Helium Accepts Back-Donation In Highly Polar Complexes: New Insights into the Weak Chemical Bond

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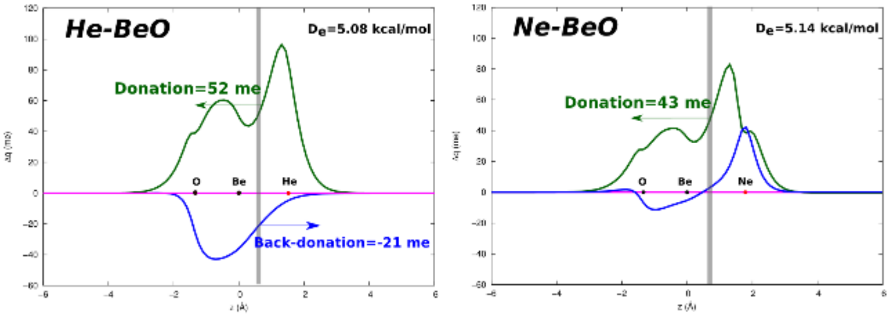
ABSTRACT: We studied the puzzling stability and short distances predicted by theory for helium adducts with some highly polar molecules, such as BeO or AuF. On the basis of high-level quantum-chemical calculations, we carried out a detailed analysis of the charge displacement occurring upon adduct formation. For the first time we have unambiguously ascertained that helium is able not only to donate electron density, but also, unexpectedly, to accept electron density in the formation of weakly bound adducts with highly polar substrates. The presence of a large dipole moment induces a large electric field at He, which lowers its *2p* orbital energy and enables receipt of π electron density. These findings offer unprecedented important clues towards the design and synthesis of stable helium compounds.

TOC GRAPHICS



KEYWORDS back-donation - bond theory - charge transfer - helium complexes - quantum chemistry

Helium, the most abundant element in the universe besides hydrogen, is unique among the noble gases (Ngs),[1-8] in that no neutral compounds involving it are experimentally known except a very recently reported Na_2He adduct, synthesized under high-pressure conditions.[9, 10] There is, therefore, a very long-standing and keen interest among chemists in taming helium's proverbial inertia.[7, 11-21] It is universally accepted that the Ngs bind predominantly through dispersion and induction, with a small charge-transfer (CT) component in the case of the heavier Ngs. Therefore, suitable candidates for the formation of energetically stable neutral complexes with Ngs are highly polar molecules.[19, 22] Beryllium oxide, with a permanent dipole moment of 7.5 D,[23] is a fitting example and, indeed, BeO adducts with the heavier Ngs, Ar, Kr and Xe, are long known.

There is here, however, a well-known, surprising anomaly regarding helium, which was the main motivation of the present work and wherein - as we have discovered - lies the key to helium chemistry. Because induction is the largely prevailing component of the bond, bond strength is expected to increase with Ng atomic number and polarizability.[15, 17, 24] This is indeed the case in a wide range of known examples in very different energy regimes, from weakly bound van der Waals complexes[25] (interaction energy of the order of a few meV) to Ng adducts with alkali and alkaline-earth cations[26] (10-20 kcal/mol). In this respect, helium, with a covalent radius of only 0.46 Å,[27] a very high ionization potential (24.6 eV), a vanishing electron affinity and a polarizability of 0.204 $Å^3$,[28] is universally regarded as a tiny hard ball, with a spherical, tightly contracted and inert electron cloud. But, in striking contrast with this picture, not only an unexpectedly large binding energy was predicted for the He-BeO complex already by early, pioneering theoretical work,[13] but recent, very accurate *ab initio* calculations have confirmed that helium should bind BeO even more strongly than neon (5.1 vs 4.9 kcal/mol, respectively),[7] despite the latter having nearly twice the polarizability. Remarkably, too, helium penetrates much nearer the Be atom than would be expected from the general Ng trend (see Figure S1 in the Supporting Information, SI). It is further puzzling that cationic adducts such as Ng-Li^+ or Ng-Be^{2+} show the expected (polarizability-based) stability trend (see Figure S2 in SI), while the anomalous inversion between He and Ne adduct stability is again encountered for other Be-containing substrates, such as BeNH and $BeCN_2$,[15] and even more pronounced in systems with strong electron acceptors, such as metal halides MX (M = Cu, Ag, Au; X = F, Cl).[29,16] In particular, the He complex with AuF is computed to be more stable than the Ne one by as much as 4 kcal/mol and the He-metal distance is as much as 0.5-0.6 Å shorter than the Ne-metal one. [16]

