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Complexes of Helium with Neutral Molecules: Progress toward a Quantitative Scale of Bonding Character

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ABSTRACT

The complexes of helium with nearly thirty neutral molecules (M) were investigated by various techniques of bonding analysis and symmetry adapted perturbation theory (SAPT) calculations. The main investigated function was the local electron energy density $H(\boldsymbol{r})$, analyzed, in particular, so to estimate the degree of polarization (DoP) of He in the various He(M). As we showed recently (J. Comput. Chem. **2019**, 40, 2318-2328), the DoP is a quantitative index that is generally informative about the role of induction and dispersion in non-covalent noble gas complexes. As a more quantitative evidence in this regard, we presently ascertained a positive correlation between the DoP(He) of the He(M) and the percentage contributions of induction and dispersion to their SAPT binding energies. Based also on the explicit evaluation of the charge transfer (CT), accomplished through the study of the charge-displacement function, we derived a quantitative scale that ranks the He(M) according to their dispersive, inductive, and CT bonding character. Our taken approach could be conceivably extended to other types of non-covalent complexes.

Introduction

The complexes of the noble-gas atoms (Ng) with neutral molecules (M) have attracted, over the years, unceasing experimental and theoretical interest.[1] Besides playing a role in diverse physical and chemical processes, the Ng(M) are prototypical examples of weak, non-covalent interactions (NCIs).[2] In general, the latter comprise[3] (besides the ubiquitous repulsive term), three major attractive components, namely the dispersion energy, the electrostatic energy between the frozen densities of the interacting fragments (both of "physical" character), and the polarization energy, the latter including the "physical" contribution of the induction, and the "chemical" contribution of the charge transfer (CT). The Ng(M) are, in particular, usually perceived as typical van der Waals molecules,[4,5] held together by the favorable balance between dispersion and repulsion. The Ng, however, while generally resistant to share their electrons so to form true ionic or covalent bonds, sensibly respond to the in case polarization exerted by the ligands. Thus, even for complexes with non-polar molecules, the binding energies may include not only inductive, but also CT stabilizing components, whose in case occurrence marks the transition from a purely (or nearly purely) "physical" contact to a more specific "chemical" bond.[6-11] In particular, searching for a mode to analyze this transition, we recently obtained evidence[12] for a new quantitative index that is generally informative about the bonding character of non-covalent Ng complexes. We termed it as the *degree of polarization* (DoP) of Ng, as it measures, in essence, the mode and the extent of the Ng polarization exerted by the ligand. Based on the study of a large group of exemplary species, including the Ng(H_2), Ng(N_2), Ng(HX) (X = F, Cl, Br, I), Ng(Na^+), and Ng(F^-) (Ng = He-Xe), we ascertained that, if the DoP(Ng) is positive or negative but small in magnitude, the complex is stabilized, mainly, by dispersion. If the DoP(Ng) is negative and relatively large, the Ng is polarized opposite to the ligand; the stabilization energy may include an inductive component, but no CT is expected. On the other hand, if the DoP(Ng) is relatively large and positive, the Ng is polarized toward the ligand, and the role of the induction may arrive up to the occurrence of the CT. Interestingly, the DoP(Ng) unraveled to be strictly correlated with the molecular electrostatic potential (MEP)[13] at the contact point between Ng and the binding partner. In essence, the local anisotropies of the electronic distribution of the ligand, mapped by the MEP, polarize the Ng in different modes and to different extents, and this determines the overall character of the interaction, signed by the DoP(Ng).To corroborate this interpretation, and to gain further insights into the DoP(Ng) as an index of bonding character, we decided to explore, in particular, the capability of the DoPto signal the bonding situation of neutral helium complexes. The He-M interaction energies are, in fact, generally small, and typically dominated by the dispersion, so that the qualitative, and, especially, quantitative catching of additional bonding components is a challenge for any method of bonding analysis.[14-16] The presently-obtained obtained results confirmed the physical interpretation of the DoP, its strict relationship with the MEP, and its effective use as a qualitative, but also quantitative, index of bonding character.

Methodology

In the present study we analyzed the local electron energy density $H(\boldsymbol{r})$,[17] the reduced density gradient (RDG) and its related NCI indices,[18,19] and the charge displacement (CD) function,[20] combined with the classical theory of Atoms-in-Molecules (AIM),[21] and symmetry-adapted perturbation theory (SAPT) calculations.[22,23] The $H(\boldsymbol{r})$, the $\rho(\boldsymbol{r})$, the RDG, and the NCI indices were analyzed with the Multiwfn program,[24] using the wfn or wfx files generated by single-point calculations performed with the Gaussian 03[25] or Gaussian 09[26] at the CCSD[27] level of theory, with the Dunning's correlation-consistent triple-zeta basis set aug-cc-pVTZ(aVTZ)[28-32] (the convergence criteria were 10^{-8} hartree on the energy and 10^{-6} on the change in the cluster amplitudes). The two-(2D) plots of the $H(\boldsymbol{r})$ were as well produced with the Multiwfn, and include the standard contour lines belonging to the patterns $\pm k \times 10^n$ (k = 1, 2, 4, 8; n = -5 ÷ 6), together with the contour lines corresponding to the critical points specifically located by the topological analysis of the $H(\boldsymbol{r})$. The 3D plots of the $s(\boldsymbol{r})$ and the $H(\boldsymbol{r})$ were produced with the Visual Molecular Dynamics (VMD) program.[33] The CD analysis was carried out at the CCSD/aVTZ level of theory using MOLPRO,[34] also employed to calculate the CCSD(T) complexation energies extrapolated at the complete basis set limit (CBS),using a three point extrapolation procedure.[35] The SAPT calculations were performed with the SAPT2016,[36] using G09 for the integrals calculation. The employed basis set, denoted here as aVTZ/mbf, combined the aVTZ with a set of extra 3*s*3*p*2*d*1*f* mid-bond functions[37,38] (three *s* and three *p* functions with exponents 0.9, 0.3, 0.1, two *d* functions with exponents 0.6 and 0.2, and one *f* function with exponent 0.3) placed at the mid-distance between He and the adjacent atom (for the linear species), or the center-of-mass (CM) of the ligand (for the T-shaped species). All the quantities are expressed in atomic units [for $\rho(\boldsymbol{r})$, 1 au = 1 ea_0^{-3} = 6.7483 e Å^{-3}; for $H(\boldsymbol{r})$, 1 au = 1 hartree a_0^{-3} = 6.7483 hartree Å^{-3}].

The analysis of the *H*(*r*): the DoP(Ng)

As described previously,[17] the analysis of the $H(\boldsymbol{r})$is informative about diverse types of bonding motifs, including those occurring in Ng compounds. We recall here the details most relevant to the definition of the DoP(Ng) (*vide supra*).

