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Noble Gas Endohedral Complexes of C_{60} Buckminsterfullerene

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Equilibrium geometries and binding energies (corrected for basis set superposition error) of single and multiple noble gas atom complexes of C_{60} are calculated at DFT and MP2 levels of theory using basis sets including polarization functions. B3LYP and MP2 give similar van der Waals dispersion interactions, predicting repulsive energies for the He and Ne complexes of about 1 kcal/mol, and higher energies for the larger noble gas atom complexes. As expected, C_{60} is resilient to deformation in all cases studied, with the geometry of the fullerene cage barely affected by the presence of multiple noble gas atoms inside.

Introduction

Since the discovery of the hollow buckminsterfullerene,[1] the idea of putting atoms and small molecules inside the relatively large interior of fullerenes has intrigued scientists. Possible uses for endohedral complexes of C_{60} range from the biological[2] to the electrical.[3] Doping the graphite with metals before vaporization[4] forms stable metallofullerenes,[5] with one[6] or more[7,8] metal atoms inside the fullerene. Methods of incorporation of noble gas atoms into intact fullerenes include molecular beams[9] and high-pressure, high-temperature conditions.[10] Multiple noble gas atom complexes have been created using the former.[9] Using the latter, complexes of He, Ne, Ar, Kr, and Xe of C_{60} have been created, with a yield of about one per thousand.[12] Advances in the technology may possibly lead to higher yields of incorporation forming complexes with multiple noble gas atoms inside C_{60}. The notation $X_n@C_{60}$ is used here to denote noble gas atoms inside buckminsterfullerene.

$He@C_{60}$ has been found to be stable with respect to chemical manipulation of the outside of the fullerene and subsequent NMR analysis.[13] Experimental studies of high-temperature decomposition of fullerenes with noble gas atoms inside have determined that the activation barrier for the release of noble gas atoms from C_{60} to be about 90 kcal/mol.[14] It has been proposed that a window mechanism is responsible for the passage of noble gas atoms in and out of fullerenes.[15] There have been chemically opened C_{60} windows,[16,17] to possibly facilitate the incorporation of atoms and small molecules. Theoretical studies on windows[18] and on the passage of He through windows[19] have also been performed, but at this time, however, theory predicts more than twice the activation barrier determined experimentally.[20] In this work, we present optimized geometries and high-accuracy energy calculations of single and multiple noble gas atom complexes of C_{60}, probing the effects and quantitatively assessing the interactions between these trapped atoms and the fullerene cage encasing them.

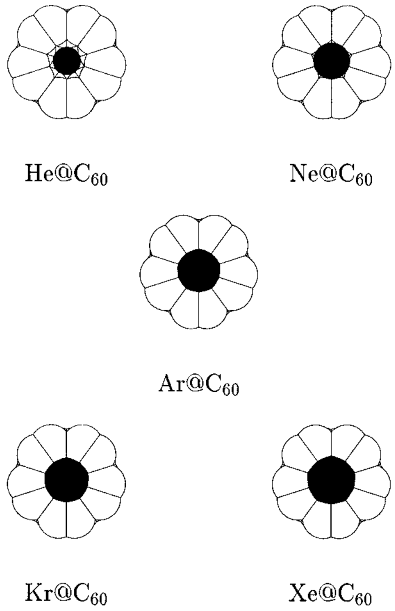

Figure 1. van der Waals[30] based space filling diagram of $X@C_{60}$ (X = He, Ne, Ar, Kr, and Xe; C_{60} cavity[29] = 1.71 Å).

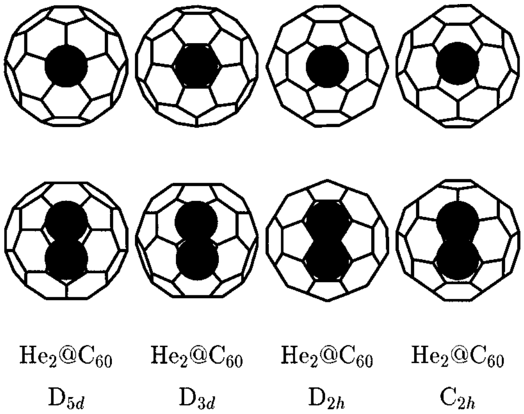

Figure 2. Two views of four isomers of $He_2@C_{60}$ (D_{5d}, D_{3d}, D_{2d}, and D_{2h} symmetries).