It thus appears that helium's binding mode cannot be described solely by the induction component as expected from the atomic properties. On the basis of our experience in the study of weakly-bound systems,[30, 31] also specifically involving Ng species,[25, 29, 32-34] we surmise that an additional CT component plays a role in the bond. To investigate this, we study the so-called charge-displacement (CD) function,[29] a well-established approach that permits in a simple yet powerful way to assess and quantify the electron displacement occurring upon formation of the Ng-X bond. We recall that the CD function, $\Delta q(z)$, gives, at each point z along an axis joining two interacting fragments, the in principle exact electronic charge that, upon formation of the complex, has been displaced from right to left across the plane perpendicular to the axis through z (see SI for details).

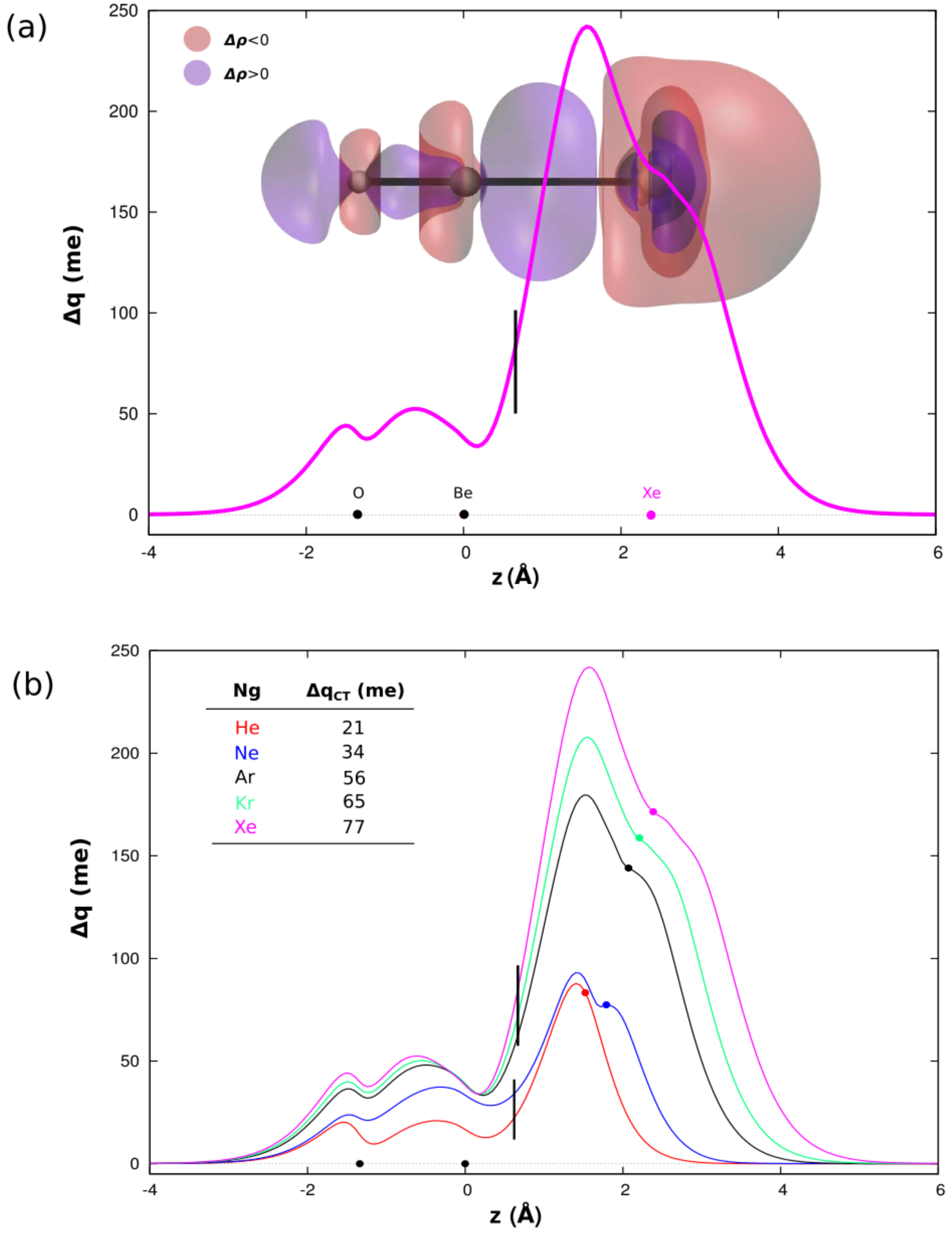


Figure 1. CD curves of a) Xe-BeO b) Ng-BeO aggregates. The dots on the dashed line represent the z coordinate of the nuclei. The vertical solid lines identify the isodensity boundary. The background in a) shows the 3D isodensity plot of the electron density change for the Xe-BeO

complex formation ($\Delta\rho = \pm 8 \times 10^{-5}$ me/bohor^3, negative / positive values in light red / light violet).

The results of the CD analysis of the Ng-BeO adducts are reported in Figure 1. Panel a) displays, for a more detailed illustration, the CD curve for the Xe-BeO complex, with, in the background, the 3D contour plot of the electron density difference between the complex and the non-interacting fragments. This plot shows that the Xe electron cloud is strongly polarized by the electric dipole of BeO, with Xe undergoing a charge depletion / accumulation in the region opposite / towards BeO. A certain amount of charge rearrangement is also present on BeO itself, with electron loss taking place at both atomic sites and