The $H(\boldsymbol{r})$ is the sum of the kinetic energy density $G(\boldsymbol{r})$, and the potential energy density $V(\boldsymbol{r})$. The former is always positive, and the latter is always negative. Thus, at variance with the $\rho(\boldsymbol{r})$, that is, invariably, positive, the $H(\boldsymbol{r})$ may be positive, negative, or null. In particular, in the inner atomic regions, $G(\boldsymbol{r})$ is, typically, lower than $|V(\boldsymbol{r})|$, and $H(\boldsymbol{r})$ is negative. On the other hand, in the outer atomic regions, $G(\boldsymbol{r})$ is, typically, higher than $|V(\boldsymbol{r})|$, and $H(\boldsymbol{r})$ is positive. The $H(\boldsymbol{r})$ is also minimum (most negative) at the nucleus, and progressively increases (sometimes being locally null or positive), until becoming definitely null at a distance, indicated as R^{-}, that is typical of each atom. For $R > R^{-}$, the $H(\boldsymbol{r})$ is positive, and becomes vanishingly small at the largest distances, passing through a point of maximum. Thus, the $H(\boldsymbol{r})$ partitions the atomic space in two well-recognizable regions, namely an inner one of negative values (that sometimes encloses tiny inner sub-region[s] of positive values), indicated as $H^{-}(\boldsymbol{r})$, and an outer one of positive values (that sometimes encloses tiny inner sub-region[s] of negative values), indicated as $H^{+}(\boldsymbol{r})$. The boundary of these two regions falls at a distance R^{-}, that is typical of each atom; at this distance, $H(\boldsymbol{r} = R^{-}) = 0$. Interestingly, when two atoms form a chemical bond, their $H^{-}(\boldsymbol{r})$ and $H^{+}(\boldsymbol{r})$ regions combine in modes that signal the character of the interaction. In particular, for typical covalent bonds, the atoms overlap all the contour lines of their $H^{+}(\boldsymbol{r})$ regions, and part of the contour lines of their inner $H^{-}(\boldsymbol{r})$ regions, the bond appearing as a continuous region of negative values of $H(\boldsymbol{r})$, plunged in a zone of positive values. The interaction is signed by a (3,+1) critical point of the $H(\boldsymbol{r})$ (denoted here as HCP), falling on the bond axis. On the other hand, in weak NCIs (like those occurring in the presently-investigated helium complexes), the involved atoms or molecules overlap only part of their $H^{+}(\boldsymbol{r})$ regions, their $H^{-}(\boldsymbol{r})$ regions remaining, instead, not overlapped. The bond thus appears as two clearly distinguishable regions of negative values of $H(\boldsymbol{r})$, separate by a region of positive values. At variance with the covalent bonds, these non-covalent contacts are not generally signed by a HCP. This arises, essentially, from the bell shape of the $H(\boldsymbol{r})$ in the outer $H^+(\boldsymbol{r})$ region (further details are given in Ref. 17), that sometimes prevents the formation of a true HCP along the bond axis. In cases like these, the interaction is conveniently signed by including, in the plotted $H(\boldsymbol{r})$, the bond critical point (BCP) located from the analysis of the $\rho(\boldsymbol{r})$ (the classical AIM[21]). In fact, the study of diverse non-covalent species, including numerous Ng(M) complexes, unraveled that, when located analytically, the HCP falling on the axis of a non-covalent bond is quite close to the corresponding BCP. The DoP(Ng) is, in particular, defined in terms of the BCP falling on the Ng-M axis, and the size of the $H^-(\boldsymbol{r})$ region of Ng. For any free Ng, the latter is spherical (the corresponding R^- periodically increases from 1.1147 a_0 for He to 3.0180 a_0 for Xe), and encloses the majority of the electronic charge (ca. 70% for He, and ca. 90%-98% for the other congeners). Due to these highest electron populations, the shape and size of the $H^-(\boldsymbol{r})$ region of any Ng are sensitive to the in case polarization exerted by the ligands; the DoP(Ng) measures, in particular, the size deviation occurring along the Ng-M axis expressed by the equation:

$$\mathrm{DoP(Ng)} = \frac{R^-_{\mathrm{Ng-BCP}}(\mathrm{Ng}) - R^-(\mathrm{Ng})}{R^-(\mathrm{Ng})} \times 100 \qquad (1)$$

where $R^-_{\mathrm{Ng-BCP}}(\mathrm{Ng})$ is the radius of the $H^-(\boldsymbol{r})$ region of Ng along the axis formed by Ng and the AIM BCP located on the Ng-M bond path, and $R^-(\mathrm{Ng})$ is the radius of the $H^-(\boldsymbol{r})$ region of the free atom. Further details about the properties of the DoP(Ng) are discussed in our recent study.[12]

The NCI analysis

The NCI analysis relies[18,19] on the study of the RDG defined by the equation:

$$s(\boldsymbol{r}) = \frac{1}{2(3\pi^2)^{\frac{1}{3}}} \frac{|\nabla\rho(\boldsymbol{r})|}{\rho(\boldsymbol{r})^{\frac{4}{3}}} \tag{2}$$

Low-value $s(\boldsymbol{r})$ isosurfaces (typically 0.3-0.6) appear among atoms undergoing any type of interaction, the NCIs emerging, in particular, by considering the spatial regions of low $\rho(\boldsymbol{r})$ (typically at around 0.05 ea_0^{-3}). The low-$s(\boldsymbol{r})$/low-$\rho(\boldsymbol{r})$ isosurfaces are, in turn, mapped in terms of the sign(λ_2)$\rho(\boldsymbol{r})$, λ_2 being the second eigenvalue ($\lambda_1 < \lambda_2 < \lambda_3$) of the Hessian matrix of $\rho(\boldsymbol{r})$. In essence, the sign of λ_2 is used to distinguish between attractive ($\lambda_2 < 0$), and repulsive interactions ($\lambda_2 > 0$), and the value of the $\rho(\boldsymbol{r})$ is exploited to rank the corresponding strength. In practice, the NCIs are visualized in 3D space by plotting the low-value isosurfaces of the $s(\boldsymbol{r})$, colored by the sign(λ_2)$\rho(\boldsymbol{r})$. Standard employed color codes are blue for highly attractive interactions (*e.g.* hydrogen bonds), green for weak interactions (*e.g.* bonds dominated by the dispersion), and red for repulsive interactions, such as the steric clashes.

The CD analysis

The CD analysis relies on the expression:[20]

$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} \Delta\rho(x, y, z')dz' \tag{3}$$

$\Delta\rho$ being the difference between the electron density of the complex, and that of the isolated constituting fragments, placed at their positions in the complex. At each point along the bond axis$z$, Δq measures the net electron charge that, upon formation of the complex, flows from right to left across the plane perpendicular to z. Thus, a negative Δq corresponds to a flux of charge from left to right. This provides a concise, but insightful snapshot of the whole electron cloud rearrangement arising as the consequence of the intermolecular potential effect. The evaluation of $\Delta q(z)$ along an axis joining the two interacting species is immediately helpful for a qualitative assessment of occurrence and extent of CT. In particular, the curve obviously suggests CT when it is appreciably different from zero, and it does not change sign in the region between the fragments. On the other hand, the CT may be uncertain (both in magnitude and direction) if the curve crosses zero in the same region. When the CT takes place, it is convenient to come up with a definite numerical estimate, which can be done by taking the value of the CD curve at a specific point between the fragments. Based on previous studies,[6-11,39,40] we choose to separate the fragments and to extract the CT at the so-called isodensity boundary (IB), *i.e.* at the point along z where the electron densities of the non-interacting fragments become equal.