Computational Details

Single noble gas atom complexes are considered to have icosahedral symmetry and are depicted in Figure 1. He and Ne atoms fit inside their carbon cages without overlap of van der Waals radii, while for the larger noble gas atoms, some overlap occurs. The four isomers of the $He_2@C_{60}$ and the $He_3@C_{60}$ complexes and the $He_4@C_{60}$ complex studied in this work are shown in Figures 2 and 3. For the two noble gas atom endohedral complexes, we chose to study a D_{5d} isomer (with the noble gas atoms aligned on the principal axis intersecting two pentagons), a D_{3d} isomer (with the principle axis intersecting two hexagons), and a C_{2h} and D_{2h} isomers (with principal axis intersecting the two symmetry distinct 6−6 and

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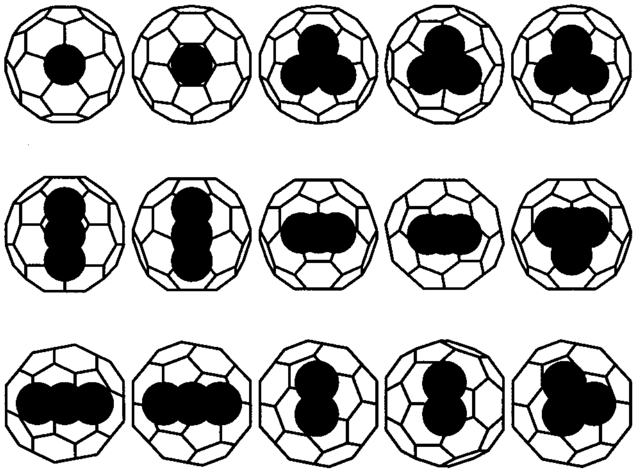

$He_3@C_{60}$ D_{5d} $He_3@C_{60}$ D_{3d} $He_3@C_{60}$ C_{3v} $He_3@C_{60}$ D_3 $He_4@C_{60}$ C_{3v}

Figure 3. Three views of four isomers of $He_3@C_{60}$ (D_{5d}, D_{3d}, C_{3v}, and D_3 symmetries) and $He_4@C_{60}$ (C_{3v} symmetry).

TABLE 1: $X@C_{60}$ (X = He, Ne, Ar, Kr, and Xe) Optimized Radii and Bond Lengths (Å)

	system	C_{60} radius	6−6 bond	5−6 bond
3−21G/LSDA	C_{60}	3.538	1.389	1.450
	$He@C_{60}$	3.537	1.388	1.450
	$Ne@C_{60}$	3.537	1.388	1.449
	$Ar@C_{60}$	3.536	1.388	1.449
	$Kr@C_{60}$	3.537	1.388	1.449
	$Xe@C_{60}$	3.538	1.389	1.450
6-31G**/LSDA	C_{60}	3.529	1.392	1.442
	$He@C_{60}$	3.529	1.392	1.442
	$Ne@C_{60}$	3.528	1.392	1.441
	$Ar@C_{60}$	3.529	1.392	1.442
	$Kr@C_{60}$	3.528	1.392	1.442
3-21G/B3LYP	C_{60}	3.555	1.391	1.459
	$He@C_{60}$	3.555	1.391	1.459
	$Ne@C_{60}$	3.554	1.390	1.459
	$Ar@C_{60}$	3.556	1.391	1.459
	$Kr@C_{60}$	3.557	1.391	1.460
	$Xe@C_{60}$	3.559	1.392	1.461
6-31G**/B3LYP	C_{60}	3.550	1.395	1.453
	$He@C_{60}$	3.550	1.395	1.453
	$Ne@C_{60}$	3.549	1.395	1.453
	$Ar@C_{60}$	3.551	1.396	1.454
	$Kr@C_{60}$	3.551	1.396	1.454