accumulation in the internuclear region and on the left side of O. A similar picture attains for the other Ngs – see Figures 1b) and S3 in the SI. Remarkably, Δq is positive everywhere in the molecular region for all complexes, proving that, everywhere along the internuclear axis, and in particular in the region between Ng and Be, there is a net shift of charge in the direction from Ng towards BeO. Therefore we may safely assume that a non-negligible CT component, indicative of some degree of covalency, is present in the interaction. This feature has been previously ascertained for complexes of Ar, Kr, and Xe [25, 29, 32, 33] and for He and Ne adducts with CCl_4.[32] The rough bell shape of the CD function around the Ng site is representative of, and usefully quantifies, the Ng polarization mentioned above.

The CD curves have a steep negative slope at the Ng site, indicating a pronounced electron depletion. Note further that the CD function of all systems, except that of helium which has only *s* electrons, exhibits a shoulder feature very close to the Ng position, originating from the different contribution of the *s* and *p* filled shells, which generates an asymmetry in the polarization along *z*. The CD curves nicely visualize the expected decrease in the extent of the charge displacement/polarization on going from the heavier to the lighter atoms. In fact, a correlation might be expected between the amplitude of the CD function and the atomic polarizability, and this is indeed roughly the case, again with the remarkable exception of the He complex: despite helium having about half the polarizability of Ne, the CD curves of their adducts are quite similar both in the position and value of their maximum (87 vs 93 me). At the Ng position, the CD function for He-BeO (84 me) is even larger that of Ne-BeO (77 me). This may again be related to He ability to get appreciably closer to Be than expected, with consequent enhanced induction.

