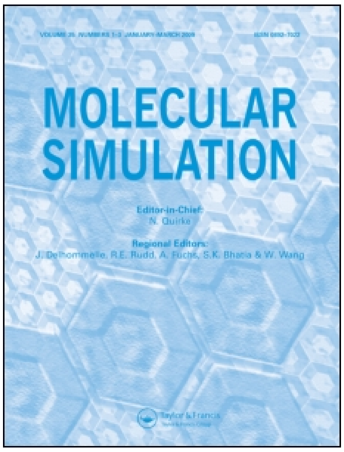

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Computational screening of metallofullerenes for nanoscience: $Sr@C_{74}$

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Computational screening of metallofullerenes for nanoscience: Sr@C_{74}

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Density-functional theory calculations are presented for Sr@C_{74} where C_{74} is either the isolated pentagon rule (IPR) cage or two cages with a pentagon–pentagon junction. Their relative thermodynamic production yields are evaluated using the calculated terms and it is shown that the IPR-based endohedral prevails at relevant temperatures. The encapsulation Gibbs energy is also combined with the saturated metal pressure as the combined term allows for evaluation of the relative production yields in a metallofullerene series.

Keywords: metallofullerenes; stability islands; optimized syntheses; Gibbs-energy evaluations; saturated metal vapors; carbon-based nanotechnology

1. Introduction

Empty C_{74} fullerene [1] has been somewhat elusive, however, various related endohedral C_{74}-based species have been known and studied vigorously like Ca@C_{74} [2,3], Sm@C_{74} [4,5], Sr@C_{74} [6], Ba@C_{74} [7], La@C_{74} [8–10], Eu@C_{74} [11], Yb@C_{74} [12–14], Sc_2@C_{74} [15] or Er_3@C_{74} [16]. In the Yb@C_{74} case, even two isomers were isolated [12]. As there is just one [17] C_{74} cage that obeys the isolated pentagon rule (IPR), namely of D_{3h} symmetry, a non-IPR structure is to be present in one Yb@C_{74} [14,18] (as it is the case with Ca@C_{72} [19] or La@C_{72} [20]). The C_{74} IPR cage was experimentally confirmed for Ca@C_{74} [3], Ba@C_{74} [7], La@C_{74} [10], one Yb@C_{74} [12], and indicated for Sm@C_{74} [4] and Sr@C_{74} [6].

The C_{74} metallofullerene family has also attracted computational interest [21–24]. First such computations were performed for Ca@C_{74} [2,21–23] and it was shown that the non-IPR encapsulations are not significant for Ca@C_{74} (in contrast to Ca@C_{72} [25,26]). The present paper deals with calculations of Sr@C_{74}, possible isomeric C_{74} cages, and estimation of production yields, consistently using the Gibbs energies as required by high temperatures [27,28]. Moreover, also saturated metal pressure (extracted from observed data [29]) is taken into consideration with the yield evaluations.

2. Calculations

The computations treat a set of three metallofullerene isomers, using the carbon cages investigated [2,21–23,30] with Ca@C_{74}, namely the unique D_{3h} C_{74} IPR cage and two non-IPR cages concluded from dianion energetics. In the previous computations the cages have been labeled by some code numbers that are also used here, combined with the symmetry of the empty cage: 1/D_{3h}, 4/C_1, and 103/C_1 (Figure 1).

The geometry optimizations were carried out using density functional theory (DFT), namely employing Becke's three parameter functional [31] with the non-local Lee–Yang–Parr correlation functional [32] (B3LYP) in the combined basis set of the 3-21G basis for C atoms and the LanL2DZ basis set [33] with the effective core potential (ECP) for the metal atoms (denoted here by 3-21G ~ dz). The B3LYP/3-21G ~ dz geometry optimizations were carried out with the analytically constructed energy gradient as implemented in the Gaussian 03 program package [34].

In the optimized B3LYP/3-21G ~ dz geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same B3LYP/3-21G ~ dz 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* ~ dz level. The Gibbs energies were evaluated using the rotational–vibrational partition functions constructed [35] from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. Although the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, the new observations [36] supply some arguments to expect

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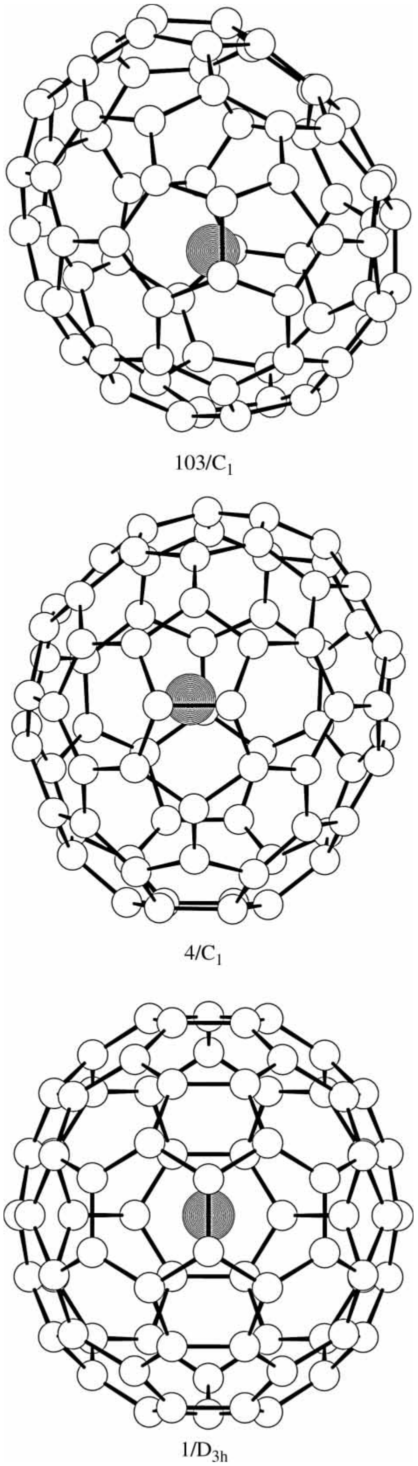
103/C_1