The SAPT calculations

The SAPT interaction energy, E_{int}^{SAPT}, was computed by including the following terms:

$$E_{int}^{SAPT} = E_{elst}^{(10)} + E_{exch}^{(10)} + E_{ind,r}^{(20)} + E_{exch-ind,r}^{(20)} + \delta E_{int,r}^{HF}$$

$$+ E_{elst,r}^{(12)} + {}^{t}E_{ind}^{(22)} + {}^{t}E_{exch-ind}^{(22)} + E_{disp}^{(20)} + E_{exch-disp}^{(20)} + E_{elst,r}^{(13)}$$

$$+ \varepsilon_{exch}^{(1)}(CCSD) + E_{disp}^{(21)} + E_{disp}^{(22)} \qquad (4)$$

According to the notation standard in SAPT,[22,23] the first (1/2) and the second (0/1/2) number superscript in parenthesis indicates, respectively, the first-/second-order perturbation term, and the zeroth-/first-/second-order correction. The notations in subscript indicate the classical (Coulombic) electrostatic energy (*elst*), the exchange term that results from the antisymmetrization of the wave-function (*exch*), the induction energy (*ind*), and the dispersion energy (*disp*). The "*r*" indicates that a given component has been computed by including the coupled Hartree-Fock (HF) response for the perturbed system. The $\delta E_{int,r}^{HF}$ term collects the contributions to the supermolecular HF energy beyond the second-order of intermolecular operator, the ${}^{t}E_{ind}^{(22)}$ is the part of $E_{ind}^{(22)}$ not included in $E_{ind,r}^{(20)}$, and $\varepsilon_{exch}^{(1)}(CCSD) = E_{exch}^{(1)}(CCSD) - E_{exch}^{(10)}$is the part of $\varepsilon_{exch}^{(1)}(\infty)$ with intra-monomer excitations at the CCSD level of theory.

The terms of equation (4) were grouped so to express the E_{int}^{SAPT} as the sum of the electrostatic (E_{elst}), inductive (E_{ind}), dispersive (E_{disp}), and exchange components (E_{exch}). We used, in particular, two distinct decomposition schemes, indicated here as SAPT(*EDA1*) and SAPT(*EDA2*). In the SAPT(*EDA1*), the E_{elst} and the E_{ind}include their exchange contributions, and the term $\delta E_{int,r}^{HF}$ is included into E_{ind}:

$$E_{elst}(EDA1) = E_{elst}^{(10)} + E_{elst,r}^{(12)} + E_{elst,r}^{(13)} \qquad (5a)$$

$$E_{ind}(EDA1) = E_{ind,r}^{(20)} + E_{exch-ind,r}^{(20)} + {}^{t}E_{ind}^{(22)} + {}^{t}E_{exch-ind}^{(22)} + \delta E_{int,r}^{HF} \qquad (5b)$$

$$E_{disp}(EDA1) = E^{(20)}_{disp} + E^{(21)}_{disp} + E^{(22)}_{disp} + E^{(20)}_{exch-disp} \qquad (5c)$$

$$E_{exch}(EDA1) = E^{(10)}_{exch} + \varepsilon^{(1)}_{exch}(CCSD) \qquad (5d)$$

The SAPT(*EDA2*) does not include the $\delta E^{HF}_{int,r}$, and all the exchange contributions are grouped into E_{exch}:

$$E_{elst}(EDA2) = E^{(10)}_{elst} + E^{(12)}_{elst,r} + E^{(13)}_{elst,r} \qquad (6a)$$

$$E_{ind}(EDA2) = E^{(20)}_{ind,r} + + \, {}^{t}E^{(22)}_{ind} \qquad (6b)$$

$$E_{disp}(EDA2) = E^{(20)}_{disp} + E^{(21)}_{disp} + E^{(22)}_{disp} \qquad (6c)$$

$$E_{exch}(EDA2) = E^{(10)}_{exch} + \varepsilon^{(1)}_{exch}(CCSD) + E^{(20)}_{exch-ind,r} + \, {}^{t}E^{(22)}_{exch-ind} + E^{(20)}_{exch-disp} \quad (6d)$$

Results and Discussion

The investigated He(M) complexes: geometries and stabilities

The helium complexes investigated in the present study are shown in Figure 1.

<Figure 1 near here, please>

Figure 1. CCSD(T)/aVTZ optimized bond distances (a_0) of the He(M) complexes.

They were chosen so to cover expectedly different bonding characters, and include HeAr, the linear He-XX and T-shaped He(X_2)-T (X = H, N, Cl, Br), the linear isomeric He-HY and He-YH (Y = F, Cl, Br), He-HCN and He-NCH, He-CO and He-OC, He-FCl and He-ClF, and the additional helium-chlorine complexes He-ClBr, He-ClCN, He-ClCCH, He-ClZH (*Z* = O, S), and He-ClZH$_3$ (*Z* = C, Si). Their geometries were first fully optimized at the MP2/aVTZ level of theory, fixing the symmetry as C_{2v} for the

He(X_2)-T,C_{3v} for the He-ClZH$_3$, C_s for the He-ClZH (with a linear He-Cl-Z arrangement), and $C_{\infty v}$ for all the other species. Within these constraints, with the only exception of He(H_2)-T (a first-order saddle point), all the complexes were characterized as true minima on the potential energy surface. We also noticed a slightly non-linear He-Cl-Z alignment (by ca. 1-2°) of the He-ClZH (Z = O, S), both complexes adopting the *trans* configuration. Most importantly, the MP2/aVTZ optimized parameters of the M moieties resulted, invariably, quite similar to the experimental geometries of the free molecules. Therefore, we fixed the bond distances and the bond angles of M at their experimental value(s) [the employed data are listed in Table S1 of the supplementary information (SI)], and re-optimized at the CCSD(T)/aVTZ level of theory the distance of He from the adjacent atom, or, for the T-shaped He(X_2)-T (X = H, N, Cl, Br), the distance of He from the CM of X_2. The obtained values (a_0) are quoted in Figure 1, and the full CCSD(T)/aVTZ Cartesian coordinates are given in the SI. Using these geometries, we calculated the SAPT complexation energies of the He(M), E_{int}^{SAPT}, and partitioned the terms appearing into Equation (4) (listed in Table S2) according to the decomposition schemes SAPT(*EDA1*) and SAPT(*EDA2*). The obtained values are reported in Tables 1 and 2.