A reasonable estimate of the CT between Ng and BeO occurring upon formation of the complex can be obtained from the value of the CD function at a specific point between the fragments. As amply discussed in previous work,[29, 35] a plausible choice, especially in case of small weakly interacting system, is the “isodensity boundary”, i.e. the point on *z* axis where the electron densities of the non-interacting fragments become equal. The top left inset in Figure 1 b) reports the Δq values across this boundary (Δq_{CT}), ranging from 21 me (He) to 77 me (Xe). Although such undisputable net CT component is present in all the Ng-BeO bonds, we see that it increases, perhaps not surprisingly, with the atomic number. Therefore, the puzzling enhanced stability of the helium complex compared to the others still eludes an explanation in these simple terms. Note that, in the Ne-Xe series, the estimated CT correlates linearly almost perfectly with the Ng-BeO bond length, while the helium data deviate again somewhat, with a bond length detectably smaller than would be expected (see Figure S1 in SI).

In order to seek further for an explanation, we proceeded to examine the different symmetry (C_{2v} subgroup) components of the CD function, as is done for example in coordination chemistry to isolate the donation and back-donation components of the bond[35, 36] (see the SI for additional details). Of course, the present situation of a weak interaction is substantially different from coordination bonds, but the decomposition of the CD function may nonetheless reveal contributions of different nature to the density displacement. Let us first consider the He-BeO complex. As clearly depicted in Figure 2(a), the symmetry decomposition of the CD function shows that the global CT from He to BeO emerges from the sum of a positive, larger A_1 component and two negative, smaller B_1 and B_2 components. The CD curve for the A_1 symmetry, similar to the total CD discussed earlier, is everywhere positive, describing a net displacement of electrons from He towards BeO (donation component). Quite surprisingly, the CD curves for the B_1 and B_2 symmetries (identical in the present case), which correlate with filled π_x and π_y molecular orbitals of BeO and the empty p_x or p_y atomic orbitals of He, are evidently negative in the bond region and describe a charge flux in the opposite direction, that is from BeO to He. There is a large polarization of the BeO π density towards He, which actually reaches far into the inter-fragment region and even beyond the He site, thus revealing the presence of a back-donation component. Since donation is everywhere larger than back-donation, they add up to the net positive CD curve and net donation we have discussed earlier. At the isodensity boundary, the net CT of nearly 30 me emerges from a donation component of 52 me and a back-donation of 21 me, divided in two identical B_1 and B_2 terms. The 3D contour plots of the symmetry components of the density deformation, shown in the insets of Figure 2(a), provide an alternative view of this picture, evidencing the unsuspected B_1 and B_2 density accumulation (light violet) in the He-Be internuclear region and the density depletion (light red) at the O atom. It thus emerges from the present analysis that the He-BeO bond is characterized not only by a CT component from He towards the strongly dipolar BeO molecule, but also by an opposite and quite large back-donation component, which contributes to bringing He closer to the interacting partner and tightening the bond. Given the obvious relevance of this finding, we also examined its dependence on the spatial partitioning separating the fragments and repeated the density difference integration over the volumes defined by the zero-flux surfaces of the Quantum Theory of Atoms in Molecule.[37] The resulting CT values are entirely comparable (see Figure S7 and the discussion in the SI).

By striking contrast, and consistently with the stability and bond length trend we seek to understand, we see from Figure 2(b) that the back-donation component is entirely absent in Ne-BeO: the B_1 and B_2 components of the CD function vanish in the Ne-Be bond region and, in fact, become positive and reinforce the electron cloud polarization at the Ne atom. We also computed the C_{2v} symmetry components of the CD function at different distances between the He/Ne and BeO fragments, finding the same qualitative trend as at the equilibrium geometry (see Figures S18-S20 in SI). A similar picture holds true for the heavier Ngs (see the Figures S8-S10 in SI). It is superfluous to finally point out that back-donation cannot occur in the Ng-Be^{2+} and Ng-Li^{+} systems. We also computed the symmetry decomposed CD function for the He-$BeCO_3$ and Ne-$BeCO_3$ (see Figures S21). For the He-$BeCO_3$ complex, we still found a larger A_1 component and two negative, smaller (and not equivalent) B_1 and B_2 components, while for the Ne-$BeCO_3$ complex all the symmetry components are positive. We can therefore conclude that, also with the $BeCO_3$ substrate, helium is able to accept electron density while neon does not.