TABLE 2: 3-21G/LSDA $X_n@C_{60}$ (X_n = He_2, Ne_2, He_3, and He_4) Optimized Radii (Å)

	av C_{60} radius	min C_{60} radius	max C_{60} radius
C_{60} (I_h)	3.538		
$He_2@C_{60}$ (D_{5d})	3.537	3.536	3.543
$He_2@C_{60}$ (D_{3d})	3.538	3.535	3.541
$He_2@C_{60}$ (D_{2h})	3.537	3.535	3.546
$He_2@C_{60}$ (C_{2h})	3.538	3.535	3.545
$Ne_2@C_{60}$ (D_{5d})	3.537	3.534	3.550
$Ne_2@C_{60}$ (D_{3d})	3.537	3.533	3.546
$He_3@C_{60}$ (D_{5d})	3.541	3.524	3.594
$He_3@C_{60}$ (D_{3d})	3.542	3.522	3.585
$He_3@C_{60}$ (C_{3v})	3.538	3.534	3.553
$He_3@C_{60}$ (D_3)	3.538	3.533	3.552
$He_4@C_{60}$ (C_{3v})	3.538	3.531	3.557

5−6 bonds between two hexagons, and a hexagon and a pentagon, respectively.) $He_3@C_{60}$ complexes considered in this work have linear noble gas atom arrangements with D_{5d} and D_{3d} symmetries, as well as more realistic planar orientations with C_{3v} and D_3 symmetries. The $He_4@C_{60}$ complex investigated here has C_{3v} symmetry. These particular choices of $X_n@C_{60}$ complexes are certainly not exhaustive but deem representative of their respective classes.

DFT methods have been shown to predict bond lengths to a few thousandths of an angstrom[21] and energies to a few kcal/mol.[22] In this paper, icosahedral complex geometries are optimized at the local spin density approximation (LSDA)[23] and Becke's three-parameter exchange with Lee, Yang, and Parr's correlation (B3LYP) hybrid functional[24] levels of theory, with 3-21G and 6-31G** basis sets, except for $Xe@C_{60}$ calculations, where no 6-31G** basis is available. Second-order Moller−Plesset perturbation (MP2)[25] single-point energy calculations are also performed on these geometries. Multiple noble gas atom complex geometries are optimized at the 3-21G/LSDA level of theory and followed by 3-21G/B3LYP single-point energy calculations. A representative set of molecules including all the icosahedral complexes except $Xe@C_{60}$, the D_{5d} symmetry $He_2@C_{60}$ isomer, the planar D_3 $He_3@C_{60}$ complex, and $He_4@C_{60}$ are chosen for calculations at the 6-311G**/B3LYP//3-21G/B3LYP level of theory.

In this paper, a negative binding energy (BE, the energy of the products minus the energy of the reactants) represents an exothermic reaction. BE overestimation because of basis set superposition error (BSSE) is obtained in this study using the counterpoise method.[26] The corrected binding energy (CBE) is the BSSE subtracted from the BE. We also refer to the energy difference between the C_{60} in the $X_n@C_{60}$ geometry configuration of the complex and the C_{60} at equilibrium as C_{60} "strain."

All calculations in this study were carried out using a developmental version of the GAUSSIAN suite of programs.[27] Density functional theory (DFT) applications entail a new weight scheme that has been shown to significantly decrease CPU time.[28] GAUSSIAN DFT methods, by default, use a pruned 75 × 302 (radial × angular) grid that neglects points based on an atomic distance threshold. We found this grid to be too sparse for the high-symmetry molecules studied here. Icosahedral geometries, with the default grids, are not predicted to be the lowest energy isomer of single noble gas atom complexes. These problems are eliminated in calculations using the larger 75 × 590 point grid, which is utilized throughout this study with DFT methods.

Results

Optimized icosahedral $X@C_{60}$ (X = He, Ne, Ar, Kr, and Xe) radii and the two symmetry distinct cage bond lengths are presented in Table 1. The experimentally determined C_{60} radius[29] is best reproduced at the 3-21G/B3LYP level of theory. Differences in radii between levels of theory and basis set, however, are less than 0.03 Å. As the size of the noble gas atom inside the fullerene increases, the radius of the complex first slightly decreases, and then increases, around the point van der Waals radii begin to overlap. Within level of theory and basis set, radii, and bond lengths are very similar to that of buckminsterfullerene at equilibrium, with differences in radii at most 0.003 Å.