<Tables 1 and 2 near here, please>

We first compared our predicted geometries and interaction energies with the accurate values available from the literature[11,41-51] for the majority of the presently-investigated He(M) systems (the only still unreported species are the He-ClR, R = CN, CCH, OH, SH, CH_3, SiH_3).With respect to these benchmark values (listed in Table S3), typically obtained at the CCDS(T) or SAPT levels of theory with very large basis sets, the bond distances quoted in Figure 1, and the E_{int}^{SAPT} listed in Tables 1 and 2 feature a mean unsigned deviation (MUD), respectively, of 0.0908a_0, and 1.20 cm^{-1}. As a further test comprising all the presently-investigated He(M), we compared the $E_{int}^{SAPT}$with the presently-predicted CCSD(T)/CBS complexation energies (see Table S3), and noticed, again, a MUD of only 2.07 cm^{-1}. Overall, these check calculations suggest that, besides strictly comparable, our SAPT/CCSD(T) data are also of good accuracy. Particularly for the interaction energies, we first note that the absolute E_{int}^{SAPT} are, generally, small, and range between -9.69 cm^{-1} for He(H_2)-T and -63.21 cm^{-1} for He-ClF. Values like these clearly point to weak NCIs, and, in fact, the attractive part of the interaction is, invariably, dominated by the dispersion (see Tables 1 and 2). The latter contribution is, indeed, crucial in determining, for example, the higher stability of He-HH, He(N_2)-T, and He-OC with respect, respectively, to their isomeric He(H_2)-T, He-NN, and He-CO. In general, however, for any pair of isomeric He(HX) (X = H, F, Cl, Br, CN), He(ClF), He(Cl_2), and He(Br_2), the relative stability of the two isomers is a subtle balance between the exchange term and the various attractive components. For example, as already noted previously,[46] He-HF is definitely more stable than He-FH, but He-ClH and He-BrH are more stable than the corresponding H-coordinated isomers, the difference increasing on going from Cl to Br. We also note that, in line with the recent discussion of the isomeric He(Cl_2),[10,11] the E_{ind} of the linear He-ClCl is more negative than the corresponding term of the He(Cl_2)-T (-9.23 *vs* -5.24 cm^{-1} with the SAPT(*EDA1*)), the difference of these terms mirroring, essentially, the difference of the corresponding interaction energies (-47.19 *vs* -43.72 cm^{-1}). But the most relevant results were obtained by evaluating the *percentage* contributions of E_{elst}, E_{ind}, and E_{disp} to the total attractive part of the interaction ($E_{elst} + E_{ind} + E_{disp}$). Thus, as shown in Tables 1 and 2, for both SAPT(*EDA1*) and SAPT(*EDA2*), the %(E_{elst}) is, invariably, at around 10-12%, with a single lower value of ca. 8.5% for He(H_2)-T. In essence, the role of the electrostatic term is (nearly) independent on the nature of M. On the other hand, the percentage contributions of induction and dispersion span appreciably larger ranges (between ca. 2-4 and32-36%, and ca. 56-58 and 88-89%, respectively), and, in particular, as shown in Figures S1 and S2, they are, roughly, inversely related. Thus, at variance with the electrostatic term, the inductive term is quite sensitive to the nature of M, and, for species such as He-HF and He-HCN, it may arrive to get close (even though invariably minor) to the dispersive one. As discussed in the subsequent paragraphs, this dependence is effectively caught, in particular, by the DoP(He), and this is beyond the presently-proposed scale of bonding character.

The DoP(He) of the He(M) complexes and its relationship with the MEP

The non-covalent character of all the He(M) complexes clearly emerged by examining the NCI descriptors, the $H(\boldsymbol{r})$, and the $\rho(\boldsymbol{r})$. The quantitative data are collected in Table 3, and some illustrative graphs, obtained, in particular, for the exemplary He(HCN), He(H_2), and He-ClCCH, are shown in Figure 2.

<Table 3 and Figure 2 near here, please>

Figure 2. From left to right, NCI isosurfaces (green disk; isovalue = 0.5), 2D-plots of the $H(\boldsymbol{r})$ (solid/brown and dashed/blue lines corresponde, respectively, to positive and negative values), and 3D-plots of the $H(\boldsymbol{r})$ = 0 hartree a_0^{-3} isosurfaces of the He(HCN), He(H_2), and He-ClCCH.

First, for any He(M) system, the 2D plot of the $s(\boldsymbol{r})$ *vs* the sign(λ_2)$\rho(\boldsymbol{r})$ featured only one spike at the low density region, corresponding to the non-covalent contact between He and M. The bonding region is best caught by examining the 3D-plots of the isosurfaces of the $s(\boldsymbol{r})$ (fixed as 0.5), colored by the sign(λ_2)$\rho(\boldsymbol{r})$ that progressively increases from blue (-0.05 au) to red (0.05 au). As shown in the left column of Figure 2, a disk-shaped green area invariably appears between the two interacting fragments, and this is typical of weak, van der Waals contacts. Consistently, at the He-M BCP located from the AIM analysis (see Table 3), the ρ(BCP) is small (between 0.00068 ea_0^{-3} for He(H_2)-T and

0.0037 ea_0^{-3} for He-HF), and, typically, at around 0.0015-0.0020 ea_0^{-3}. The $\nabla^2\rho$(BCP) and H(BCP) are as well invariably small and positive, as typical for NCIs.[21] The analysis of the $H(\boldsymbol{r})$ confirmed this assignment. As shown in the 2D-plots of Figure 2 (central column), the $H^{-}(\boldsymbol{r})$ regions of both He and M are perfectly closed, and separated by a wide region of positive values of $H(\boldsymbol{r})$. The covalent bond(s) of M are also invariably signed by a HCP falling on the corresponding bond axis. The boundary of the $H^{-}(\boldsymbol{r})$ regions of He and M correspond to the $H(\boldsymbol{r})$ = 0 hartree a_0^{-3} isosurfaces, that appear in 3D as shown in the right column of Figure 2. The space region between these two isosurfaces includes the AIM BCP, whose position, combined with the size of the $H(\boldsymbol{r})$ = 0 hartree a_0^{-3} isosurface of He along the He-M or He-CM axis, furnished, through equation (1), the DoP(He) of the various He(M). The obtained values, quoted in Table 3, span between -0.511 (He-NCH) and 1.62 (He-HF), and this rather large range confirms that, even for the least polarizable He, the DoP(Ng) sensibly signals the different effects exerted by the ligands. In particular, based on our previous study,[12] a positive/negative DoP(He) indicates an electronic cloud of He that is polarized toward/opposite to M. We also showed previously that, rather than mirroring the total atomic charges of M, the polarization effects signed by the DoP(Ng) are best related to the *local* electronic distributions of the ligands as mapped, in particular, by their molecular electrostatic potential (MEP).[13] In this regard, rather than using the MEP of the *free* molecules projected on an arbitrarily-chosen isodensity surface (*e.g.* the ρ = 0.0010 or 0.0020 ea_0^{-3} customarily taken in the literature[52]), we used the MEP(BCP), namely the MEP evaluated at the AIM BCP of the complex (taken as the contact point between Ng and the ligand), and established nearly linear correlations between the DoP(Ng) and the MEP(BCP). We confirm here a good linear dependence (r^2 = 0.996) between the DoP(He) of the He(M) and the corresponding MeP(BCP). But it is also reasonable to speculate that, for the same value of the MEP(BCP), the polarization of

He by M is inversely related to the distance of the BCP from Ng, *R*(BCP). As a matter of fact, using the data quoted in Table 3, we found a nearly-linear correlation (r^2 = 0.998) between the DoP(He) and the MEP(BCP)/*R*(BCP) expressed by the equation:

$$\mathrm{DoP(He)} = 0.0449 \times \frac{\mathrm{MEP(BCP)}}{R\mathrm{(BCP)}} - 0.0294 \qquad (7)$$

(see Figure 3), that actually reproduces the DoP(He) quoted in Table 3 with a MUD of only 0.017.