4/C_1

1/D_{3h}

Figure 1. B3LYP/3-21G ~ dz optimized structures of three Sr@C_{74} isomers.

it around or above 1500 K. Thus, the computations discussed here are centered around the temperature.

Relative concentrations (mole fractions) x_i of m isomers can be evaluated [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:

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

where R is the gas constant and T 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 inter-isomeric thermodynamic equilibrium. The electronic partition function for Equation (1) was constructed by direct summation of the TD B3LYP/3-21G ~ dz electronic excitation energies though only singlet excited electronic states were considered according to the recommendation [37]. The chirality contribution was included accordingly [38].

Let us note that in addition to the conventional RRHO treatment in Equation (1), a further modified approach for description of the encapsulate motions can be considered [39], following findings [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 Equation (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. For example, for the 1/D_{3h} species the D_{3h} symmetry is employed though its statical symmetry (i.e. after the geometry optimization) is just C_{2v}.

3. Results and discussion

Table 1 reports the separation energetics computed at two levels of theory, both in the B3LYP/3-21G ~ dz optimized geometries. In fact, the lower-level B3LYP/3-21G ~ dz separation energies agree reasonably well with the B3LYP/6-31G* ~ dz//B3LYP/3-21G ~ dz computations. The 4/C_1 and 103/C_1 isomers are quite close in energy in both treatments. As far as the charge transfer is concerned, it amounts at the B3LYP/3-21G ~ dz level to about 2.02–2.04 electrons donated to the cage.

Temperature development of the relative concentrations of the three Sr@C_{74} isomers in the FEM

Table 1. Sr@C$_{74}$ relative potential energies $\Delta E_{\mathrm{pot,rel}}$ computed in the B3LYP/3-21G $\sim$ dz optimized geometries.

	$\Delta E_{\mathrm{pot,rel}}$ (kcal/mol)	
Species[a]	B3LYP/3-21G $\sim$ dz[b]	B3LYP/6-31G* $\sim$ dz[b]
$103/C_1$	15.81	18.37
$4/C_1$	15.76	17.48
$1/D_{3h}$	0.0	0.0

[a] See Figure 1. [b] See the text for the abbreviation.

treatment are presented in Figure 2. In the temperature region around 1500 K, the $1/D_{3h}$ species is clearly prevailing while the two non-IPR cage related isomers $4/C_1$ and $103/C_1$ represent just a few percent of the equilibrium isomeric mixture. The proportions are in agreement with the observation [6] in which just one Sr@C$_{74}$ species was isolated and concluded to employ the IPR carbon cage. Consequently, in the following evaluations we can also limit ourselves to the $1/D_{3h}$ structure.

Let us move now to the more general problem, stabilities of the endohedrals with different stoichiometries.

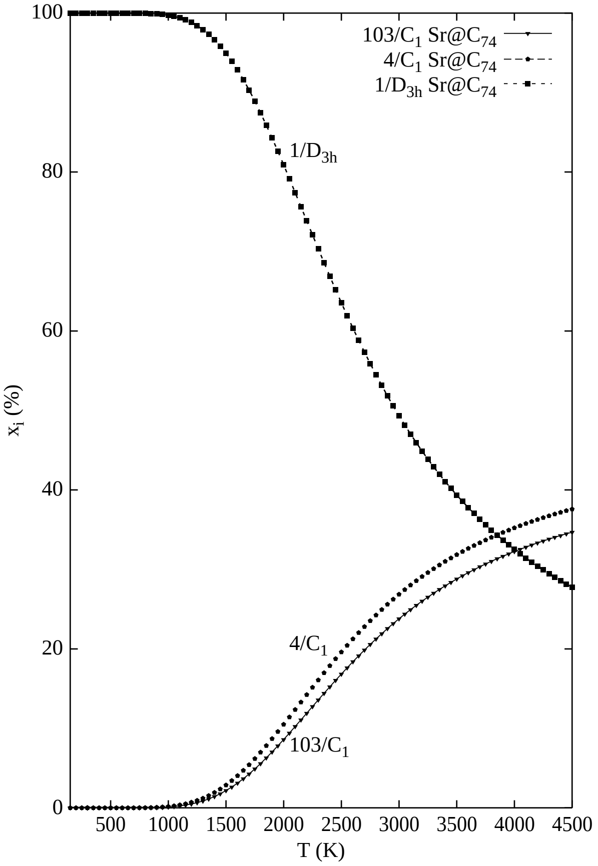

Figure 2. Relative concentrations of the Sr@C$_{74}$ isomers computed with the B3LYP/6-31G* $\sim$ dz energetics, B3LYP/3-21G $\sim$ dz entropy, and FEM treatment.

