31G*	EA 3-21G	EA 6-31G*	triplet	singlet
103/C_1	1.69	6.82	6.28	3.00	2.52	0.759	0.943
4/C_1	1.67	6.66	6.11	2.74	2.27	0.930	1.125
1/C_{2v}	1.67	6.67	6.11	3.02	2.53	0.657	0.859

[a] Computed in the B3LYP/3-21G∼CEP-4G geometries (see Table 1); the values evaluated at the B3LYP/3-21G∼CEP-4G (coded by 3-21G) and B3LYP/6-31G*∼CEP-4G (6-31G*) level; energy terms in eV.

oriented in such a way that a pentagon−pentagon pair appears in the central area of the cage).

The present geometry optimizations were primarily carried out using density-functional theory (DFT), namely employing Becke's three-parameter functional[26] combined with the nonlocal Lee−Yang−Parr correlation functional[27] (B3LYP) in the following combined basis set: 3-21G basis for C atoms and the CEP-4G basis set[28−30] with the CEP effective core potential on Yb (46 core electrons). The combined basis set is denoted here by 3-21G∼CEP-4G. The B3LYP/3-21G∼CEP-4G geometry optimizations were carried out with the analytically constructed energy gradient, using results from preliminary B3LYP/CEP-4G optimizations. Only singlet electronic states were submitted to the geometry optimizations. The reported computations were performed with the Gaussian 03 program package.[31]

In the optimized B3LYP/3-21G∼CEP-4G geometries the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same B3LYP/3-21G∼CEP-4G optimized geometries higher-level single-point energy calculations were also performed, using the standard 6-31G* basis set for C atoms, i.e., the B3LYP/6-31G*∼CEP-4G level. Moreover, the SDD (Stuttgart/Dresden) basis set[32,33] was also employed (with the SDD effective core potential for Yb - 28 core electrons) for the single point calculations; however, for the carbon atoms the SDD, 6-31G*, or 6-311G* basis set was stepwise used (Table 1). In addition, for the three lowest isomers, the geometry optimizations were also carried out at the B3LYP/6-31G*∼SDD level. The electronic excitation energies were evaluated by means of time-dependent (TD) DFT response theory[34] at the B3LYP/3-21G∼CEP-4G level (using the Gaussian 98 program).

Relative concentrations (mole fractions) x_i of m isomers can be expressed[35] through their partition functions q_i and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H^{o}_{0,i}$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula

$$x_i = \frac{q_i \exp[-\Delta H^{o}_{0,i}/(RT)]}{\sum_{j=1}^{m} q_j \exp[-\Delta H^{o}_{0,j}/(RT)]} \qquad (1)$$

where R is the gas constant, and T is the absolute temperature. Equation 1 is an exact formula that can be directly derived[35] from the standard Gibbs energies of the isomers, supposing the conditions of the interisomeric thermodynamic equilibrium. Rotational−vibrational partition functions were constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. No frequency scaling is applied as it is not significant[36] for the x_i values at high temperatures. The geometrical symmetries of the optimized cages were determined not only by the Gaussian built-in procedure[31] but also primarily by a procedure[37] which considers precision of the computed coordinates. The electronic partition function was constructed by directed summation from the TD B3LYP/3-21G∼CEP-4G electronic excitation energies. Finally, the chirality contribution was included accordingly[38] (for an enantiomeric pair its partition function q_i is doubled).

3. Results and Discussion

Table 1 reports the separation energetics computed at several levels of theory, mostly in the B3LYP/3-21G∼CEP-4G optimized geometries. At all the levels, the energy order of isomers is the same. Moreover, with an exception of the two simplest treatments, the separation energetics is considerably consistent. The picture is also not changed after the geometry reoptimizations at the B3LYP/6-31G*∼SDD level. The 1/C_{2v} endohedral based on the IPR C_{74} cage is after about 13 kcal/mol followed by the 4/C_1 isomer, the 103/C_1 structure is about 17 kcal/mol above the lowest isomer, while the other endohedrals are located more than 30 kcal/mol higher. Interestingly enough, for the Yb central location in the 1/C_{2v} cage the energy is computed about 51 and 43 kcal/mol higher at the B3LYP/3-21G∼CEP-4G and B3LYP/6-31G*∼CEP-4G level, respectively, than in the optimized off-center location shown in Figure 1. The shortest Yb−C B3LYP/3-21G∼CEP-4G distances are rather uniform as they vary between 2.54 and 2.59 Å. As far as the charge transfer is concerned, it amounts in the B3LYP/3-21G∼CEP-4G approach to about 1.7 electrons donated to the cage (cf. Table 2).

