Spatial quenching of a molecular charge-transfer process in a quantum fluid: The Cs\textsubscript{x} - C\textsubscript{60} reaction in superfluid helium nanodroplets

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The first section of this Supporting Material contains a table with parameters of our PPM model. Section 2 presents one table and three figures regarding the MCSCF+ D\textsubscript{as} calculations on neutral fragments, extending the appendix of the main manuscript. Section 3 contains density plots for shorter and larger distances than what is shown in the main manuscript. Section 4 compares the CDFT results of various functionals for the charge-neutral interaction of the triplet Cs\textsubscript{2} dimer with a C\textsubscript{60} fullerene.
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References
1 Pairwise Potential Model for the He-C\textsubscript{60} Interaction

Table 1: Parameters defining the dispersionless and dispersion contributions to the He/C\textsubscript{60} interaction energy using the pairwise additive potential model proposed in this work.

<table>
<thead>
<tr>
<th>( R_c / \text{\AA} )</th>
<th>( A / \text{eV} )</th>
<th>( \alpha / \text{\AA}^{-1} )</th>
<th>( \beta / \text{\AA}^{-2} )</th>
<th>( \gamma_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.0</td>
<td>1191.268</td>
<td>4.182</td>
<td>-0.110</td>
<td>-0.83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( C_6^X / \text{eV}\cdot\text{\AA}^6 )</th>
<th>( C_8^X / \text{eV}\cdot\text{\AA}^8 )</th>
<th>( \beta^X / \text{\AA}^{-1} )</th>
<th>( \gamma_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X=\text{C} )</td>
<td>9.897</td>
<td>1975.2</td>
<td>3.487</td>
</tr>
<tr>
<td>( X=\text{He} )</td>
<td>0.678</td>
<td>0.266</td>
<td>4.763</td>
</tr>
</tbody>
</table>

As mentioned in the appendix of the main manuscript, a pairwise potential model (PPM) has been developed to fit ab-initio interaction energies for the He-C\textsubscript{60} interaction. Table 1 lists the PPM parameters while Figure 1 plots the PPM total and dispersion energies as a function of the distance from the He atom to the C\textsubscript{60} mass center, comparing them with those obtained at DFT-SAPT level by Hesselmann and Korona.\textsuperscript{1} Notice that the PPM reproduces both total and dispersion He/C\textsubscript{60} interaction energies rather accurately.

2 Dispersion-corrected MCSCF calculations of Neutral States

As mentioned in the appendix of the main manuscript, state-average (two-state) MCSCF calculations have been performed to describe the van-der-Waals neutral Cs-C\textsubscript{60} and Cs\textsubscript{2}-C\textsubscript{60} interactions, with the latter in the electronic triplet and singlet states. The Cs and Cs\textsubscript{2} species were located along the C\textsubscript{3} axis of fullerene, with the Cs–Cs axis oriented perpendicularly to the C\textsubscript{3} axis. For Cs we used the same basis set as in the B97M-V calculations (see Section 2.1 of the main manuscript) but employed the polarized correlation-consistent double-\( \zeta \) basis sets of Dunning and collaborators\textsuperscript{2} for carbon atoms. To define the MCSCF active space we
considered the $5s$ orbitals from the Cs and Cs$_2$ species along with frontier $\pi$-type molecular orbitals of the C$_{60}$ fragment. Although the active space was rather restrictive, it allowed us to obtain the two states correlating asymptotically to Cs$_x$+C$_{60}$ and Cs$_x^+$+C$_{60}^-$ fragments at the long-range potential region. It was tested that the wave-function of the state correlating to neutral Cs$_x$/C$_{60}$ fragments is strongly dominated by a single reference configuration.

For the Cs$_2$(triplet)-C$_{60}$ complex, Figure 2 shows the two MCSCF potential energy curves as a function of the distance, denoted $R$, between the Cs$_2$ and fullerene mass centers. Note that the two states in this figure have radically different character. The ground state describes the strong Coulomb interaction between a negatively charged fullerene and a positively charged cesium dimer. In contrast, the excited state corresponds to the interaction of a neutral Cs$_2$ with a fullerene (physisorption) and correlates asymptotically to Cs$_2$+C$_{60}$. In the long-range region (i.e. at distances larger than about 7 Å), our Mulliken population analysis showed that the Cs$_2$ monomer is kept neutral in the state correlating to Cs$_2$+C$_{60}$. 

