Hexa-Aqua Transition Metal Complexes

Aqueous pKₐ values for hexa-aqua complexes of first and second row transition metals are computed using a combination of quantum chemical and electrostatic methods. On page 69, Gegham Galstyan and Ernst-Walter Knapp report the computed pKₐ values show very good agreement with measured pKₐ values with a root mean square deviation of 1 pH unit. Compared to previous approaches, the precision of the method is systematically improved.

Molecular Dynamics

On page 79, Robin M. Betz and Ross C. Walker report on Paramfit, a new program that generates force field parameters for molecular dynamics simulation by minimizing the difference between ab-initio quantum and classical energies of a set of input molecular conformations. The program incorporates a novel minimization algorithm capable of reliably locating global minima, shown by testing on various surfaces like the three-dimensional Rastrigin function illustrated here, which features numerous attractive local minima. Several molecular conformations of a small peptide used for demonstrating the program’s efficacy on biological systems are also shown at the border. Structures like these are input into Paramfit, along with associated quantum energies, and are used to generate parameters of interest.

Rare Gas Encapsulation

Encapsulating rare-gas atoms into fullerenes smaller than C₆₀ quickly becomes repulsive and follows an exponential law with decreasing number of carbon atoms. The reason comes from a rather rigid cage structure that determines the space available inside the fullerene. On page 88, Rebecca Sure, Ralf Tonner, and Peter Schwerdtfeger provide detailed insight into rare-gas fullerene interactions ranging from C₅₀ to C₆₀ and from He to Ar using Grimme’s dispersion corrected density functional theory. The maximum inscribing inner sphere inside a fullerene cage gives a good qualitative picture for the space available.

Coming Soon

Clarifying and illustrating the electronic energy transfer pathways in trimeric and hexameric aggregation state of cyanobacteria allophycocyanin within the framework of Förster theory

Yanliang Ren et al.

The electronic energy transfer is a fundamental key in the development of synthetic light-harvesting devices. Insight into the EET pathways in cyanobacteria allophycocyanin trimer and hexamer is gained by the first principle calculations within the framework of Förster theory.

DOI: 10.1002/jcc.23770

Isolated pentagon rule violating endohedral metallofullerenes explained using the Hückel rule: A statistical mechanical study of the C₈₄ isomeric set

Timothy Fuhrer et al.

A systematic, temperature dependent, statistical thermodynamic study is presented of the 24 possible isolated pentagon rule fullerene isomers of C₈₄ as well as two of the experimentally known non-IPR isomers (S1365 and S1383), at several different charges (0, −2, −4, and −6). Based on the results, the Hückel rule is a valid explanation for the stability of fused pentagons in endohedral metallofullerenes.

DOI: 10.1002/jcc.23774
A Systematic Study of Rare Gas Atoms Encapsulated in Small Fullerenes using Dispersion Corrected Density Functional Theory

Rebecca Sure,*[a] Ralf Tonner,[b] and Peter Schwerdtfeger*[c]

The most stable fullerene structures from C_{20} to C_{60} are chosen to study the energetics and geometrical consequences of encapsulating the rare gas elements He, Ne, or Ar inside the fullerene cage using dispersion corrected density functional theory. An exponential increase in stability is found with increasing number of carbon atoms. A similar exponential law is found for the volume expansion of the cage due to rare gas encapsulation with decreasing number of carbon atoms. We show that dispersion interactions become important with increasing size of the fullerene cage, where Van der Waals forces between the rare gas atom and the fullerene cage start to dominate over repulsive interactions. The smallest fullerenes where encapsulation of a rare gas element is energetically still favorable are He_{C_{48}}, Ne_{C_{52}}, and Ar_{C_{58}}. While dispersion interactions follow the trend Ar > Ne > He inside C_{60} due to the trend in the rare gas dipole polarizabilities, repulsive forces become soon dominant with smaller cage size and we have a complete reversal for the energetics of rare gas encapsulation at C_{50}. © 2014 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.23787

