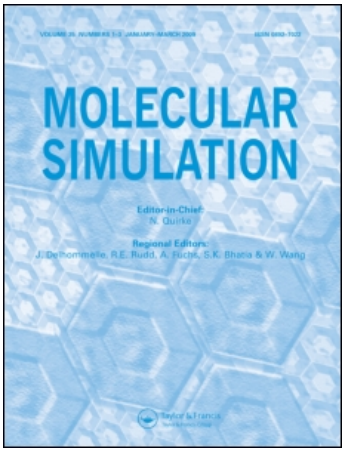

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Computations of production yields for $Ba@C_{74}$ and $Yb@C_{74}$

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Computations of production yields for Ba@C_{74} and Yb@C_{74}

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The paper reports computations for two C_{74}-based endohedrals—Ba@C_{74} and Yb@C_{74}. A set of six C_{74} cages is considered, namely one cage with isolated pentagons, three isomers with a pentagon–pentagon junction, two structures with one pentagon–pentagon pair and one heptagon. However, the endohedral based on the cage with isolated pentagons is the most important species in both systems. Special interest is paid to the Gibbs energy-based evaluations of the production abundances for different metallofullerenes, for the first time including saturated metal pressures into consideration. The computations show that the saturated metal pressures can substantially modulate the production yields.

Keywords: Metallofullerenes; Carbon-based nanotechnology; Molecular electronics; Optimized syntheses; Gibbs-energy evaluations; Saturated metal vapors

1. Introduction

Although empty C_{74} fullerene [1] is not yet available in solid form, several related endohedral species have been known like Ca@C_{74} [2,3], Sr@C_{74} [4], Ba@C_{74} [5], La@C_{74} [6–8], Eu@C_{74} [9], Yb@C_{74} [10], Sc_2@C_{74} [11] or Er_3@C_{74} [12]. In the Yb@C_{74} case, two isomers were in fact isolated [10]. 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]. Obviously, with Yb@C_{74}, a non-IPR cage should be involved as it is the case of Ca@C_{72} [14] (empty C_{72} could also not be isolated yet, possibly owing to solubility problems [2,15–17]).

The metallofullerene family is naturally of computational interest. First, such computations were performed for Ca@C_{74} with considerations of selected non-IPR cages [2,16,18,19]. However, the non-IPR encapsulations are not significant with Ca@C_{74}, in contrast to Ca@C_{72} [20,21]. The present paper surveys the computations also for the Ba@C_{74} and Yb@C_{74} species. In order to respect high temperatures in fullerene/metallofullerene preparations, the Gibbs energies are used [22,23] for stability considerations.

2. Computations

The computations treat a set of six metallofullerene isomers, using the carbon cages investigated with Ca@C_{74}, namely the three structures selected previously from dianion energetics [2,18], and three additional cages with non-negligible populations as empty C_{74} cages [24,25]. In the computations [18,19,24], 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–see figure 1. 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. The remaining two species, $368/C_1$ and $463/C_1$, contain a pentagon/pentagon pair and one heptagon.

The present geometry optimizations were primarily carried out using density-functional theory (DFT), namely employing Becke's three parameter functional [26] with the non-local Lee–Yang–Parr correlation functional [27] (B3LYP) in a combined basis set introduced and tested in the past [16]. In the case of Ba@C_{74}, the combined basis set consists of the 3-21G basis for C atoms and a dz basis

