

## Computed Encapsulation Energetics for Metallofullerenes

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**Abstract:** Some alkali and alkaline-earth metals can be now encapsulated in fullerenes. For example, Li@C<sub>60</sub> and Li@C<sub>70</sub> can be produced by the low-energy bombardment method while Ca@C<sub>74</sub>, Sr@C<sub>74</sub>, and Ba@C<sub>74</sub> can be prepared by high-temperature syntheses. Hence, their computations at higher levels of theory are also of interest. In the report, the computations are carried out on Li@C<sub>60</sub>, Li<sub>2</sub>@C<sub>60</sub> and Li<sub>3</sub>@C<sub>60</sub> with the B3LYP and MPWB1K density-functional theory (DFT) treatment in the standard 3-21G and 6-31G\* basis sets. The computed energetics suggests that Li<sub>x</sub>@C<sub>60</sub> species could be produced for several small *x* values if the Li pressure is enhanced sufficiently. The B3LYP DFT approach is also applied to Mg@C<sub>74</sub>, Ca@C<sub>74</sub>, Sr@C<sub>74</sub>, and Ba@C<sub>74</sub> and production populations are thus rationalized.

**Keywords:** Endohedral fullerenes; carbon-based nanotechnology; molecular modeling; molecular electronic structure; metallofullerene stabilities.

### INTRODUCTION

There has been a renewed interest [1-22] in systems containing alkali metals and fullerenes, in particular Li@C<sub>60</sub> and Li@C<sub>70</sub> produced by low energy ion implantation [11,13,14] in bulk amounts. Recently, such systems have also been subjected to more advanced computations [19-22], especially in the studies by Gurin [19,20]. The vibrational spectra were obtained [13,14] for Li@C<sub>60</sub> and Li@C<sub>70</sub>. Li<sub>2</sub>@C<sub>60</sub> was also evidenced in observations [11] though in a small amount compared to Li@C<sub>60</sub>. In addition to alkali metals, even alkaline-earth metals can be encapsulated into fullerene cages and actually a whole reaction series Ca@C<sub>74</sub>, Sr@C<sub>74</sub>, and Ba@C<sub>74</sub> is now available from high-temperature techniques [23-25]. The observations moreover suggest a qualitative information on their relative populations. The recent experimental progress makes computations of the species even more interesting and, in particular, some theoretical rationalization of the observed relative stabilities would be useful. In the report, the computations are carried out on Li@C<sub>60</sub>, Li<sub>2</sub>@C<sub>60</sub>, and Li<sub>3</sub>@C<sub>60</sub>, and also on Mg@C<sub>74</sub>, Ca@C<sub>74</sub>, Sr@C<sub>74</sub>, and Ba@C<sub>74</sub>, using the density-functional theory (DFT) treatments. The report supplies illustrative examples what kind of information can be obtained from calculations for such metallofullerene systems. Both potential energy and Gibbs free energy terms are evaluated. The study for the first time allows for computational rationalization of the observed relative populations for metallofullerene reaction series.

### COMPUTATIONS

The geometry optimizations were carried out with Becke's three parameter functional [27] with the non-local Lee-Yang-Parr correlation functional [28] (B3LYP) in the standard 3-21G basis set (B3LYP/3-21G). The geometry optimizations were carried out with the analytically constructed energy gradient as implemented in the Gaussian program package [29]. Although the 3-21G basis set is a small basis, its application has been customary for fullerene geometries owing to the computational demands (though a check with larger basis sets would in future be useful).

In the optimized B3LYP/3-21G 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, i.e., the B3LYP/6-31G\* level (or, more precisely, B3LYP/6-31G\*\*/B3LYP/3-21G). As Li@C<sub>60</sub> and Li<sub>3</sub>@C<sub>60</sub> are radicals, their computations were carried out using the unrestricted B3LYP treatment for open shell systems (UB3LYP). The ultrafine integration grid was used for the DFT numerical integrations throughout.

Recently, Zhao and Truhlar [30-35] performed a series of test DFT calculations with a conclusion [35] that the MPWB1K functional (the modified Perdew and Wang exchange functional MPW [36] and Becke's meta correlation functional [37] optimized against a kinetics database) is the best combination for evaluations of nonbonded interactions with a relative averaged mean unsigned error of only 11%. The MPWB1K functional is also applied in this report.