Figure 2 presents the key output of this study−temperature development of the relative concentrations of the six Yb@C_{74} isomers at high temperatures where the fullerene/metallofullerene electric-arc synthesis happens. The enthalpy component of the Gibbs energy is taken from the B3LYP/6-311G*∼SDD//B3LYP/3-21G∼dz calculations, the entropy part is evaluated at the B3LYP/3-21G∼CEP-4G entropy level, actually using two different approaches. Regardless of the entropy evaluation, the 1/C_{2v} endohedral species derived from the only C_{74} cage with the isolated pentagons comes as a major isomer at any reasonable temperature. The 4/C_1 endohedral with one pentagon−pentagon junction in the cage represents the second most populated species and should be identified with the minor isomer observed[1] though there is still one non-negligible species, 103/C_1. To reproduce the observed production ratio, within the conventional RRHO approach to the partition functions in eq 1 temperature should reach about 1850 K when the 1/C_{2v}, 4/C_1,

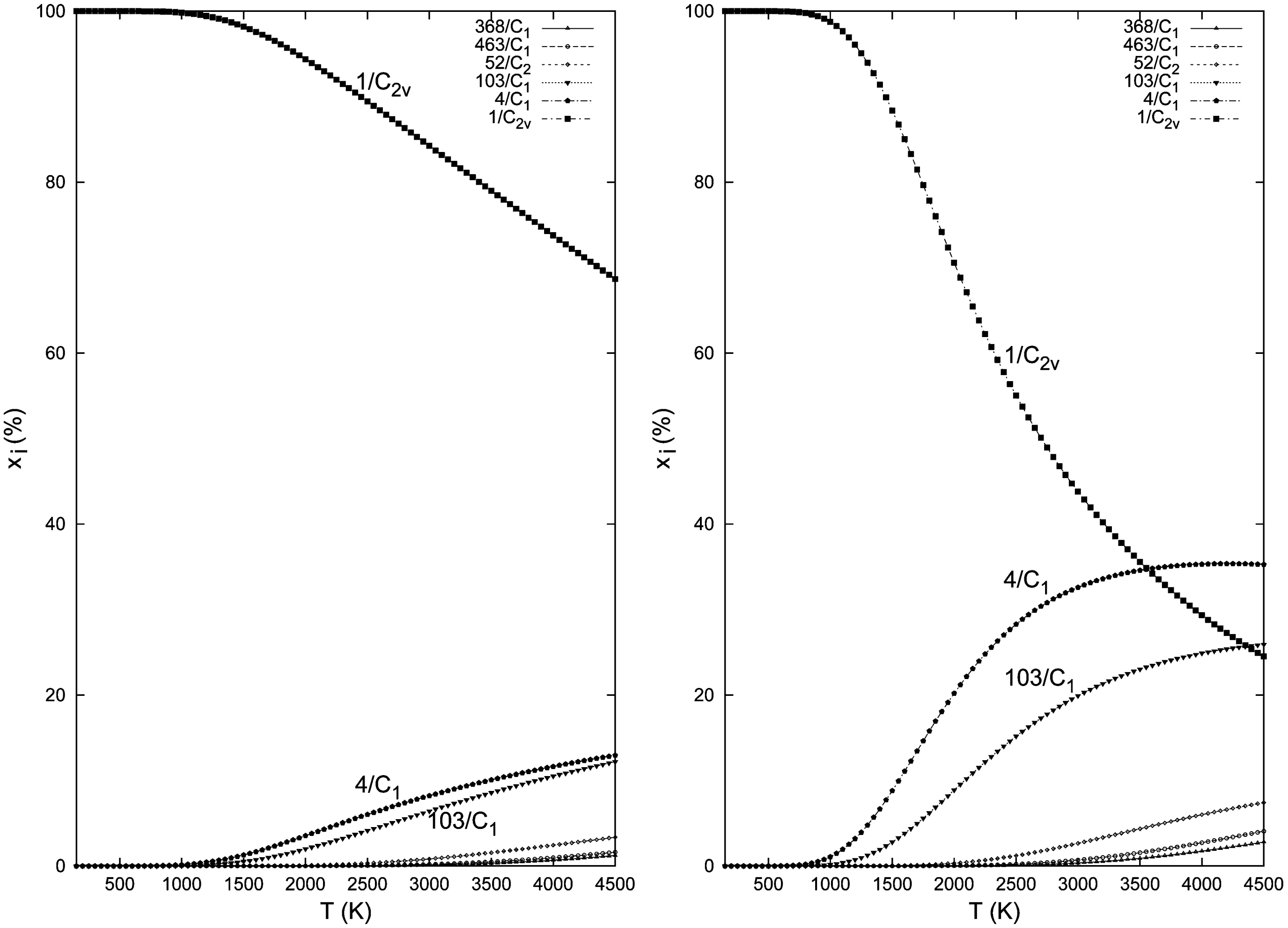

Figure 2. Relative concentrations of the Yb@C_{74} isomers (Figure 1) based on the B3LYP/6-311G*∼SDD energetics and the B3LYP/3-21G∼CEP-4G entropy, using the RRHO (left) and FEM (right) treatment.

and 103/C_1 species compose 95.7, 2.8, and 1.5% of the equilibrium isomeric mixture, respectively. It should be, however, realized that the observed relative abundances are roughly estimated from chromatography peak areas.

In addition to the conventional RRHO treatment with eq 1, also a modified approach to description of the encapsulate motions can be considered,[39] following findings[14,16,40] that the encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations[41]). One can expect that if the encapsulate is relatively free then, at sufficiently high temperatures, its behavior in different cages will bring about the same contribution to the partition functions. However, such uniform contributions would then cancel out in eq 1. This simplification is called[39] free, fluctuating, or floating encapsulate model (FEM) and requires two steps. In addition to removal of the three lowest vibrational frequencies (belonging to the metal motions in the cage), the symmetries of the cages should be treated as the highest (topologically) possible, which reflects averaging effects of the large amplitude motions. There are several systems[39,42] where the FEM approach improves agreement with experiment. In the Yb@C_{74} case, the FEM treatment reduces the temperature for the reproduction of the observed ratio[1] to about 1200 K with 96.1, 3.2, and 0.7% for the 1/C_{2v}, 4/C_1, and 103/C_1 isomer, respectively. Although it is true that the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, the new observations[43] supply some support to expect it around 1500 K so that the FEM treatment would be in a better agreement with the experiment.[1]

Some electronic properties of the three most stable isomers of Yb@C_{74} are summarized in Table 2. In particular, the computed ionization potentials and electron affinities are supplied as the terms could be measured in the gas-phase. The terms have rather uniform values for the isomers. The same is true for the formal Mulliken charge on the Yb atom. Excitation energies for the first electronic excited triplet and singlet state are listed, too.

In fact, it has been pointed out recently that very low excited electronic states can be present in some fullerenes such as C_{80}[44] or even the C_{74} IPR cage,[45] thus influencing the electronic partition function significantly. However, the aspect is not particularly important for the Yb@C_{74} system as, for example, the lowest triplet state of the 1/C_{2v}, 4/C_1, and 103/C_1 endohedral is computed about 0.7, 0.9, and 0.8 eV, respectively, above the related singlet ground state (Table 2). Interestingly enough, there is a suggestion[25] that the electronic partition function based on the singlet electronic states only could actually produce more realistic results for fullerene relative concentrations in the fullerenic soot. Nevertheless, in the Yb@C_{74} case the conclusions would not be changed as the suppression of the triplet states in the electronic partition function has a rather negligible effect on the relative concentrations.

In conclusion, the computations support the experimental finding of two Yb@C_{74} isomers and point out that the major species should have the IPR cage, while the minor one should contain one pentagon−pentagon junction in the carbon cage.

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