Optimized geometries of the multiple noble gas atom complexes are listed in Table 2. All average radii are within 0.001 Å of each other and buckminsterfullerene at equilibrium, excluding the linear $He_3@C_{60}$ complexes, which have distortions smaller than 0.005 Å. However, maximum and minimum radii of the complexes, compared to the radius of optimized C_{60}, display an unequal distortion of the fullerene. There is an increase of the radius associated with the carbon atoms closest to the axis or plane of the noble gas atoms, while the radii of the carbons located perpendicular to the axis or plane are decreased. The maximum radius of the fullerene is smaller

TABLE 3: X@C_{60} (X = He, Ne, Ar, Kr, and Xe) Binding Energies (kcal/mol)

	He@C_{60}	Ne@C_{60}	Ar@C_{60}	Kr@C_{60}	Xe@C_{60}
3-21G/LSDA//3-21G/LSDA	−1.1	−2.6	−16.6	−18.3	−21.1
6-31G**/LSDA/3-21G/LSDA	−2.1	−5.9	−11.3	−24.6	
6-31G**/LSDA//6-31G**/LSDA	−2.1	−5.9	−11.1	−24.6	
3-21G/B3LYP//3-21G/LSDA	0.8	−1.2	3.7	8.6	20.8
6-31G**/B3LYP//3-21G/LSDA	0.9	−2.3	6.9	1.8	
6-31G**/B3LYP//6-31G**/B3LYP	0.6	−2.6	6.0	1.1	
3-21G/MP2//3-21G/B3LYP	0.1	−0.7	3.9	10.5	25.0
6-31G**/MP2//3-21G/B3LYP	0.2	−1.2	7.5	4.8	
6-31G**/MP2//6-31G**/B3LYP	0.1	−1.0	8.0	4.7	

TABLE 4: X@C_{60} (X = He, Ne, Ar, Kr, and Xe) BSSE Corrected Binding Energies (kcal/mol)

	He@C_{60}	Ne@C_{60}	Ar@C_6	Kr@C_{60}	Xe@C_{60}
3-21G/LSDA//3-21G/LSDA	−0.3	0.0	−10.6	−8.6	−9.2
6-31G**/LSDA/3-21G/LSDA	−1.3	−2.2	−9.0	−10.1	
6-31G**/LSDA//6-31G**/LSDA	−1.3	−2.2	−8.8	−10.0	
3-21G/B3LYP//3-21G/B3LYP	1.3	1.0	8.7	17.5	31.3
6-31G**/B3LYP//3-21G/B3LYP	1.2	0.7	8.2	14.8	
6-31G**/B3LYP//6-31G**/B3LYP[a]	1.4	0.9	8.4	15.0	
3-21G/MP2//3-21G/B3LYP	0.6	1.1	8.3	18.7	36.3
6-31G**/MP2//3-21G/B3LYP	0.6	1.1	8.7	17.2	
6-31G**/MP2//6-31G**/B3LYP[c]	0.6	1.3	9.2	17.1	

[a] Corrected.

TABLE 5: X@C_{60} (X = He, Ne, Ar, Kr, and Xe) C_{60} Strains (kcal/mol)

	He@C_{60}	Ne@C_{60}	Ar@C_{60}	Kr@C_{60}	Xe@C_{60}
3-21G/LSDA//3-21G/LSDA	0.0	0.0	0.0	0.0	0.0
6-31G**/B3LYP//3-21G/LSDA	0.1	0.3	0.5	0.4	0.1
3-21G/B3LYP//3-21G/B3LYP	0.0	0.0	0.0	0.0	0.1

when the noble gas atoms face open rings, rather than facing carbon−carbon bonds because of the increased noble gas−carbon atom repulsion in the latter case. Also, the maximum radius is larger for complexes with noble gas atoms facing pentagons than for those facing hexagons on the surface of the fullerene. Linear He_3@C_{60} complexes are the most distorted of all the systems studied.

The icosahedral complex BEs listed in Table 3 show very little dependence on geometry. LSDA predicts that as the size of the noble gas atom inside C_{60} increases, the complex becomes more stable. B3LYP and MP2 predict more realistic repulsive energies, except for the Ne@C_{60} complex. CBEs are presented in Table 4. LSDA still overbinds, but to a lesser extent than without the BSSE correction. B3LYP and MP2 CBEs are very much in agreement, regardless of basis set used. Most importantly, Ne@C_{60} is no longer bound, and the trend of increased destabilization with larger noble gas atoms is observed, except for the B3LYP prediction that Ne@C_{60} is more stable than He@C_{60}. C_{60} strain of the icosahedral complexes studied here is presented in Table 5. Only at the 3-21G/B3LYP//3-21G/LSDA level of theory does the geometry deformation create a noticeable energetic strain on the fullerene. In almost all of the other cases, the C_{60} strain is less than 0.05 kcal/mol.