<Figure 3 near here, please>

Figure 3. DoP(He) of the He(M) complexes *vs* the corresponding MEP(BCP)/*R*(BCP).

Equation (7) predicts also that the DoP(He) is positive/negative for a MEP(BCP)/*R*(BCP) higher/lower than 0.65 kcal mol$^{-1}a_0^{-1}$. Using an *average* *R*(BCP) of 2.590 a_0 (derived from the data quoted in Table 3), this corresponds to a MEP(BCP) higher/lower than 1.70 kcal mol^{-1}. Interestingly, this threshold is, essentially, the MEP of the free He, predicted to range between ca. 0.6 and ca. 2.6 kcal mol^{-1} for a mapped isodensity surface between 0.00050 and 0.0020 ea_0^{-3}. In addition, based on the data quoted in Table S3, we noticed that the MEP(BCP) predicted for the various He(M) positively correlates (r^2> 0.98) with the MEP of the *free* M (taken along/perpendicular to the bond axis for the linear/T-shaped complexes), the best dependence (r^2 = 0.9896) occurring with the MEP evaluated at the 0.0010 ea_0^{-3} isodensity surface, MEP(0.0010). In essence, as a rule of thumb, if the MEP(0.0010) of a ligand M at the site coordinating He is higher/lower than ca. 2-3 kcal mol^{-1}, the interacting helium is polarized toward/opposite to it, the ensuing effect increasing by increasing (more positive or more negative) the value of the MEP. These different modes of polarization are signed by the

DoP(He), that also strictly mirrors the different role of the various binding components. This is best discussed in the subsequent paragraph.

The DoP(He) as an index of bonding character

Table 4 reports the percentage contributions of the induction energy, %(E_{ind}), of the He(M) complexes listed according to a decreasing value of the DoP(He).

<Table 4 near here, please>

This mode of ranking clearly unravels that, for both SAPT(*EDA1*) and SAPT(*EDA2*), the studied complexes can be divided into three groups. The first one includes the fourteen species between He-ClSH and He-CO. Their DoP(He) falls between -0.200 and 0.200, and their %(E_{ind}) is, invariably, lower than ca. 5-6%. They are, thus, assigned as dispersive (DISP) in character. The second group includes the twelve complexes between He-HF and He-BrH. Their DoP(He) is higher than 0.200, and progressively increases up to 1.62; the corresponding %(E_{ind}) is, invariably, higher than 5%, and increases up to ca. 32-34% for He-HF. In these systems, the He is polarized toward the ligand, and their bonding character is, therefore, assigned as dispersive/inductive(+) (DISP/IND$^+$). At least in principle, these complexes may also feature the contribution of the CT (*vide infra*). The third group includes He-FH and He-NCH. Their DoP(He) is lower than -0.200 (-0.386 and -0.511, respectively), and their %(E_{ind}) is higher than 6% (ca. 7-8 and ca. 11-12%, respectively). Their He atom is polarized opposite to the ligand, and they are, therefore, assigned as dispersive/inductive(-) (DISP/IND$^-$). In systems like these, no CT is expected. In essence, as shown in Figure 4, DoP(He)/%(E_{ind}) plane can be partitioned into three major zones: the right one includes the complexes of DISP/IND$^+$ character [DoP(He) > 0.200, %(E_{ind}) progressively increasing from left to right], the left one includes the complexes of DISP/IND$^-$ character [DoP(He) < -0.200, %(E_{ind}) progressively increasing from right to left], and the central one includes the complexes of DISP character [-0.200 < DoP(He) < 0.200, %(E_{ind})<5-6%].

<Figure 4 near here, please>

Figure 4. %(E_{ind}) of the He(M) complexes *vs* the corresponding DoP(He) evaluated by (a) SAPT(*EDA1*) and (b) SAPT(*EDA2*).

For both SAPT(*EDA1*) and SAPT(*EDA2*), the dependence of %(E_{ind}) on the DoP(He) is best expressed by a third-order polynomial:

$$\%(E_{ind}) = -A \times [\mathrm{DoP(He)}]^3 + B \times [\mathrm{DoP(He)}]^2 - C \times [\mathrm{DoP(He)}] + D \qquad (8)$$

with SAPT(*EDA1*)/SAPT(*EDA2*) coefficients *A* = 7.388/6.9765, *B* = 23.689/22.523, *C* = 0.256/0.502, and *D* = 4.204/3.452. Their correlation coefficients are 0.963/0.982, and this slight difference mirrors a points distribution of Figure 4b that is slightly sharper than that of Figure 4a. In any case, for both SAPT(*EDA1*) and SAPT(*EDA2*), equation (8) reproduces the %(E_{ind}) quoted in Table 4 with a MUD, respectively, of 0.92 and 0.56, that reduces to 0.61 and 0.54 when one considers, in particular, the complexes of DISP character. As mentioned above, the %(E_{ind}) and %(E_{disp}) are, nearly, inversely related. Consistently, for both SAPT(*EDA1*) and SAPT(*EDA2*), the curves interpolating the values of %(E_{disp}) plotted *vs* the DoP(He) (shown in Figures S3 and S4) resulted complementary to those shown in Figure 4, and, again, well fitted by a third-order polynomial. The correlation coefficients, albeit slightly lower than those obtained for equation (8), are, still, as high as 0.942 and 0.957.

Concerning the role of the CT

The He(M) complexes featuring a negative value of the DoP(He) are assigned as DISP or DISP/IND$^-$, and no CT is expected. In these systems, in fact, the He atom is polarized opposite to the ligand. On the other hand, in the systems featuring a positive value of the DoP(He), particularly those of DISP/IND$^+$ character, the polarization of He toward the ligand may be large enough to promote a CT from the noble gas. To unambiguously ascertain the presence of a CT in the He(M) interaction, the most reliable approach is to analyze the electron density changes occurring upon formation of the complexes by means of the CD analysis. The CD function defines, at each point along a selected axis joining two interacting species, the amount of electron charge which is displaced across a plane perpendicular to the axis, as a consequence of the interaction. The resulting snapshot of the CD across the entire system nicely points out the presence and extent of CT in weakly interacting systems REF, such as the ones at hand here.