Introduction

Directly after the discovery of C_{60} by mass spectrometry,[1] Smalley and coworkers provided evidence for the formation of a stable La@C_{60} complex,[2] demonstrating that fullerenes are able to encapsulate atoms (or molecules) inside their carbon cage.[3] Few years later, the same group reported the synthesis of larger lanthanum containing fullerenes such as La@C_{70}, La@C_{74}, La@C_{82}, as well as K@C_{60}.[4,5] In the same year, Schwarz and coworkers observed the first endohedral fullerenes enclosing a noble gas atom from high-energy collisions, that is, He_{C_{60}} and He_{C_{70}}.[6–8] Since then, many different endohedral fullerenes have been synthesized[9] or studied by computational methods.[10,11] Prime examples are the encapsulation of H_{2}O inside C_{60} heavy atoms such as Ba in C_{60} or more recently Pb in C_{80}.[15] endohedral fullerenes containing neon, argon, or heavier rare gas atoms,[16–21] metal clusters such as La_{2} in C_{72},[22] or even another fullerene cage forming so-called buckyonions with C_{20}+2n@C_{20}+2n (m<n, m ≠ 1).[23–27] For a recent comprehensive review on endohedral fullerenes see Popov et al.[9] or Lu et al.[28]

In order for a fullerene to be able to encapsulate an atom, cluster or a molecule, there must be sufficient “empty” space inside the fullerene cage, otherwise the interaction between the encapsulated atom (molecule) and the fullerene cage becomes repulsive and energetically unfavorable. This is why some of the molecules or atomic clusters inside a fullerene cage require a larger cage radius than is available in C_{60}.[9] Schwarz et al. as well as Saunders et al. showed experimentally that all rare gas atoms up to xenon fit into C_{60},[19,29] which was verified theoretically by Thiel and coworkers for He.[30] In a recent paper, it was demonstrated that a large number of rare gas atoms is required to increase the internal pressure to the point where the C_{60} cage breaks.[31] Here, we take the opposite approach by studying the stability of endohedral rare gas fullerenes starting from the smallest Ng@C_{20} up to Ng@C_{60} (Ng = He, Ne, Ar), using the most stable isomer for each class of fullerenes. If there is enough space inside the fullerene cage to accommodate a rare gas atom, that is, the repulsive forces between the atom and the carbon framework are small, dispersive type of interactions need to be taken into account.[32] For example, Autschbach showed that without the inclusion of dispersive type of interactions, encapsulating Xe into C_{60} is energetically not favorable.[33] A case study on hydrogen filled endohedral fullerenes nH_{2}@C_{60} and nH_{2}@C_{70} showed that simple dispersion corrected density functionals yield good results for the energetics of the encapsulation.[34]

Concerning rare gas encapsulation into fullerenes, there are already a number of theoretical studies on C_{60} available.[10][35–45] (but few on smaller fullerenes)[30][46–51]. For example, Straka and

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Table 1. Properties of fullerenes $C_n\text{/(}N=20+2n\text{)}$ (numbering of the isomers stems from lexicographically ordered face-spiral pentagon indices$^{[56]}$): HOMOLUMO gap $\Delta\text{LUMO}$ in eV, smallest $r_{\text{min}}$ and largest $r_{\text{max}}$ bond lengths, maximum nonbonding distance $d_{\text{max}}$, maximum inner sphere radius $R_{\text{RES}}$ in Å, relative energy $\Delta E$ with respect to the energetically lowest isomer, and the total energy $\Delta\text{E}_{\text{RES}}$ per carbon atom relative to $C_{60}$ in kcal/mol.