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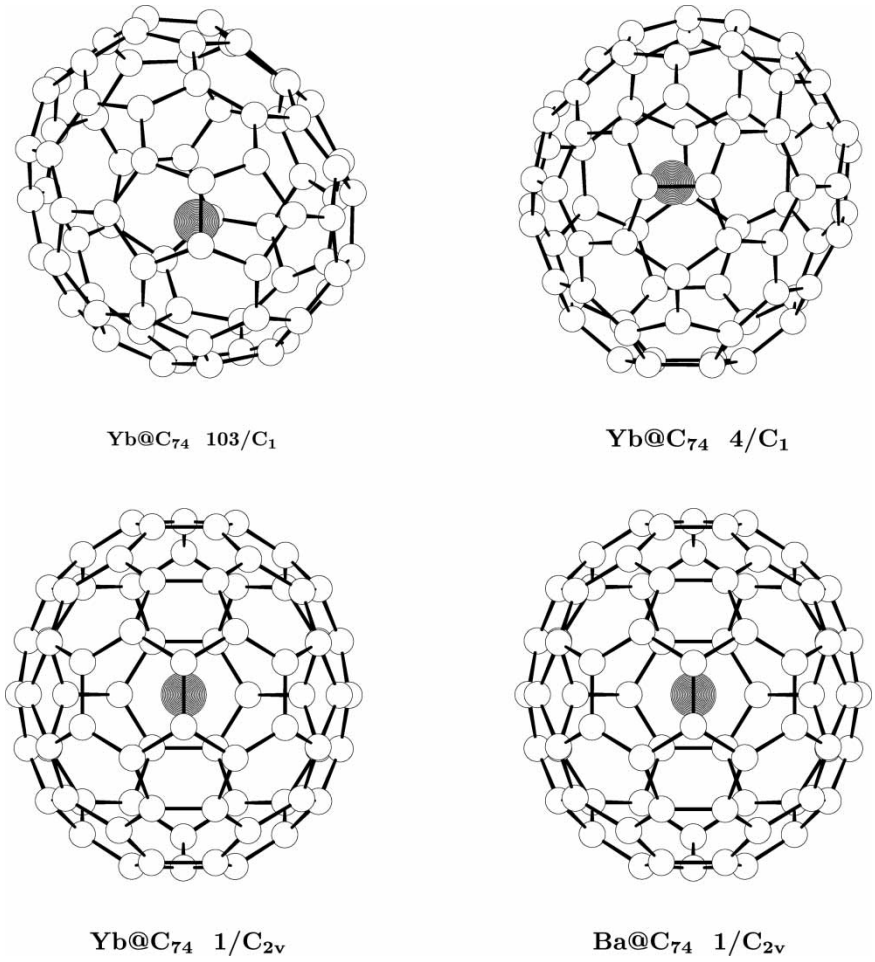

Figure 1. B3LYP/3-21G ~ CEP-4G optimized structures of three Yb@C_{74} isomers and B3LYP/3-21G ~ dz structure of the lowest Ba@C_{74} species.

set [28] with the effective core potential (ECP) on Ba (denoted here by 3-21G ~ dz) while with Yb@C_{74} (where the dz-type basis set [28] is not available for Yb) the 3-21G basis on C atoms is combined with the CEP-4G basis set [29,30] employing the compact effective (pseudo) potential (CEP) for Yb (denoted here by 3-21G ~ CEP-4G). The B3LYP/3-21G ~ dz or B3LYP/3-21G ~ CEP-4G geometry optimizations were carried out with the analytically constructed energy gradient. All the species are considered in singlet spin states. The relativistic effects are respected in the ECP/CEP terms. The basis set superposition error was not estimated for the dimerization energies. The reported computations were performed with the Gaussian 03 program package [31].

In the optimized B3LYP/3-21G ~ dz or B3LYP/3-21G ~ CEP-4G geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same 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 single-point treatment for Ba@C_{74} and the B3LYP/6-31G*~CEP-4G level with Yb@C_{74}. Moreover, in the latter case, the Stuttgart/Dresden (SDD) basis set [32,33] was also employed (with the SDD ECP for Yb) for the single-point calculations, and for the carbon atoms the SDD, 6-31G*, or 6-311G* basis set was stepwise used. 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 ~ dz or B3LYP/3-21G ~ CEP-4G level.

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 $\Delta H^o_{0,i}$ by a compact formula:

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

where R is the gas constant and T the absolute temperature. 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

Table 1. The computed* products of the encapsulation equilibrium constant† $K_{X@C_n,p}$ with the metal saturated-vapor pressure $p_{X,\mathrm{sat}}$ for Ba@C_{74} and Yb@C_{74} at a temperature $T = 1500$ K.

Endohedral	$K_{X@C_{74},p}$ (atm^{-1})	$p_{X,sat}$ (atm)	$p_{X,sat}K_{X@C_{74},p}$	$p_{X,sat}K_{X@C_{74},p}/p_{Ba,sat}K_{Ba@C_{74},p}$
Ba@C_{74}	1332.6	0.0261	34.82	1.00
Yb@C_{74}	81.77	1.42	116.13	3.34

* Ba@C_{74}: the potential-energy change evaluated at the B3LYP/6-31G*∼dz level and the entropy part at the B3LYP/3-21G ∼ dz level; Yb@C_{74}: the potential-energy change evaluated at the B3LYP/6-31G*∼SDD level and the entropy part at the B3LYP/3-21G ∼ CEP-4G level.
† The standard state—ideal gas phase at 101,325 Pa pressure.

determined both by the Gaussian built-in procedure [31] and by procedure [37] (including chirality [38]). The electronic partition function was constructed by direct summation of the TD B3LYP/3-21G ∼ dz or B3LYP/3-21G ∼ CEP-4G electronic excitation energies.