We applied the CD analysis to two exemplary groups, namely the helium-hydrogen complexes He-HX (X = H, F, Cl, Br, CN), and the helium-chlorine complexes He-Cl*R* (*R* = H, F, Cl, Br, CN, CCH, OH, SH, CH_3, SiH_3). The results are reported in Table 5 and Figures 5, S3-S5 (in SI), also showing the 3D contour plots of the electron density difference between the complex and the non-interacting fragments.

<Figure 5 and Table 5 near here, please>

Figure 5. CD curves of the He-NCH, He(H_2)-T, He-HH, He-ClCCH and He-HCN complexes, together with the 3D isodensity plots of the electron density change ($\Delta\rho = \pm 8\times 10^{-6}$ me a_0^{-3}) accompanying the formation of the adduct. The dots on the dashed line represent the nuclei *z* coordinates, and the vertical solid line identifies a conventional boundary between Ng and M (see text for details).

Figure 5 includes some representative CD curves, describing sizable or negligible CT in He(M) systems. Specifically, in the He-HCN complex, the HCN substrate pronouncedly polarizes the spherical He cloud, which undergoes electron charge depletion/accumulation in the region opposite/towards HCN. A sizable charge rearrangement is also evident on the HCN moiety. More importantly, the computed CD is negative everywhere, suggesting a corresponding electron flow in the direction from He to HCN. By contrast, in the He-NCH approach the CD curve indicates an inverted (less pronounced) polarization on the He center (Δq is positive), and a lacking of charge rearrangement on the NCH moiety, with the function changing sign between the two interacting partners. Therefore, the CD analysis on the He-NCH system suggests a negligible or null CT and a He charge polarization opposite to that in He-HCN. We also note that the 3D contour plots of the electron density change accompanying the complex formation ($\Delta\rho$, see Figures 5, S3-S% in SI) nicely reproduce the shape of the CD curves.

The CD analysis show that for the He complexes with M = Cl*R* (*R*=SH, CCH, Br, OH, Cl, F, CN), HX (X = Cl, Br, I), H-H (linear) a sizable CT from He to M is attained, the CD function being always negative everywhere. The amount of displaced charge can be plausibly estimated by considering the Δq value at the so-called “isodensity boundary“ (see above). For the He-HCN/He-ClCCH systems (see Figure 5) a Δq value of -0.66/-0.32 milli-electron (me) has been computed. As shown in Table 5, the HF substrate undergoes the higher CT from He (Δq = -1.08 me), while Δq values between -0.74 and 0.10 me have been computed for the remaining systems. Table 5 also reports the Δq values at the He site, related to the entity of the He polarization exerted by the ligand. These values span from -9.35 me (HF) to -0.66 me (H-H linear).

The CD analysis also suggest that for the He-Cl_2 (T-shaped), He-$ClCH_3$, He-$ClSiH_3$, He-HH (T-shaped), He-NCH systems negligible or null CT can be surmised, together with an inverted charge polarization at the He site (Δq = +3.63 me for He-NCH).

Overall, the discussed results from the CD analysis fully confirm the capability of the DoP(He) to signal the bonding character of the He(M) adducts, including the conceivable role of the CT. First, as shown in Figure 6a, for the examined He-HX and He-Cl*R*, the DoP(He) depends on $-\Delta q$(max) nearly linearly (r^2 = 0.992), the correlation coefficient further improving to 0.995 if the He-HX and He-Cl*R* are considered separately. In essence, the DoP(He) and the $-\Delta q(z = 0)$ measure the same *primary* effect, namely the polarization of He by the ligand. A progressively increased polarization of He (particularly from He to M) is also expected to enhance the role of the CT, and, in fact, as shown in Figure 6b, a positive correlation does exist between the DoP(He) of the various He-H*R* and He-Cl*R*, and the corresponding CT. The dependence is, however, not linear, thus suggesting that the actually transferred charge reflects not only the degree of polarization of He, but also the acceptor ability of M. In any case, the data clearly unravel two major points, namely that no CT occurs for a negative DoP(He), and that an appreciable CT (at least ca. 0.5 me) demands a DoP(He) of at least 0.5. For a DoP(He) positive but lower than this threshold, the role of CT is minor, and, essentially, negligible for a DoP(He) lower than 0.2.

<Figure 6 near here, please>

Figure 6. (a) $-\Delta q$(max) *vs* DoP(He) and (b) CT *vs* DoP(He) of the He-HX (X = H, F, Cl, Br, CN) and He-Cl*R* (*R* = H, F, Cl, Br, CN, CCH, OH, SH, CH_3, SiH_3) complexes.

Concluding Remarks

The present investigation clearly confirmed that the complexes of He with neutral molecules feature all the “ingredients” of NCIs, namely dispersion, electrostatics, and induction, including the CT. Due to the lowest polarizability of He, the latter contribution is, indeed, at its early incipience, and this makes the He(M) ideally suited to investigate the weakest domain of the NCIs. The role of induction and CT is, in particular, effectively signed by the DoP(He), a dimensionless index that ranks the He(M) on a scale covering three types of bonding character, namely DISP ($-0.2 <$ Dop(He) < 0.2), DISP/IND$^-$ [DoP(He) < -0.2], and DISP/IND$^+$ [DoP(He) > 0.2], the latter including the contribution of the CT for a DoP(He) > 0.5. The DoP(He) is also correlated with the MEP at the outer region of the ligand. This confirms the point repeatedly highlighted in the literature[53,54] that, even in the Coulombic σ-hole interpretation of non-covalent interactions, the inclusion of polarization is of major importance. We plan to investigate the conceivable extension of our proposed scale to the complexes of the other noble gases, and, in the perspective, to assay the applicability of our taken approach to analyze other types of NCIs.

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Keywords: bonding analysis · charge-displacement analysis ·electron energy density · helium complexes · NCI analysis · noble gas chemistry · SAPT calculations

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Table 1. Decomposition analysis of the He(M) complexes (see also Figure 1) according to SAPT(*EDA1*) (see text). The percentage contributions are with respect to $(E_{elst} + E_{ind} + E_{disp})$. Energy values in cm^{-1}.