<table>
<thead>
<tr>
<th>$C_n$</th>
<th>Isomer</th>
<th>Symmetry</th>
<th>State</th>
<th>$\Delta\text{LUMO}$</th>
<th>$r_{\text{min}}$</th>
<th>$r_{\text{max}}$</th>
<th>$d_{\text{max}}$</th>
<th>$R_{\text{RES}}$</th>
<th>$\Delta E$</th>
<th>$\Delta\text{E}_{\text{RES}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{20}$</td>
<td>1</td>
<td>$D_{2d}$</td>
<td>$A_{2u}$</td>
<td>0.731</td>
<td>1.411</td>
<td>1.518</td>
<td>4.166</td>
<td>1.950</td>
<td>0.00</td>
<td>18.148</td>
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<tr>
<td>C$_{24}$</td>
<td>1</td>
<td>$D_{6d}$</td>
<td>$A_1$</td>
<td>0.481</td>
<td>1.374</td>
<td>1.533</td>
<td>4.613</td>
<td>2.171</td>
<td>0.00</td>
<td>15.710</td>
</tr>
<tr>
<td>C$_{26}$</td>
<td>1</td>
<td>$Ih$</td>
<td>$A_1$</td>
<td>0.392</td>
<td>1.423</td>
<td>1.519</td>
<td>4.774</td>
<td>2.077</td>
<td>0.45</td>
<td>15.729</td>
</tr>
<tr>
<td>C$_{30}$</td>
<td>6</td>
<td>$D_3$</td>
<td>$A_1$</td>
<td>0.300</td>
<td>1.370</td>
<td>1.528</td>
<td>5.283</td>
<td>2.273</td>
<td>0.00</td>
<td>10.350</td>
</tr>
<tr>
<td>C$_{32}$</td>
<td>6</td>
<td>$D_3$</td>
<td>$A_1$</td>
<td>1.457</td>
<td>1.385</td>
<td>1.506</td>
<td>5.655</td>
<td>2.435</td>
<td>0.00</td>
<td>8.369</td>
</tr>
<tr>
<td>C$_{34}$</td>
<td>5</td>
<td>$C_2$</td>
<td>$A_1$</td>
<td>0.490</td>
<td>1.389</td>
<td>1.505</td>
<td>5.899</td>
<td>2.452</td>
<td>0.00</td>
<td>8.029</td>
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<tr>
<td>C$_{46}$</td>
<td>109</td>
<td>$C_2$</td>
<td>$A_1$</td>
<td>0.537</td>
<td>1.375</td>
<td>1.498</td>
<td>5.671</td>
<td>2.560</td>
<td>0.00</td>
<td>4.066</td>
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<tr>
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<td>171</td>
<td>$C_2$</td>
<td>$A_1$</td>
<td>0.733</td>
<td>1.381</td>
<td>1.490</td>
<td>6.941</td>
<td>2.735</td>
<td>0.00</td>
<td>3.384</td>
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<tr>
<td>C$_{50}$</td>
<td>271</td>
<td>$D_{5h}$</td>
<td>$A_{1g}$</td>
<td>0.307</td>
<td>1.394</td>
<td>1.471</td>
<td>6.870</td>
<td>2.958</td>
<td>0.00</td>
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<td>422</td>
<td>$C_2$</td>
<td>$A_1$</td>
<td>0.213</td>
<td>1.388</td>
<td>1.481</td>
<td>6.836</td>
<td>3.183</td>
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<td>2.512</td>
</tr>
<tr>
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<td>$C_2v$</td>
<td>$A_1$</td>
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<td>1.380</td>
<td>1.481</td>
<td>7.746</td>
<td>3.121</td>
<td>0.00</td>
<td>1.921</td>
</tr>
<tr>
<td>C$_{56}$</td>
<td>916</td>
<td>$D_2$</td>
<td>$A_1$</td>
<td>0.673</td>
<td>1.381</td>
<td>1.470</td>
<td>7.510</td>
<td>3.049</td>
<td>0.00</td>
<td>1.560</td>
</tr>
<tr>
<td>C$_{58}$</td>
<td>1050</td>
<td>$C_3v$</td>
<td>$E$</td>
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<td>1.391</td>
<td>1.468</td>
<td>7.162</td>
<td>3.255</td>
<td>0.00</td>
<td>1.260</td>
</tr>
</tbody>
</table>

[a] Saddle point on a shallow potential energy surface.

coworkers studied rare gas chemical shifts in fullerenes.$^{[52-54]}$
We also mention that Becker and coworkers found extraterrestrial helium trapped in C$_{60}$ and C$_{70}$ in the Sudbury impact structure, which was clearly identified by the $^3\text{He}/^4\text{He}$ ratio.$^{[55]}$ It is therefore, quite likely that some of the smaller fullerenes containing helium can be found and isolated, and the structure and stability of such endohedral rare gas fullerenes are therefore of interest. The aim of this systematic study is to give a comprehensive overview over structural and electronic features of all fullerenes up to C$_{60}$ including information about different electronic states and a rigid analysis of the changes upon encapsulation of a rare gas atom with special emphasis on quantifying dispersion effects.