In addition, to the conventional RRHO treatment with equation (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]). A simplified approach called [39] free, fluctuating, or floating encapsulate model (FEM) was suggested. There are several systems [39,42] where the FEM approach improves agreement with experiment.

As for the temperature intervals to be considered, it is true that the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, however, the new observations [43] supply some relevant experimental arguments to expect it around 1500 K, and the temperature is used also here for illustrative purposes in table 1. Very low excited electronic states can be present in some fullerenes like C_{80} [44] or even the C_{74} IPR cage [45] which makes the electronic partition function particularly significant at such high temperatures. 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. Incidentally, the electronic excitation energies can in some cases (like empty fullerenes) be evaluated by means of a simpler ZINDO method [46,47].

3. Results and discussion

Let us first survey, for a more complete picture, the empty C_{74} cages (B3LYP/6-31G*//B3LYP/3-21G energetics, ZINDO electronic partition functions). The relative populations computed according to equation (1) show that the sole IPR cage (D_{3h}) is prevailing. Shinohara *et al.* [48] recently recorded electronic spectrum of C_{74} anion and concluded that the cage could have D_{3h} symmetry. Moreover, it was observed by Achiba *et al.* [3] that the only available IPR C_{74} cage is actually employed also in the Ca@C_{74} endohedral species. At a temperature of 1500 K, the $1/C_{2v}$ (related to the C_{74} IPR species), $4/C_1$, and $103/C_1$ Ca@C_{74} isomeric populations are computed [19] in the FEM scheme as 88.4, 8.0, and 3.5%, respectively.

Ba@C_{74} relative stability proportions differ from those previously computed [19] for Ca@C_{74}. For example, at a temperature of 1500 K, the $1/C_{2v}$, $4/C_1$, and $103/C_1$ species when evaluated with the conventional RRHO treatment should form 99.5, 0.3 and 0.2% of the equilibrium isomeric mixture, respectively. With the more realistic FEM scheme, the relative concentration are changed to 97.8, 1.2 and 1.0%. The proportions are in agreement with the observation of Reich *et al.* [5] in which just one Ba@C_{74} species was isolated, namely possessing the IPR carbon cage.

Yb@C_{74} is actually a more interesting system as Xu *et al.* [10] isolated two isomers and even found their production ratio as 100:3. In the computations at the B3LYP/6-31G*∼SDD level, the $1/C_{2v}$ species (see figure 1) is after about 13.14 kcal/mol followed by the $4/C_1$ isomer, the $103/C_1$ structure is about 16.98 kcal/mol above the lowest isomer while the other endohedrals are located more than 30 kcal/mol higher. The still higher B3LYP/6-311G*∼SDD approach gives about the some energetics as the $4/C_1$ isomer is placed 13.30 kcal/mol and the $103/C_1$ structure 16.99 kcal/mol above the $1/C_{2v}$ species.

The computed Yb@C_{74} energy and entropy parts are then converted [49] into the relative isomeric concentrations. In order to reproduce the observed [10] production isomeric ratio (100:3) within the conventional RRHO approach, temperature should reach about 1850 K when the $1/C_{2v}$, $4/C_1$, and $103/C_1$ species compose 95.7, 2.8, and 1.5% of the equilibrium isomeric mixture, respectively. The FEM treatment reduces the temperature for the reproduction of the observed ratio [10] 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. The ratios at 1500 K would be changed to 88.4, 8.8, 2.8% in the FEM treatment. Thus, the computations support the experimental finding [10] 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. A similar situation could be met with Ca@C_{74} but rather not with Ba@C_{74}.

There is a more general stability problem [50–53] related to fullerenes and metallofullerenes, viz. the absolute stability of the species or the relative stabilities of clusters with different stoichiometries. We shall illustrate the issue just on the most stable (i.e. $1/C_{2v}$) structures of Ba@C_{74} and Yb@C_{74}, thus ignoring the

remaining five isomers in each set. This choice is well supported by the computed relative isomeric populations, showing that the $1/C_{2v}$ structure is clearly prevailing in both cases. Let us consider formation of a metallofullerene:

$$X(g) + C_n(g) = X@C_n(g). \tag{2}$$

Under equilibrium conditions, we shall deal with the encapsulation equilibrium constant $K_{X@C_n,p}$:

$$K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \tag{3}$$

expressed in the terms of partial pressures of the components. Temperature dependency of the encapsulation equilibrium constant $K_{X@C_n,p}$ is described by the van't Hoff equation:

$$\frac{\mathrm{d}\ln K_{X@C_n,p}}{\mathrm{d}T} = \frac{\Delta H^o_{X@C_n}}{RT^2} \tag{4}$$

where $\Delta H^o_{X@C_n}$ stands for the (negative) standard change of enthalpy upon encapsulation. Let us further suppose that the metal pressure is close to the respective saturated pressure $p_{X,\mathrm{sat}}$. With this presumption, we shall deal with a special case of clustering under saturation conditions [54,55]. While the saturated pressures $p_{X,\mathrm{sat}}$ for various metals are known from observations [56,57], the partial pressure of C_n is less clear as it is obviously influenced by a larger set of processes (though, p_{C_n} should exhibit a temperature maximum and then vanish). Therefore, we avoid the latter pressure in our considerations at this stage. The computed equilibrium constants $K_{X@C_n,p}$ show a temperature decrease as it must be the case with respect to the van't Hoff equation (4) for the negative encapsulation enthalpy. However, if we consider the combined $p_{X,\mathrm{sat}}K_{X@C_n,p}$ term:

$$p_{X@C_n} \sim p_{X,\mathrm{sat}}K_{X@C_n,p}, \tag{5}$$

that directly controls the partial pressures of various $X@C_n$ encapsulates in an endohedral series (based on one common C_n fullerene), we get a different picture. The considered $p_{X,\mathrm{sat}}K_{X@C_n,p}$ term can frequently (though not necessarily) be increasing with temperature which would form a basic scenario for a temperature enhancement of metallofullerene formation in the electric-arc technique. An optimal production temperature could be evaluated in a more complex model that also includes temperature development of the empty fullerene partial pressure. If we, however, want to evaluate production abundances for two metallofullerenes like $Ba@C_{74}$ and $Yb@C_{74}$, just the product $p_{X,\mathrm{sat}}K_{X@C_{74},p}$ term can straightforwardly be used. Let us consider a temperature of 1500 K as the observations [43] suggest that fullerene synthesis should happen in the temperature region. The results in table 1 show for 1500 K that the $p_{\mathrm{Ba,sat}}K_{\mathrm{Ba@C_{74},p}}$ quotient is about three times smaller than the $p_{\mathrm{Yb,sat}}K_{\mathrm{Yb@C_{74},p}}$ product term. The ratio is enabled by a higher saturated pressure of Yb compared to Ba though the equilibrium constants show the reversed order. The B3LYP/6-31G*∼dz potential-energy change upon Ba encapsulation into the IPR C_{74} cage is $\Delta E = -59.5$ kcal/mol while the B3LYP/6-31G*∼SDD term for Yb encapsulation is computed at −55.9 kcal/mol. Although the energy terms are likely still not precise enough, their errors could be comparable and thus they should cancel out in the relative term $p_{X,\mathrm{sat}}K_{X@C_{74},p}/p_{\mathrm{Ba,sat}}K_{\mathrm{Ba@C_{74},p}}$. Let us mention that the combined basis sets require in the Gaussian program specification through a GEN keyword and for the sake of consistency the GEN approach is to be used even with empty cages (for example, the GEN-consistent approach gives for the B3LYP/6-31G*∼dz $La@C_{60}$ encapsulation energy [58] the value −54.7 kcal/mol). Let us also note that the FEM treatment is not used in a full extent with the product quotient $p_{X,\mathrm{sat}}K_{X@C_{74},p}$ evaluation as the three lowest vibrational frequencies are not removed in contrast to the isomeric treatment by equation (1), and also the electronic partition functions were ignored in the quotient evaluations. Finally, this new stability criterion also suggests (as $Yb@C_{74}$ should come in higher yields than $Ba@C_{74}$) that the conditions for the isolation of a minor isomer are more convenient in the $Yb@C_{74}$ case (in addition to the computed higher fraction of the non-IPR species in the case of Yb encapsulation compared to Ba [59]).

Various endohedral cage compounds have been suggested [60–62] as possible candidate species for applications. Low potential barriers for a three-dimensional rotational motion of encapsulates in the cages [14,16,40,63–65] or at least large amplitude oscillations [66,67] can be a significant factor. The low barriers are responsible for simplifications of the NMR patterns at room temperature. This simplification is made possible by a fast, isotropic endohedral motions inside the cages that yield a time-averaged, equalizing environment [60,61,68] on the NMR timescale. The internal motion can however be restricted by a cage derivatization [41,69,70].

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