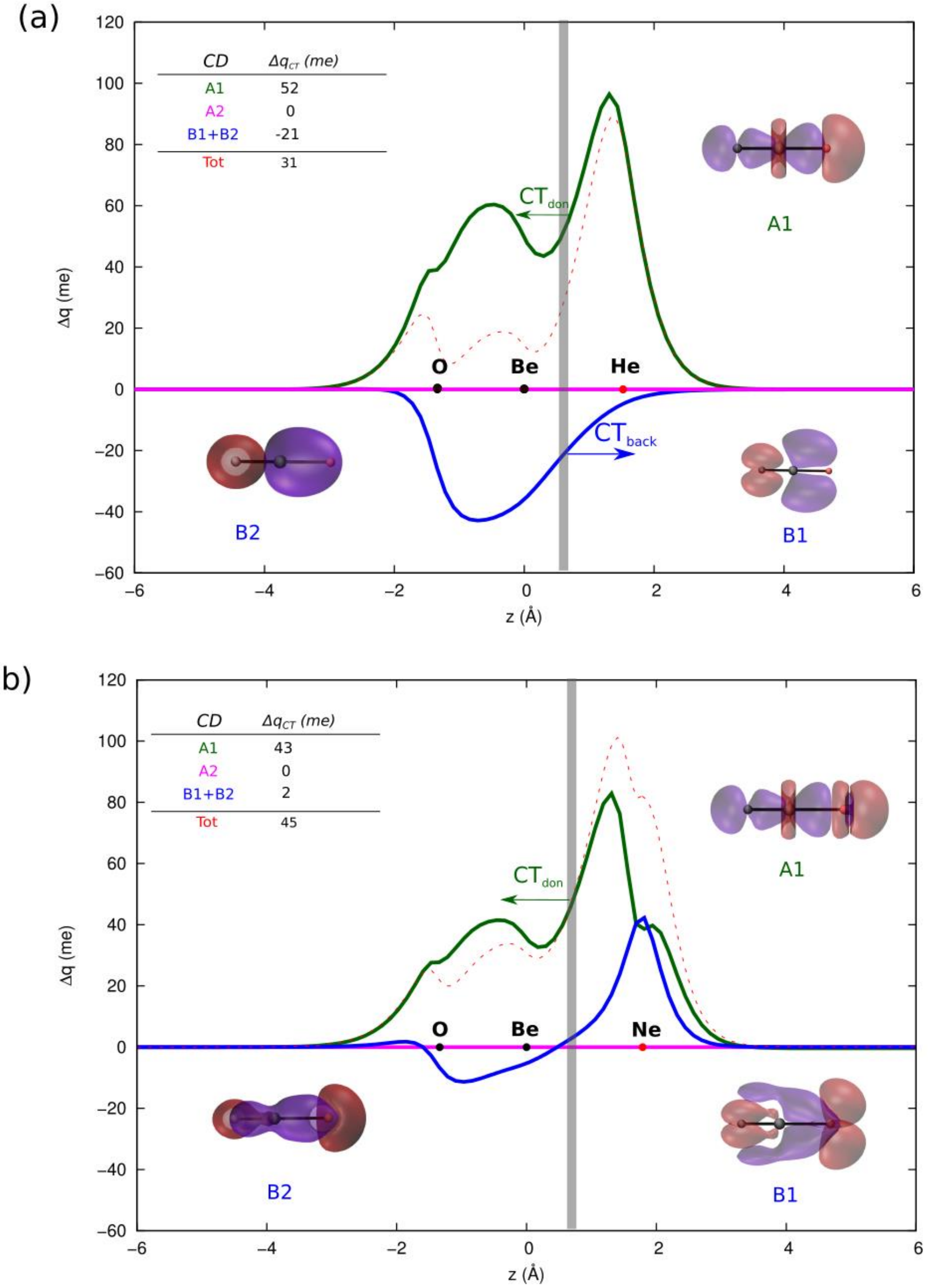


Figure 2. CD curves associated with the total electron density difference Δρ (red dashed lines) and with its C_{2v} symmetry components for (a) He-BeO and (b) Ne-BeO complexes. The dots on the axis mark the *z* coordinate of nuclei. The vertical lines identify the isodensity boundary. The

inset shows the 3D isodensity surfaces ($\Delta\rho_{A1} = \pm\ 8 \times 10^{-5}$ and $\Delta\rho_{B1/B2} = \pm\ 8 \times 10^{-4}$ me / bohr^3), with light red / light violet surfaces (negative / positive values) identifying charge depletion / accumulation areas.

The BeO capability to donate electron density to He may be strictly related to the presence of the oxygen atom, promoting a certain contribution of the Be atomic excited state configuration ($1s^2\ 2s^0\ 2p^2$). Consideration of the recently synthesized neutral beryllium - carbene complex,[38] where a π back-donation interaction from the Be filled *2p* atomic orbitals to the carbene ligand was argued to stabilize the complex, prompted us to investigate the Be*(^{1}D)-He system, where He interacts with Be in its ^{1}D excited state ($1s^2\ 2s^2 \rightarrow 1s^2\ 2s^0\ 2p^2$). By large Full Configuration Interaction calculations, we find that the lower lying $^1\Delta$ state of the adduct (correlating at large distance with Be*(^{1}D) and He in its ^{1}S ground state) presents an energy minimum at short distance (1.41 Å) of about 10 kcal/mol below the dissociation limit – see Figure S12 in SI. This is an unprecedented large value for the interaction energy of He in neutral systems. Remarkably, the ability of He to accept electrons from Be* is significantly enhanced with respect to He-BeO adduct, as clearly shown from the CD curves in Figure S13 of SI. To further generalize our results, we also applied the symmetry-decomposed CD analysis to the He and Ne complexes with AuF, which is known to act as a strong electron acceptor in the interaction with Ngs.[29, 39] The results are reported in Figure 3 and clearly show that the metal fluoride adducts display a CT pattern similar to those of BeO. A clear back-donation component is present in the helium compound and entirely absent in the neon one. In fact, the results show that the metal fluoride is able to back-donate electron density to helium even more efficiently than BeO.