**Computational Methods**

In all cases, the least strained fullerene isomers having the smallest pentagon neighbor index $N_p$ were considered (for the definition of the pentagon neighbor index see Ref. [56]). Moreover, previous theoretical work on fullerenes in the range from C$_{28}$ to C$_{60}$ also helped to identify the most stable isomers.$^{[57-59]}$ For most of the fullerences just one or two isomers had to be considered. The exceptions are C$_{46}$ and C$_{48}$, which exhibit seven and four relatively stable isomers, respectively. For the fullerenes with more than one stable isomer, point-group symmetry, or more than one possible electronic state, for example due to Jahn–Teller distortions, the structure with the lowest total electronic energy was determined. For example, C$_{50}$ exhibits Jahn–Teller distortion leading to a deviation from ideal icosahedral symmetry $I_h$ into $D_{3d}$ with a predicted $A_{2u}$ electronic ground state.$^{[58]}$ C$_{24}$ ($D_{6d}$) has a triplet, C$_{28}$ ($T_{d}$) a quintet and C$_{58}$ ($C_{3v}$) a triplet state as predicted ground states.

All geometry optimizations and single-point calculations were carried out using the TURBOMOLE 6.3.1. program suite.$^{[60]}$ The functional Perdew-Burke-Ernzerhof (PBE)$^{[61,62]}$ developed by Perdew-
Becke-Emzerhof was used together with polarized split-valence triple-ζ basis sets (def2-TZVPP) to keep the basis set superposition error (BSSE) small. The BSSE was not included in our analysis (for a recent critical account see Baerends et al.). However, for the sake of completion we give the BSSE for the rare-gas insertion into the largest and smallest fullerenes considered (in kcal/mol): He@C_{20} 0.62; Ne@C_{20} 1.55; Ar@C_{20} 1.81; He@C_{60} 0.49; Ne@C_{60} 1.07; Ar@C_{60} 1.01. The geometry optimizations were performed with and without inclusion of the Grimme dispersion correction scheme (D3) applying the Becke-Johnson damping. A tighter energy convergence criterion (10^-8 a.u.) and a larger numerical quadrature grid (m5) for integration of the exchange-correlation contribution were used in all cases. For all calculations the resolution of identity approximation for Coulomb integrals applying a matching auxiliary basis set was used.

Geometry optimizations of the empty fullerene cages were performed using the corresponding symmetric structure as a starting point. However, no symmetry constraints were applied for the optimizations of the fullerenes and endohedral clusters. The stationary points were analyzed at the corresponding computational level via calculations of the Hesse matrix. In a few cases (see Table 1) small imaginary frequencies indicating a saddle point with a shallow potential hypersurface were obtained. Distortions along the imaginary modes yielded a local minimum with lowered symmetry as indicated in the Tables. For the energetics discussed here, we include zero-point vibrational (ZPVE) effects, even if these are rather small compared to the accuracy of the density functional approximation applied. The point-group symmetry was determined with the TURBOMOLE module DEFINE using a threshold in Cartesian coordinates of 5×10^-5 Å.

The topological analyses for the various fullerene cages were performed using the program Fullerene (version 4.4). This program was also used to generate the input coordinates for all fullerene cages via the face-spiral algorithm of Manolopoulos and Fowler followed by a force-field optimization.

**Results and Discussion**

The results from electronic structure calculations for C_{20+2n} (n = 0, 2, 3, 4, . . . , 20) are shown in Table 1 (note that C_{22} does not
Teller distorted singlet states of DFT is not able to correctly find the singlet state of D_n number of hexagons exist as a regular fullerene. In its ideal Ih symmetric structure, C_{20} is of multireference character and conventional Kohn–Sham density functional theory (DFT) is not able to correctly describe this state. Instead, we compared the possible Jahn–Teller distorted singlet states of D_{3d} and D_{2h} symmetry, and the triplet electronic states of C_{5v} and D_{3d} symmetry. We found the singlet state of D_{3d} symmetry the lowest in energy. For C_{24} the singlet state of D_{6h} symmetry is lower in energy than the D_{6h} triplet. In case of C_{28} we did not find a singlet or triplet state that is lower in energy than the quintet state, which is of T_d symmetry. For C_{58} the C_{5v} triplet state has a slightly lower energy compared to the C_{2h} singlet.

All other fullerenes exhibit singlet ground states. However, the fullerenes C_{36}, C_{40}, C_{44}, C_{46}, C_{48}, and C_{56} have two or more isomers (not counting the enantiomers) with the same pentagon neighbor index, and all these needed to be considered (only the most stable isomers are listed in Table 1).