Figure 1: He/C$_{60}$ total (left panel) and dispersion (right panel) interaction energies as a function of the distance from the He atom to the C$_{60}$ mass center, as obtained with the DFT-SAPT approach by Hesselmann and Korona$^1$ and our pairwise potential model. The He atom is located along the C$_3$ symmetry axis of fullerene.
At distances shorter than about 7 Å, however, the excited state was identified with an excited charge-transfer state via redistribution of the electronic charge localized in the fullerene fragment. Hence, the neutral Cs$_{2}$ + C$_{60}$ potential energy curve was extrapolated at the potential wall region by fitting to an exponential function. From Figure 2 it can be seen that the crossing between ionic and neutral potential energy curves at MCSCF level takes place at long distances (ca. 8 Å), as it is typically found for interactions governed by the harpoon mechanism.\textsuperscript{3} Moreover, preliminary calculations adding dynamical correlation energy contributions to the MCSCF interaction energies show that the crossing region moves to intermolecular distances even larger (ca. 10.5 Å).

![Figure 2: Cs$_2$(triplet)-C$_{60}$ interaction energies as a function of the distance between the corresponding mass centers along the C$_3$ symmetry axis, obtained with the MCSCF method. The Cs$_2$ molecule is oriented perpendicularly to the C$_3$ symmetry axis of fullerene.](image)
An obvious flaw of the MCSCF approach is the lack of dynamical correlation. To include these contributions (see also appendix of the main manuscript) we performed CCSD(T) calculations for the Cs/C₆H₆ and Cs₂(triplet,singlet)/C₆H₆ complexes. In the next step, the correlation CCSD(T) energies were fitted to the effective interatomic pairwise Dₐs functional. Figure 3 compares the calculated CCSD(T) correlation energies with those fitted via the functional Dₐs. The root-mean-square errors of these fits were below 1 meV and 0.1 meV for the Cs₂(triplet)/benzene and Cs/benzene complexes, respectively. In contrast with the original Dₐs approach, where the parameters were fitted for a given training set of molecules, we tune the Dₐs function for the considered system (fullerene) using a small representative cluster (benzene). This procedure has been validated for the adsorption of noble-gas and metal atoms on carbon-based substrates. Finally, the functional Dₐs was used to estimate the dispersion Cs-C₆₀ and Cs₂-C₆₀ energies. As can be seen in Figure 2, the van der Waals Cs₂(triplet)-C₆₀ interaction potential becomes attractive when the long-range dispersion correction is taken into consideration. As an additional test, preliminary calculations were carried out by adding dynamical correlation contributions to the MCSCF interaction energies via multi-state second-order multi-reference perturbation theory (MS-CASPT2), as implemented in the MOLPRO program. These two-state MS-CASPT2 calculations were carried out for the Cs₂(singlet)-C₆₀ complex and the same multi-configurational space as in the precedent MCSCF computations: MCSCF+Dₐs and MS-CASPT2 potential energy curves for the neutral Cs₂-C₆₀ complex agreed very well to each other, with energy differences below 7% at the well region. However, further SAPT-DFT calculations for the Cs₂-C₆₀ complex indicated that both our MCSCF+Dₐs and MS-CASPT2 procedures might underestimate the attractive van-der-Waals-type interaction (e.g., by a factor of 1.4 at a distance of 12 Å).
Figure 3: Cs/C₆H₆ and Cs₂(triplet)/C₆H₆ interaction energies as functions of the distance between the corresponding mass centers along the C₆ symmetry axis, as obtained with the CCSD(T) method and the parametrization of the Dₐₕ functional. The Cs₂ molecule is oriented perpendicularly to the C₆ symmetry axis.
3 Additional He-DFT contour plots

Figure 4: Contour plots of the helium density for a distance of 10 Å between the fullerene and (a) a single Cs atom, (b) the triplet Cs$_2$ dimer in collinear configuration, (c) the triplet Cs$_2$ dimer in T-shaped (c) configuration. The density is plotted in units of Å$^{-3}$. Note that the bulk value for the density of liquid helium is 0.02185 atoms per Å$^3$.

Figure 5: Contour plots of the helium density for a distance of 30 Å between the fullerene and (a) a single Cs atom, (b) the triplet Cs$_2$ dimer in collinear configuration, (c) the triplet Cs$_2$ dimer in T-shaped (c) configuration. The density is plotted in units of Å$^{-3}$. Note that the bulk value for the density of liquid helium is 0.02185 atoms per Å$^3$. 
4 CDFT results for triplet Cs$_2$ with various functionals

Figure 6: Interaction of a fullerene with a triplet Cs$_2$ dimer in T-shaped configuration, calculated with three different functionals.

References