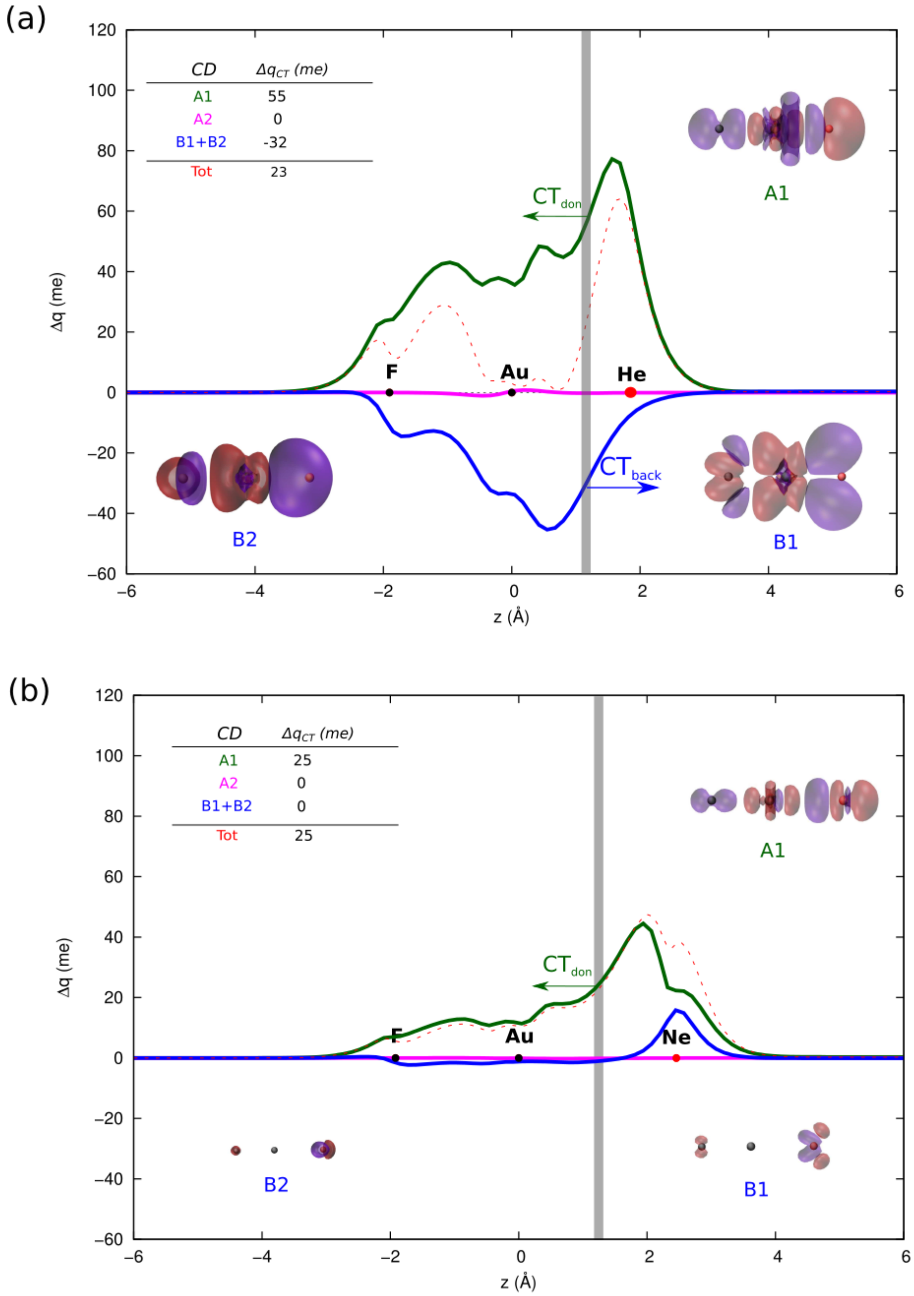


Figure 3. CD curves associated with the total electron density difference Δρ (red dashed lines) and with its C_{2v} symmetry components for (a) He-AuF and (b) Ne-AuF complexes. The dots on the axis mark the z coordinate of nuclei. The vertical lines identify the isodensity boundary. The inset shows the 3D isodensity surfaces ($\Delta\rho_{A1} = \pm\ 8 \times 10^{-5}$ and $\Delta\rho_{B1/B2} = \pm\ 8 \times 10^{-4}$ me / bohr^3),

with light red / light violet surfaces (negative / positive values) identifying charge depletion / accumulation areas.