CBEs and C_{60} strains of the multiple noble gas atom complexes are presented in Table 6. The lowest energy isomer of the He_2 @C_{60} complex is C_{2h}, rather than D_{3d}, which has the least distortion. BSSE is very large in the case of the Ne_2@C_{60} complexes. Linear He_3@C_{60} isomers are more unstable than the planar isomers by almost a factor of 3. He_4@C_{60} has the largest CBE of all the complexes studied. C_{60} strain of the multiple noble gas atom complexes is a very small contribution to the total energy. Only in the unrealistic case of linear He_3@C_{60} is the C_{60} strain over 1 kcal/mol. In all other cases of multiple noble gas atom complexes examined, the strain due to the deformation of C_{60} is 0.5 kcal/mol or less.

CBEs of the representative set of molecules calculated with the 6-311G** basis set are listed in Table 7. BSSEs are reduced on the average by almost 60%. CBEs are within 1 kcal/mol of the CBEs calculated with the smaller basis sets, so BSSE consideration is crucial to calculate accurate BEs for these systems, regardless of basis set size, at least up to 6-311G**. The binding energy of the He_2@C_{60} complex is predicted to be similar to that of Ar@C_{60}. Noble gas atom complex configurations display C_{60} strains less than 1 kcal/mol, even for the He_4@C_{60} complex.

TABLE 6: 3-21G/B3LYP//3-21G/LSDA X_n@C_{60} (X_n = He_2, Ne_2, He_3, and He_4) BSSE Corrected BEs and C_{60} Strains (kcal/mol)

	corr BE	C_{60} strain		corr BE	C_{60} strain
He_2@C_{60} (D_{5d})	8.6	0.3	He_3@C_{60} (D_{5d})	47.1	1.4
He_2@C_{60} (D_{3d})	8.5	0.2	He_3@C_{60} (D_{3d})	45.6	1.1
He_2@C_{60} (D_{2h})	8.5	0.3	He_3@C_{60} (C_{3v})	17.4	0.2
He_2@C_{60} (C_{2h})	8.4	0.2	He_3@C_{60} (D_3)	17.4	0.3
Ne_2@C_{60} (D_{5d})	27.0	0.5	He_4@C_{60} (C_{3v})	28.3	0.2
Ne_2@C_{60} (D_{3d})	27.0	0.5			

TABLE 7: 6-311G/B3LYP//3-21G/B3LYP X_n@C_{60} BSSE Corrected BEs**

	corr BE		corr BE
He@C_{60} (I_h)	1.3	He_2@C_{60} (D_{5d})	7.2
Ne@C_{60} (I_h)	1.1	Ne_2@C_{60} (D_{5d})	24.8
Ar@C_{60} (I_h)	7.2	He_3@C_{60} (D_3)	17.0
Kr@C_{60} (I_h)	13.8	He_4@C_{60} (C_{3v})	29.1

Conclusions

High-level density functional and perturbation theory calculations are performed on several noble gas atom complexes with C_{60}. Fully optimized radii of the icosahedral complexes, and the average radii of the multiple noble gas atom complexes differ from that of C_{60} at equilibrium by only a few thousandths of an angstrom. The B3LYP and MP2 interaction energies for the smaller noble gas atom complexes of He and Ne are consistently predicted by both methods to be slightly repulsive, about 1 kcal/mol. It is interesting to note that B3LYP and MP2 predictions are very similar for the problem under consideration. These energies are much more repulsive for the other noble gas atom complexes, around 7 and 14 kcal/mol for Ar@C_{60} and Kr@C_{60}, and from 7 to 30 kcal/mol for the He_2@C_{60} and He_4@C_{60} complexes. As expected, C_{60} is resilient to deformation in all cases studied, with strains of the fullerene in the geometry of the complex less than 0.5 kcal/mol for the single noble gas atom complexes and less than 1 kcal/mol for all multiple noble gas atom complexes studied with realistic geometries.

Recent studies of the equilibrium constants for noble gas fullerene compounds[20,32] together with the results obtained in this paper indicate that there is appreciable disagreement between experiment and theory. The highly repulsive noble gas C_{60} interactions predicted for Ar and Kr in this paper are not compatible with experiments yielding macroscopic amounts of the endohedral compounds. Evidently, further theoretical and experimental work is needed to settle these interesting questions.

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