M	E_{elst}	E_{ind}	E_{disp}	E_{exch}	E_{int}^{SAPT}[a]	%(E_{elst})	%(E_{ind})	%(E_{disp})
HeAr	-4.85	-1.66	-39.55	25.98	-20.08	10.53	3.60	85.87
He-HH	-2.62	-1.48	-23.09	16.34	-10.85	9.64	5.44	84.92
He(H_2)-T	-1.74	-0.77	-17.92	10.74	-9.69	8.52	3.77	87.71
He-NN	-5.15	-1.75	-40.42	31.15	-16.17	10.88	3.70	85.42
He(N_2)-T	-6.29	-2.45	-49.42	34.89	-23.27	10.82	4.21	84.97
He-ClCl	-12.95	-9.23	-89.10	64.09	-47.19	11.64	8.29	80.07
He(Cl_2)-T	-14.95	-5.24	-97.02	73.49	-43.72	12.76	4.47	82.77
He-BrBr	-15.46	-12.11	-95.94	74.71	-48.80	12.52	9.80	77.68
He(Br_2)-T	-11.83	-4.72	-83.97	59.10	-41.42	11.76	4.70	83.54
He-HF	-12.66	-46.79	-76.26	96.77	-38.94	9.33	34.48	56.19
He-FH	-7.2	-4.74	-51.68	37.53	-26.09	11.32	7.45	81.23
He-HCl	-10.12	-17.12	-65.25	61.68	-30.81	10.94	18.51	70.55
He-ClH	-7.92	-3.26	-62.76	41.56	-32.28	10.71	4.41	84.88
He-HBr	-13.45	-16.91	-74.65	79.03	-25.98	12.81	16.10	71.09
He-BrH	-10.45	-5.35	-72.93	53.38	-35.35	11.78	6.03	82.19
He-HCN	-11.73	-24.87	-68.60	78.27	-26.93	11.15	23.64	65.21
He-NCH	-6.38	-6.84	-43.17	36.82	-19.57	11.31	12.13	76.56
He-CO	-4.24	-2.11	-31.11	23.70	-13.76	11.32	5.63	83.05
He-OC	-6.65	-2.08	-50.41	38.31	-20.83	11.24	3.52	85.24
He-FCl	-8.61	-3.26	-66.21	42.11	-35.97	11.02	4.18	84.80
He-ClF	-19.94	-21.99	-117.57	96.29	-63.21	12.50	13.79	73.71
He-ClBr	-14.06	-8.58	-90.85	69.87	-43.62	12.39	7.56	80.05
He-ClCN	-9.60	-10.72	-78.22	53.00	-45.54	9.74	10.88	79.38
He-ClCCH	-9.69	-5.97	-78.10	51.48	-42.28	10.33	6.37	83.30
He-ClOH	-14.25	-9.36	-94.97	69.55	-49.03	12.02	7.89	80.09
He-ClSH	-11.32	-5.53	-78.79	56.74	-38.90	11.84	5.78	82.38
He-ClCH_3	-9.19	-4.01	-68.90	46.61	-35.49	11.20	4.88	83.92
He-ClSiH_3	-9.07	-3.88	-63.71	47.75	-29.21	11.83	5.06	83.11

[a] $E_{int}^{SAPT} = E_{elst} + E_{ind} + E_{disp} + E_{exch}$.

Table 2. Decomposition analysis of the He(M) complexes (see also Figure 1) according to SAPT(*EDA2*) (see text). The percentage contributions are with respect to $(E_{elst} + E_{ind} + E_{disp})$. Energy values in cm^{-1}.

He(M)	E_{elst}	E_{ind}	E_{disp}	E_{exch}	$\delta E_{int,r}^{HF}$	E_{int}^{SAPT}[a]	%(E_{elst})	%(E_{ind})	%(E_{disp})
HeAr	-4.85	-1.39	-40.74	28.54	-1.64	-20.08	10.32	2.96	86.72
He-HH	-2.62	-0.86	-23.83	17.70	-1.24	-10.85	9.59	3.15	87.26
He(H_2)-T	-1.74	-0.43	-18.42	11.65	-0.75	-9.69	8.45	2.09	89.46
He-NN	-5.15	-1.54	-41.72	33.65	-1.41	-16.17	10.64	3.18	86.18
He(N_2)-T	-6.29	-1.87	-51.21	38.42	-2.32	-23.27	10.59	3.15	86.26
He-ClCl	-12.95	-8.65	-92.45	72.17	-5.31	-47.19	11.36	7.58	81.06
He(Cl_2)-T	-14.95	-4.51	-100.58	81.38	-5.06	-43.72	12.45	3.76	83.79
He-BrBr	-15.46	-11.48	-99.65	84.82	-7.03	-48.80	12.21	9.07	78.72
He(Br_2)-T	-11.83	-3.78	-86.67	65.64	-4.78	-41.42	11.56	3.70	84.74
He-HF	-12.66	-43.62	-79.45	105.31	-8.52	-38.94	9.32	32.14	58.54
He-FH	-7.2	-4.95	-53.60	41.31	-1.65	-26.09	10.95	7.53	81.52
He-HCl	-10.12	-14.31	-67.86	67.10	-5.62	-30.81	10.96	15.51	73.53
He-ClH	-7.92	-2.91	-64.87	46.06	-2.74	-32.28	10.47	3.84	85.69
He-HBr	-13.45	-13.00	-78.02	86.31	-7.82	-25.98	12.88	12.44	74.68
He-BrH	-10.45	-5.13	-75.53	59.75	-3.99	-35.35	11.47	5.63	82.90
He-HCN	-11.73	-22.42	-71.43	84.29	-5.64	-26.93	11.11	21.24	67.65
He-NCH	-6.38	-6.18	-44.65	39.58	-1.94	-19.57	11.15	10.80	78.05
He-CO	-4.24	-1.76	-32.12	26.09	-1.73	-13.76	11.12	4.62	84.26
He-OC	-6.65	-1.78	-52.14	41.21	-1.47	-20.83	10.98	2.94	86.08
He-FCl	-8.61	-3.61	-68.63	47.48	-2.60	-35.97	10.64	4.47	84.89
He-ClF	-19.94	-22.53	-122.31	109.87	-8.30	-63.21	12.10	13.67	74.23
He-ClBr	-14.06	-7.62	-94.49	78.65	-6.10	-43.62	12.10	6.56	81.34
He-ClCN	-9.60	-11.17	-80.82	59.28	-3.23	-45.54	9.44	11.00	79.56
He-ClCCH	-9.69	-6.27	-80.74	57.54	-3.12	-42.28	10.02	6.48	83.50
He-ClOH	-14.25	-9.12	-98.59	78.41	-5.48	-49.03	11.68	7.48	80.84
He-ClSH	-11.32	-4.66	-81.75	63.64	-4.81	-38.90	11.58	4.77	83.65
He-ClCH_3	-9.19	-3.18	-71.32	51.83	-3.63	-35.49	10.98	3.80	85.22
He-ClSiH_3	-9.07	-2.93	-66.00	52.48	-3.69	-29.21	11.62	3.76	84.62

[a] $E_{int}^{SAPT} = E_{elst} + E_{ind} + E_{disp} + E_{exch} + \delta E_{int,r}^{HF}$.

Table 3. Data obtained from the analysis of the $H(\boldsymbol{r})$ and the $\rho(\boldsymbol{r})$ of the He(M) complexes (see also Figure 1). All distances R are in a_0.