The fullerene cages investigated show a mean minimal bond distance between two carbon atoms of 1.390 Å. The T_d symmetric isomer of C_{58} exhibits the largest value of 1.431 Å and C_{60} the lowest of 1.370 Å. The mean maximal bond distance of two carbon atoms is 1.492 Å, whereas C_{26} shows the largest value of 1.543 Å, and C_{58} the smallest value of 1.453 Å. There is no clear correlation between the bond distances and the number of carbon atoms and thus the size of the fullerene cage. This is most likely due to the bond distances in fullerenes being directly correlated to the Pauling bond order for each C–C bond in a specific isomer, which can be derived from the many possible Kekulé structures (perfect matchings) of a fullerene (there are 12,500 such structures for C_{60}). The maximal nonbonding distance between two carbon atoms related to the cage diameter increases roughly in a linear fashion with increasing number of carbon atoms. The exception is found for C_{60}, where the two different bond distances are small compared to the other fullerenes. This indicates a more stable and spherical (less prolate) shape as will be analyzed in more detail below. For the stability of the bare fullerene cage, we list the relative stabilities with respect to C_{60} for the isodesmic reaction,

$$\Delta E_{\text{RS}}(N) = \frac{1}{N} \Delta E[C_60] - \frac{1}{60} \Delta E[C_{60}-h]$$

This reflects the increase in fullerene stability with increasing number of carbon atoms. In contrast, for the isomers considered here there is no clear observable trend between \(\Delta E_{\text{RS}}\) and the energetic stability. The energy gap between the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) \(\Delta E_{\text{HOMO}}\) can be as small as 0.101 eV for C_{58}C_{60} and as large as 1.653 eV as for C_{60} (compare also to the values published in Ref. [47]). We note that absolute values for band-gaps computed with GGA functionals can exhibit errors up to 50% compared to experiment. The optimized geometries of the most stable isomers are shown in Figure 1. These structures were subsequently used as starting point for the encapsulation of rare gas atoms He, Ne, and Ar, which will be discussed in the following.

To encapsulate a rare gas atom, the cavity inside the fullerene has to be large enough to avoid repulsive forces. The size of a fullerene cavity available to accommodate an atom can be estimated using the concept of the maximum inscribing empty sphere (MES), that is, the largest possible sphere with origin at \(\vec{r}_{\text{MES}}\).
The MES algorithm in program Fullerene is simplified by just keeping the vertices outside the inscribing sphere (thus allowing for slight protrusion of faces of the polyhedron), and uses a steepest descent optimization starting with \( c_{\text{MES}} \) at the bary-center of the fullerene. Once the MES radius \( R_{\text{MES}} \) and origin \( c_{\text{MES}} \) is obtained, we can estimate the condition for fitting a rare gas atom \( N_g \) inside a fullerene cage without hitting the repulsive wall,

\[
R_{\text{MES}}(C_{N_g}) \geq R_{\text{VdW}}(C) + R_{\text{VdW}}(N_g) \tag{3}
\]

using the Van der Waals radii for carbon \( R_{\text{VdW}}(C) = 1.415 \, \text{Å} \), helium \( R_{\text{VdW}}(\text{He}) = 1.40 \, \text{Å} \), neon \( R_{\text{VdW}}(\text{Ne}) = 1.54 \, \text{Å} \), and argon \( R_{\text{VdW}}(\text{Ar}) = 1.88 \, \text{Å} \). Using the \( R_{\text{MES}} \) values listed in Table 1, we see that \( N_g@C_{N_g} \) fits this criterion for \( N_g \geq 48 \) for both \( N_g = \text{He} \) and \( \text{Ne} \), and for \( \text{Ar} \) only for \( N_g = 60 \). Hence, we expect that the interaction between the encapsulated rare gas atom and the fullerene cage becomes repulsive soon with decreasing cage size. Clearly, this gives only a qualitative picture but...
and can therefore be fitted to the following expression:

$$\Delta E(n) = a e^{-bn} - c. \quad (4)$$

with the parameters listed in Table 2.