All these findings strongly suggest that back-donation to helium may be triggered in the presence of substrates with a large dipole moment, causing He to donate and lowering the He empty *2p* orbital energies, which enables He, but not other Ngs, to accept back-donation, hence to come very close to the interacting partner and reinforce the induction interaction. We undertook two further lines of investigation to definitively assess our conclusions. First of all, in order to disentangle the role of the BeO π polarization from the role of the empty helium *p* atomic orbitals in accepting back donation, we repeated the CD analysis for the He complexes with modified basis sets. In particular, we considered a TZ2P basis set without *p* or *d,* or both *p* and *d*, functions on He. The results clearly show (Figure S14 (a) in the SI) that, while the A_1 CD curves are marginally affected by the basis set modifications, the B_1/B_2 CD curves undergo a significant change upon He *p* functions removal, becoming clearly less pronounced and going to zero rapidly towards He. Remarkably, the *d* functions show almost vanishing effects on the B_1/B_2 CD curves. The same is found for the Au-He and the Be*(^{1}D)-He complexes, for which the effect of the removal of the He *p* functions is even larger (see Figures S14, S15 in the SI). It is thus confirmed that the empty *2p* functions on He play a key role in the π electron density rearrangement, by describing back-donation to He from BeO or AuF or Be*. Additionally, in order to assess on energy grounds whether the He *2p* orbitals could plausibly receive electron density from the interacting substrate, we investigated the change in the He electron affinity upon approaching a positive point charge, that is the energy of a He$^-$ ion in its lowest ^{2}P state, relative to the neutral ^1S ground state, as a function of the point-charge distance. The results (Figure S16 in the SI) show that, when He approaches the positive charge, the electron affinity increases (the ^2P state relative energy decreases), even reaching positive values. This trend demonstrates the energy lowering of the empty *p* atomic orbitals and is therefore consistent with a π back-donation of electron density to He. Remarkably, the electric field value generated by BeO at He is roughly equivalent to that of the point charge placed at no more than 2 Å.

One very interesting feature, which the absence of back-donation unmasks in the CD functions for the neon complexes (Figures 3), is that the B_1/B_2 density component of AuF remains largely unperturbed upon complex formation (the corresponding CD curves are completely flat and vanishing all over the AuF region). The Au center lacks low energy empty orbitals of the proper symmetry, so that a contribution of electron donation from the Ne $2p_x$ / $2p_y$ orbitals to AuF can be safely ruled out. A comparative study carried out on the Au^+-Ne system supports this conclusion (see Figure S17). It is only natural to assume, *a fortiori*, that such absence of AuF polarization also characterizes the B_1/B_2 density component of the He complex. If this is true, we are then led to assume that the corresponding B_1+B_2 orbital contribution ΔE_{orb} of 1.84 kcal/mol to the energy decomposition analysis (see table S3 in SI) is the stabilization energy entirely associated to CT (back-donation), the polarization contribution being negligible. Assuming that this energy varies linearly with the charge transferred and dividing it by the back-donation CT of 32 me, we roughly estimate the energy associated with the transfer of one electron as 57.5 kcal/mol, or 2.5 eV. This figure is very nicely in line with that calculated for other previously studied cases of weak interactions.[31, 40]

Summarizing, we have unambiguously identified an electron acceptor capability of the helium atom, that is able not only to donate electron density in the formation of weakly bound adducts, but also to accept electron density from suitable interacting substrates. We demonstrated that the existence of a back-donation contribution stabilizes the He complexes and explains the similar bond strength of He and Ne complexes, which defy expectations based on their known atomic properties. On the basis of the present investigation, we may surmise that the stability of the recently synthesized Na_2-He compound[9, 10] could be related to the ability of He to receive electron density from Na, a possibility enhanced by the high-pressure conditions bringing the He and Na atoms closer, and lowering the He *p* orbital energy through the strong electrostatic field induces by the Na centers. Further in-depth dedicated studies are needed to assess this surmise and we think that the present findings may be very useful to probe previously unexplored pathways for the design and synthesis of stable helium compounds.

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NOTES The authors declare no competing financial interest

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Supporting Information Available: Computational details; equilibrium bond lengths and dissociation energies; energy decomposition analysis; 3D isodensity surfaces; CD curves; He electron affinity.

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