Table 2. The product of the encapsulation equilibrium constant[a] $K_{\mathrm{Sr}@C_{74},p}$ with the metal saturated-vapor pressure[b] $p_{\mathrm{Sr,sat}}$ computed for three illustrative temperatures *T*.

T (K)	$K_{\mathrm{Sr}@C_{74},p}$ (atm^{-1})	$p_{\mathrm{Sr,sat}}$ (atm)	$p_{\mathrm{Sr,sat}}K_{\mathrm{Sr}@C_{74},p}$
1000	2.11×10^{2}	1.16×10^{-3}	0.244
1500	5.18×10^{-1}	3.55×10^{-1}	0.184
2000	2.69×10^{-2}	6.12	0.165

[a] The potential energy change evaluated at the B3LYP/6-31G* $\sim$ dz level and the entropy part at the B3LYP/3-21G $\sim$ dz level – see Table 1. [b] Extrapolated from available observed data [29].

We can consider an overall stoichiometry of a metallofullerene formation:

$$X(g) + \mathrm{C}_n(g) = X@\mathrm{C}_n(g). \tag{2}$$

The encapsulation process is thermodynamically characterized by the standard change of the Gibbs energy $\Delta G^{o}_{\mathrm{X}@C_n}$ and the related encapsulation equilibrium constant $K_{\mathrm{X}@C_n,p}$. Table 2 presents the encapsulation equilibrium constant $K_{\mathrm{Sr}@C_{74},p}$ computed for three representative temperatures at the B3LYP/6-31G* $\sim$ dz//B3LYP/3-21G$\sim$dz level.

One can introduce a simplification, namely a presumption that the reaction metal pressure is actually close to the respective saturated pressure $p_{\mathrm{X,sat}}$. With this presumption, we shall deal with a special case – clustering under saturation conditions [42–44]. While the saturated pressures $p_{\mathrm{X,sat}}$ for various metals are known from observations [29], the partial reaction pressure of empty fullerene is less clear as it is obviously influenced by a larger set of processes (though it should exhibit a temperature maximum and then vanish). As far as we deal with a metallofullerene series with one common carbon cage, we can avoid the latter pressure in our considerations and what remains is the combined $p_{\mathrm{X,sat}}K_{X@C_{n,p}}$ term:

$$p_{\mathrm{X}@C_n} \sim p_{X,sat}K_{X@C_{n,p}}, \tag{3}$$

that directly controls the partial pressures $p_{\mathrm{X}@C_n}$ of various X@C$_n$ encapsulates in the endohedral series based on just one common C$_n$ fullerene. Table 2 shows the $p_{\mathrm{Sr,sat}}K_{\mathrm{Sr}@C_{74,p}}$ term. If we want to compare production abundances for two parent metallofullerenes like Sr@C$_{74}$ and Ba@C$_{74}$, just the ratio of their $p_{\mathrm{X,sat}}K_{\mathrm{X}@C_{74,p}}$ products is used. The $p_{\mathrm{Ba,sat}}K_{\mathrm{Ba}@C_{74,p}}$ term at 1500 K evaluated at the same level of theory is 34.8, i.e. two orders of magnitude higher than that for Sr@C$_{74}$. We get about the same finding with still larger basis set, B3LYP/6-311G* $\sim$ dz, used for energetics. Hence, although the energy terms are likely still not precise enough, their errors could be comparable in the series and thus, they should cancel out in the relative term. A similar cancellation should also operate for the higher corrections to the RRHO partition functions, including motions of the encapsulate. Incidentally, the computed stability proportions do correlate with qualitative abundances known from observations. For Ba@C_{74}, even microcrystals could be prepared [7] so that a diffraction study was possible, while for Sr@C_{74} only spectra could be recorded [6] in solution.

The saturation regime is a useful simplification – it is physically well defined, however, it is not necessarily always achieved. Under some experimental arrangements, under-saturated or perhaps super-saturated metal vapors are also possible. This reservation is applicable not only to the electric-arc treatment but even more likely to newly introduced ion-bombardment production technique [45,46].

Various endohedral cage compounds have been suggested as possible candidate species for molecular memories and other future nanotechnological applications. One approach is built on endohedral species with two possible location sites of the encapsulated atom [47] while another concept of quantum computing aims at a usage of spin states of N@C_{60} [48] or fullerene-based molecular transistors [49]. Low potential barriers for a three-dimensional rotational motion of encapsulates in the cages [50,51] can be a significant factor, however, the internal motion can be restricted by an additional cage derivatization [41] allowing for a versatile control in future nanoscience applications.

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