In all cases, the PBE-D3 reaction energy $\Delta E(n)$ is lower than the PBE energy as dispersion terms are attractive, but increasingly so with increasing cage size when dispersion effects become more important. This results in a substantial difference between the PBE and PBE-D3 reaction energies for the larger cage structures. The difference between the PBE and PBE-D3 reaction energy is smallest for the helium and largest for the argon containing cage, thus correlates with the rare gas atomic dipole polarizabilities, which increases with increasing atom size. The shift toward attraction is reached earlier for the smaller rare gas atoms as expected based on the very same trend in atom sizes. In the case of helium the encapsulation becomes favorable for helium at He@C_{48}, for neon at Ne@C_{52} and for argon at Ar@C_{54} in excellent agreement with the MES estimate discussed above. Note that very large energies are required for the addition of rare-gas atoms into the smallest fullerene cages, which makes the synthesis of such endohedral fullerenes very difficult if not impossible. This can be rationalized based on the large volume expansion observed (see discussion below) and the fact that fullerenes are considered to be rather stiff and incompressible molecules. We mention that the ZPVE corrections should increase with decreasing cage radius as predicted for a confined atom (i.e. particle-in-a-box system), but this is not always the case as the changes in the cage frequencies due to encapsulation can also contribute substantially, especially in the repulsive region (see Tables 4–6). We note that our PBE-D3 value of $-2.4$ kcal/mol for the encapsulation of He into C_{30} is in excellent agreement with the MP2 value of $-2.0$ kcal/mol of Patchkovskii and Thiel. We mention that the ZPVE corrections should increase with decreasing cage radius as predicted for a confined atom (i.e. particle-in-a-box system), but this is not always the case as the changes in the cage frequencies due to encapsulation can also contribute substantially, especially in the repulsive region (see Tables 4–6). We note that our PBE-D3 value of $-2.4$ kcal/mol for the encapsulation of He into C_{30} is in excellent agreement with the MP2 value of $-2.0$ kcal/mol of Patchkovskii and Thiel.

There is a clear correlation between the endohedral encapsulation energy and the size of the atom. Figure 3 shows that for a specific fullerene cage the reaction energy $\Delta E(n)$ also increases exponentially with the size of the rare gas atom up to about C_{50}. This trend is in agreement with previous work by Breslavskaya et al. When attraction starts to dominate, this trend becomes less clear though because of the increase in the static dipole polarizability of the heavier.

### Table 6. Symmetry, electronic state, HOMO–LUMO energy gap $\Delta E_{n}$, (in eV), minimal $r_{max}$, maximal bond lengths $r_{max}$ and maximum nonbonding distance $d_{max}$ between two carbon atoms (in Å) for Ar@C_{20–2n} ($n=0, 2–20$), and reaction energies $\Delta E(n)$ (in kcal/mol) with (PBE-D3) and without (PBE) dispersion correction (not corrected for ZPVE) and ZPVE corrections (in kcal/mol) for the encapsulation of Ar.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>Symmetry</th>
<th>State</th>
<th>$\Delta E_{n}$</th>
<th>$r_{min}$</th>
<th>$r_{max}$</th>
<th>$d_{max}$</th>
<th>$\Delta E_{PBE-D3}(n)$</th>
<th>$\Delta E_{PBE}(n)$</th>
<th>ZPVE</th>
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<tr>
<td>Ar@C_{20}</td>
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<td>1A_{g}</td>
<td>0.617</td>
<td>1.455</td>
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<td>4.413</td>
<td>531.555</td>
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<td>260.715</td>
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<td>-2.319</td>
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<td>1.457</td>
<td>1.549</td>
<td>4.950</td>
<td>199.151</td>
<td>202.436</td>
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The relative change in volume \( \Delta V(n) \) and surface area \( \Delta A(n) \) upon encapsulation of a rare gas atom \( \text{Ng} \) with respect to the number of hexagons \( n \) in the fullerene \( C_{20+2n} \) (in \%). The data points were fitted to exponential functions (see text and eq. (7)).

\[
\Delta V(n) = ae^{-bn} \quad \text{and} \quad \Delta A(n) = ce^{-dn},
\]

with the fit parameters listed in Table 3.