	$H(\boldsymbol{r})$		$\rho(\boldsymbol{r})$				
He(M)	$\bar{R}_{\text{He-BCP}}$	DoP(He)[a]	R(BCP)[b]	ρ(BCP)[c]	$\nabla^2\rho$(BCP)[d]	H(BCP)[e]	MEP(BCP)[f]
HeAr	1.1151	0.0359	2.7170	0.0013	0.00586	0.00044	2.00
He-HH	1.1157	0.0897	2.8099	0.00093	0.00459	0.00038	8.56
He(H_2)-T	1.1143	-0.0359	2.9325	0.00068	0.00325	0.00028	-2.28
He-NN	1.1133	-0.126	2.6644	0.0014	0.00674	0.00053	-7.01
He(N_2)-T	1.1160	0.117	2.6866	0.0014	0.00645	0.00049	7.25
He-ClCl	1.1200	0.475	2.5144	0.0022	0.01258	0.00098	28.2
He(Cl_2)-T	1.1146	-0.00897	2.6502	0.0016	0.00807	0.00059	3.19
He-BrBr	1.1209	0.556	2.5246	0.0022	0.01185	0.00090	31.6
He(Br_2)-T	1.1145	-0.0179	2.7718	0.0012	0.00557	0.00043	1.34
He-HF	1.1328	1.62	2.3392	0.0037	0.02084	0.00149	85.5
He-FH	1.1104	-0.386	2.5048	0.0020	0.01204	0.00085	-17.5
He-HCl	1.1242	0.852	2.4943	0.0024	0.01208	0.00090	48.2
He-ClH	1.1162	0.135	2.6122	0.0016	0.00889	0.00071	9.81
He-HBr	1.1228	0.727	2.4720	0.0026	0.01256	0.00092	42.5
He-BrH	1.1177	0.269	2.5941	0.0018	0.00942	0.00075	16.8
He-HCN	1.1263	1.04	2.4210	0.0029	0.01527	0.00111	59.9
He-NCH	1.1090	-0.511	2.6655	0.0014	0.00642	0.00049	-29.6
He-CO	1.1128	-0.170	2.8169	0.00099	0.00413	0.00034	-10.1
He-OC	1.1133	-0.126	2.5617	0.0018	0.00953	0.00070	-5.13
He-FCl	1.1138	-0.0807	2.4825	0.0022	0.01298	0.00089	-1.37
He-ClF	1.1251	0.933	2.3978	0.0030	0.01931	0.00143	50.0
He-ClBr	1.1189	0.377	2.5089	0.0022	0.01246	0.00096	22.9
He-ClCN	1.1221	0.664	2.5411	0.0020	0.01173	0.00094	38.7
He-ClCCH	1.1190	0.386	2.5526	0.0019	0.01113	0.00089	23.4
He-ClOH	1.1198	0.458	2.4877	0.0023	0.01390	0.00106	27.7
He-ClSH	1.1169	0.197	2.5649	0.0019	0.01024	0.00080	13.2
He-$ClCH_3$	1.1145	-0.0179	2.6115	0.0017	0.00874	0.00069	1.52
He-$ClSiH_3$	1.1144	-0.0269	2.6267	0.0016	0.00798	0.00063	0.0288

[a] Calculated by Equation (1).

[b] Distance of the BCP from He.

[c] Electron density (ea_0^{-3}) at the BCP.

[d] Laplacian of the electron density (ea_0^{-5}) at the BCP.

[e] Energy density (hartree a_0^{-3}) at the BCP.

[f] Molecular electrostatic potential (kcal mol^{-1}) at the BCP.

Table 4. Bonding character and percentage contribution of the inductive stabilization energy of the He(M) complexes ranked by a decreasing value of the DoP(He), together with the MEP(BCP).

			%(E_{ind})		Bonding character
He(M)	DoP(He)[a]	MEP(BCP)[b]	SAPT(*EDA1*)	SAPT(*EDA2*)	DISP/IND$^+$
He-HF	1.62	85.5	34.48	32.14	DISP/IND$^+$
He-HCN	1.04	59.9	23.64	21.24	DISP/IND$^+$
He-ClF	0.933	50.0	13.79	13.67	DISP/IND$^+$
He-HCl	0.852	48.2	18.51	15.51	DISP/IND$^+$
He-HBr	0.727	42.5	16.10	12.44	DISP/IND$^+$
He-ClCN	0.664	38.7	10.88	11.00	DISP/IND$^+$
He-BrBr	0.556	31.6	9.80	9.07	DISP/IND$^+$
He-ClCl	0.475	28.2	8.29	7.58	DISP/IND$^+$
He-ClOH	0.458	27.7	7.89	7.48	DISP/IND$^+$
He-ClCCH	0.386	23.4	6.37	6.48	DISP/IND$^+$
He-ClBr	0.377	22.9	7.56	6.56	DISP/IND$^+$
He-BrH	0.269	16.8	6.03	5.63	DISP/IND$^+$
He-ClSH	0.197	13.2	5.78	4.77	DISP
He-ClH	0.135	9.81	4.41	3.84	DISP
He(N_2)-T	0.117	7.25	4.21	3.15	DISP
He-HH	0.0897	8.56	5.44	3.15	DISP
HeAr	0.0359	2.00	3.60	2.96	DISP
He(Cl_2)-T	-0.00897	3.19	4.47	3.76	DISP
He-$ClCH_3$	-0.0179	1.52	4.88	3.80	DISP
He(Br_2)-T	-0.0179	1.34	4.70	3.70	DISP
He-$ClSiH_3$	-0.0269	0.0288	5.06	3.76	DISP
He(H_2)-T	-0.0359	-2.28	3.77	2.09	DISP
He-FCl	-0.0807	-1.37	4.18	4.47	DISP
He-OC	-0.126	-5.13	3.52	2.94	DISP
He-NN	-0.126	-7.01	3.70	3.18	DISP
He-CO	-0.170	-10.1	5.63	4.62	DISP
He-FH	-0.386	-17.5	7.45	7.53	DISP/IND$^-$
He-NCH	-0.511	-29.6	12.13	10.80	DISP/IND$^-$

[a] Calculated by Equation (1).

[b] Molecular electrostatic potential (kcal mol^{-1}) at the BCP.

Table 5. Data obtained from the analysis of the CD function of the He(M) complexes together with estimated Dop(He) values.

He(M)	-Δq (z = 0) [a]	R(IB)[b]	-CT(IB)[c]	DoP(He)[d]
He-HF	9.35	2.312	1.08	1.62
He-HCN	6.65	2.387	0.66	1.04
He-ClF	5.21	2.366	0.74	0.933
He-HCl	5.08	2.463	0.52	0.852
He-HBr	4.47	2.426	0.69	0.727
He-ClCN	4.07	2.508	0.36	0.664
He-ClCl	2.67	2.475	0.40	0.475
He-ClOH	2.46	2.452	0.49	0.458
He-ClCCH	2.21	2.517	0.33	0.386
He-ClBr	2.04	2.466	0.44	0.377
He-ClSH	0.92	2.521	0.33	0.197
He-ClH	0.58	2.571	0.28	0.135
He-HH	0.66	2.779	0.10	0.0897
He(Cl_2)-T	-0.36	2.565	no CT	-0.00897
He-$ClCH_3$	-0.52	2.575	no CT	-0.0179
He-$ClSiH_3$	-0.51	2.574	no CT	-0.0269
He(H_2)-T	-0.28	2.890	no CT	-0.0359
He-NCH	-3.63	2.624	no CT	-0.511

[a] Δq (me) at z = 0 on the CD curve.

[b] Distance (a_0) of the IB from He.

[c] Charge (me) transferred from He to M at the IB.

[d] Calculated by Equation (1).