### RESULTS AND DISCUSSION

#### One atom-type stepwise encapsulations: Li<sub>x</sub>@C<sub>60</sub>

The UB3LYP approach is preferred here over the restricted open-shell treatment (ROB3LYP) as the latter actually

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Table 1. Computed encapsulation potential-energy changes  $\Delta E_{Y_x@C_n}$  (kcal/mol) for  $\text{Li}_x@C_{60}$

Species	$\Delta E_{Y_x@C_n}$	$\frac{\Delta E_{Y_x@C_n}}{x}^a$
B3LYP <sup>b</sup>		
Li@C <sub>60</sub>	-28.4	-28.4
Li <sub>2</sub> @C <sub>60</sub>	-51.1	-25.6
Li <sub>3</sub> @C <sub>60</sub>	-71.0	-23.7
MPWB1K <sup>c</sup>		
Li@C <sub>60</sub>	-34.9	-34.9
Li <sub>2</sub> @C <sub>60</sub>	-62.8	-31.4
Li <sub>3</sub> @C <sub>60</sub>	-101.0	-33.7

<sup>a</sup>The relative term related to one Li atom. <sup>b</sup>Computed at the B3LYP/6-31G\*//B3LYP/3-21G level. <sup>c</sup>Computed at the MPWB1K/6-31G\*//MPWB1K/3-21G level.

The encapsulation process is thermodynamically characterized by the standard changes of, for example, enthalpy  $\Delta H_{Y_x@C_n}^o$  or the Gibbs energy  $\Delta G_{Y_x@C_n}^o$ . In a first approximation, we can just consider the encapsulation potential-energy changes  $\Delta E_{Y_x@C_n}$  (i.e., the differences in the total electronic energy between reactants and products). Table 1 presents the terms for  $\text{Li}_x@C_{60}$ . Their absolute values increase with the increasing number of the encapsulated Li atoms. In order to have some directly comparable relative terms, it is convenient to consider the reduced  $\frac{\Delta E_{Y_x@C_n}}{x}$  terms related to one Li atom. Although the absolute values of the reduced term decrease with increasing Li content, the decrease is not particularly fast (so that, a further increase of the encapsulated Li atoms could still be possible). The MPWB1K terms are somewhat more pronounced and there is even a different trend for  $\text{Li}_3@C_{60}$  compared to B3LYP (as shown by Zhao and Truhlar [30-35], B3LYP is however not particularly reliable for such situations). The computational findings help to rationalize why also the  $\text{Li}_2@C_{60}$  species could be observed [11]. The basis set superposition error (BSSE) is not estimated for the presented values (a straightforward application of the Boys-Bernardi counterpoise method would be rather questionable in this situation, partly owing to a substantial cage deformation upon the encapsulation). However, the BSSE terms could be to some extent additive and thus, they should somewhat cancel out in a reaction series. Interestingly enough, the stabilization of metallofullerenes is mostly electrostatic as documented [45,46] using the topological concept of 'atoms in molecules' (AIM) [47,48] which shows that the metal-cage interactions form ionic (and not covalent) bonds.

The problem of the relative stabilities of clusters with different stoichiometries can also be considered in a series with variable metal, like  $\text{Mg}@C_{74}$ ,  $\text{Ca}@C_{74}$ ,  $\text{Sr}@C_{74}$ , and  $\text{Ba}@C_{74}$ . Let us consider an overall stoichiometry of a metallofullerene formation:



The encapsulation process is thermodynamically characterized by the standard changes of, for example, enthalpy  $\Delta H_{X@C_n}^o$  or the Gibbs energy  $\Delta G_{X@C_n}^o$ . The equilibrium composition of the reaction mixture is controlled by the encapsulation equilibrium constants  $K_{X@C_n,p}$ :

$$K_{X@C_n,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \quad (3)$$

expressed in the terms of partial pressures of the components. The encapsulation equilibrium constant is interrelated with the the standard encapsulation Gibbs energy change:

$$\Delta G_{X@C_n}^o = -RT \ln K_{X@C_n,p}. \quad (4)$$

Temperature dependency of the encapsulation equilibrium constant  $K_{X@C_n,p}$  is then described by the van't Hoff equation:

$$\frac{d \ln K_{X@C_n,p}}{dT} = \frac{\Delta H_{X@C_n}^o}{RT^2} \quad (5)$$

where the  $\Delta H_{X@C_n}^o$  term is typically negative (as shown by available computations and also as expected in order to get a significant stabilization) so that the encapsulation equilibrium constants decrease with increasing temperature.

Let us further suppose that the metal pressure  $p_X$  is actually close to the respective saturated pressure  $p_{X,sat}$ . While the saturated pressures  $p_{X,sat}$  for various metals are known from observations [49], the partial pressure of  $C_n$  is



highly anharmonic, however, its description is yet possible only with simple potential functions. Another option for evaluation of the entropic term could be classical molecular dynamics. As long as we are interested in the relative production yields, the anharmonic effects should at least to some extent be cancelled out in the relative quotient  $\frac{p_{X,sat} K_{X@C_{74},P}}{p_{Ba,sat} K_{Ba@C_{74},P}}$ . Incidentally, the computed stability proportions do correlate with qualitative abundances known from observations. For Ba@C<sub>74</sub> even microcrystals could be prepared [26] so that a diffraction study was possible, while for Sr@C<sub>74</sub> at least various spectra could be recorded [25] in solution, Ca@C<sub>74</sub> was studied [24] only by NMR spectroscopy, and Mg@C<sub>74</sub> is yet unknown from experiment.

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