Compared to the empty fullerene cage, the symmetry is lowered upon encapsulation of a rare gas atom, see Tables (4–6). We allowed for possible migration of the rare gas atoms from the center of mass toward the smaller endohedral complexes remains the same. Note that atom encapsulation and change in symmetry results somewhat in a larger change of the HOMO-LUMO gap than that of the empty cage. Interestingly, the minimum bond distance between two carbon atoms stays more or less constant upon rare gas encapsulation compared to the empty cage. The largest values are found for \( \text{Ng}@C_{26} \) and \( \text{Ar}@C_{20} \) and the smallest ones for \( \text{Ng}@C_{46} \).

One might ask if the encapsulation of a closed-shell atom leads to a change of the shape of the fullerene. One measure to quantify a distortion away from a spherical appearance is the isoperimetric quotient \( q_\theta \),

\[
q_\theta = 36\pi \frac{V^2}{A^3} \quad \text{with} \quad q_\theta \in [0, 1],
\]

which for an ideal sphere is \( q_\theta = 1 \). The distortion \( D \) away from spherical symmetry is then simply defined as \( D_{q_\theta} = 1 - q_\theta \). With increasing number of carbon atoms the cage becomes more "spherical" as Figure 5 (upper part) shows. \( C_{20} \) shows a distortion parameter of 24.8% whereas the parameter for \( C_{60} \) is only 9.6%. For \( C_{60} \), all carbon atoms lie on a sphere, but the volume and surface area of the cage are smaller than that of a perfect sphere. Therefore, \( D_{q_\theta} \) is not zero.

On encapsulation of a rare gas atom the distortion parameter is slightly reduced(!), that is the fullerene becomes more spherical than the empty cage for a fixed number of cage atoms. The exception is \( \text{Ar}@C_{20} \) which exhibits a slightly higher distortion parameter of 25.3% than \( C_{20} \) (24.8%). Otherwise for all fullerenes the argon cluster is the most spherical one but the difference in the distortion parameter between the diverse \( \text{Ng}@C_{20+2n} \) clusters vanishes with increasing number of carbon atoms.

Another possibility to measure the distortion from an ideal sphere is by the minimal distance sphere (MDS) criterion (relative to the smallest bond distance \( R_{\text{min}} \)), which is defined as

\[
D_{\text{MDS}} = \min_{\text{Ng}@C_{20+2n}} \frac{1}{N} \sum_{i=1}^{N} \| R_{\text{MDS}} - \| \bar{p}_i - \bar{c}_{\text{MDS}} \| \|
\]

with

\[
R_{\text{MDS}} = \frac{1}{R} \sum_{i=1}^{N} \| \bar{p}_i - \bar{c}_{\text{MDS}} \|
\]

where \( \| \cdot \| \) is the Euclidean norm, \( R_{\text{MDS}} \) is the radius of the minimum distance sphere and \( \bar{c}_{\text{MDS}} \) is its center. Compared to \( D_{q_\theta} \), the
are other definitions for distortion parameters leading to quite different values for the sphericity not considered here.\textsuperscript{[24]}

\section*{Conclusion}

In this systematic study of rare gas encapsulation into C\textsubscript{20} up to C\textsubscript{60}, we showed the importance of dispersion interactions when they start to dominate over repulsive effects. Several of the smaller fullerenes are good candidates for rare gas encapsulation. The repulsive wall starts at cage sizes smaller than He@C\textsubscript{20}, Ne@C\textsubscript{28}, and Ar@C\textsubscript{52}, but above that such fullerenes should be good targets for future syntheses. The energy required for encapsulating rare gas atoms follows a simple exponential decay law with increasing size of the fullerene cage. A similar exponential decay was found for the volume and surface area expansion of the cage upon encapsulation with increasing number of carbon atoms. Fullerenes become generally more spherical upon inclusion of a rare gas atom which was quantified with several indicators.

\section*{Acknowledgments}

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\textbf{Keywords:} fullerenes · rare gas encapsulation · density functional theory · topological aspects

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{distortion.png}
\caption{Distortion parameter D\textsubscript{MDS}, distortion from minimum distance sphere D\textsubscript{MDS} and Fowler asymmetry parameter \( \lambda \text{sym} \) for C\textsubscript{20} with different gases. The asymmetry parameter \( \lambda \text{sym} \) is defined as

\[ \lambda_{\text{sym}} = \sum_{i=1}^{N} \frac{(R_i - R_{av})^2}{R_{av}^2} \]}
\end{figure}

\begin{flushright}
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