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Van der Waals Interaction Energies of Helium, Neon, and Argon with Naphthalene

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The Hartree−Fock and the Hartree−Fock−Clementi−Corongiu methods (Clementi, E.; Corongiu, *G. Theochem.* **2001**, *543*, 39) are selected to compute van der Waals potentials in the systems He_2, HeNe, HeAr, Ne_2, NeAr, Ar_2, benzene−He, benzene−Ne, and benzene−Ar and to determine the parameters needed for HF-CC computations of van der Waals interaction energies of naphthalene−He, naphthalene−Ne, and naphthalene−Ar; shallow double wells are predicted for the above naphthalene systems.

1. Introduction

The van der Waals interactions for the systems C_6H_6−He, C_6H_6−Ne, and C_6H_6−Ar have been the subject of a number of publications[1−9] reporting both laboratory and computational data. In this work, we present a study on the van der Waals potentials for the above systems and for larger ones, specifically, $C_{10}H_8$−He, $C_{10}H_8$−Ne, and $C_{10}H_8$−Ar, the largest systems, to our knowledge, for which post-Hartree−Fock computations of van der Waals potential energies have been performed.

We use a relatively new method, the Hartree−Fock−Clementi−Corongiu, HF-CC, tested for neutral atoms, ground and excited states,[10] and a large sample of molecules.[11−13] We recall that this method is a semiempirical post Hartree-Fock, HF, technique proposed to compute the total correlation energy correction, thus also the van der Waals interactions. The HF-CC method scales the Hartree-Fock energy or the generalized Hartree-Fock energy[14−16] in the case of near degeneracy (static correlation). Data obtained from the HF wave function, like the bond order and the gross atomic charges, are used to construct the HF-CC functionals needed to compute scaling factors for the HF integrals. The HF-CC approach assumes an HF function as its zero-order approximation, and as a consequence, rather realistic basis sets not far from the HF limit are needed; note that non adequate basis sets would yield not only erratic results for the above-mentioned HF data, but also a zero-order function not consistent with the HF-CC assumptions. Full details of the HF-CC method, as used in this work, are given in ref 13.

The basis set used in the following computations is a geometrical basis set[17,18] of triple-ζ type (or better), augmented with polarization functions, specifically, (10,1/3,1) for H, (7,1/3,1) for He, (13,7,1/3,3,1) for C, (13,10,1) for Ne, and (17,12,1) for Ar. With this basis set, the HF and the HF-CC energies (in parentheses) for the $H(^2S)$, $He(^1S)$, $C(^3P)$, $Ne(^1S)$, and $Ar(^1S)$ atoms are −0.49999, (−0.49999), −2.86160, (−2.90371), −37.68715, (−37.844949), −128.5470 (−128.93821), and −526.81724 hartrees, (−527.54344 hartrees), respectively; note that the energy difference between the HF and the HF-CC values agrees to the fourth decimal figure in hartrees with accurate correlated energies for atomic systems.[19] Larger basis sets would be preferable; however, due to our computer hardware limitations, computations with a larger basis set would be unfeasible for the large molecules we are interested in. We recall that the near to HF limit values[17] for $He(^1S)$, $C(^3P)$, $Ne(^1S)$, and $Ar(^1S)$ are −2.86160, −37.68862, −128.54710, and −526.81751 hartrees.

The HF-CC model[13] divides the correlation energy of a molecule into the sum of the correlation energy of the component atoms (at dissociation) and a "leftover", the "molecular extra correlation energy".[20] The correlation energy of the atom "*a*" at infinite separation is obtained by scaling the HF integrals with the factors

$$[1 - \alpha_\nu S_\nu,(Z,a)^{\beta_\nu}/n^{\gamma_\nu}] \qquad (1)$$

defined in refs 10 and 11; $S_\nu(Z,a)$ designates the atomic functional for the atom "*a*" with "*n*" electrons, and the index $\nu = 1, 2, 3$, and 4 specifies, respectively, the nuclear-electron, the kinetic, the coulomb, and the exchange HF integrals to be scaled. The atomic semiempirical constants α, β, and γ are determined once for always for atoms and ions.[10] However, when "atom *a* is in the molecule", the scaling factors of eq 1 assume the modified form

$$[1 - \alpha_\nu \mathrm{S}_\nu(\mathrm{Z},\mathrm{Z}')_a{}^{\beta_\nu}/n^{\gamma_\nu}] \qquad (2)$$

where $S_\nu(Z,Z')_a$ designates the molecular functional for atom *a* with atomic number *Z* and gross charge *Z*′, the latter being obtained from the HF function (Mulliken's gross charge[21]). The HF-CC molecular functional is given below:

$$S_\nu(Z,Z')_a = S_\nu(Z,a) + (Z'_a - Z_a)\Delta S(Z,a) + k(Z_a)\sum_b B_{a,b}R_{ab}(r_{ab}{}^{-3}) + w(Z_a) \qquad (3)$$

where ΔS designates the difference between the neutral atom value for $S_\nu(Z\ a)$ and its corresponding ionic values $S_\nu(Z,a^+)$ or $S_\nu(Z,a^-)$; see ref 13 for the full definition of these terms. Further, for the atoms *a* and *b* in a molecule, we designate the bond order matrix element as B_{ab}, the internuclear separation as r_{ab}, and the sum of the covalent radii for the atoms *a* and *b* (taken

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from standard literature) as R_{ab}. Finally, we indicate as $w(Z_a)$ the van der Waals term:

$$w(Z_a) = \sum_b \{k_1(Z_a)\exp(-r_{ab}) + [k_2(Z_a)/r_{ab}^{\ 6} + k_3(Z_a)/r_{ab}^{\ 8}][I_a I_b \alpha_a \alpha_b/(I_a + I_b)] + B_{a,b}\} \quad (4)$$

where I_a, I_b, α_a, and α_b are the first ionization potentials and the polarizabilities of atoms a and b, respectively. In eq 4, we have included the term $1/r_{ab}^8$ (not present in ref 13, but often suggested; see, for example, studies by Dunker and Gordon,[22] Duquette et al.,[23] early applications for example by Kolos et al.,[24] and more recent work by Aziz[25]).

Physically, with the modification from the atomic scaling factors in eq 1 to the molecular scaling factors in eq 2, it is recognized that in a molecule there might be charge transfer, such as that for ionic bonds; therefore, there is need of a correction proportional to the charge transferred (either lost or gained) given by the $(Z' - Z)$ term of eq 3. In addition, the electronic structure of atom a (in the molecule) is modified, due to hybridization, thus the need of a term containing the bond order, which we assume to be proportional to the atom's electronic structure rearrangement, charge-transfer apart. Finally, there can be van der Waals forces acting on the atoms; with eq 4, we assume that the van der Waals interaction energy is pairwise, to a first approximation.

The HF-CC molecular semiempirical constants are $k(Z_a)$, $k_1(Z_a)$, $k_2(Z_a)$, and $k_3(Z_a)$. For approximated computations yielding computed atomization energies within 3−4 kcal/mol from experimental values, $k(Z_a)$ is proportional to the number of valence electrons via a simple three-parameter expression;[13] for more accurate determinations, more parameters are needed.[13] The van der Waals term is constructed to allow flexibility in the determination of the shape of the potential energy surface, an important feature for potentials compatible with a variety of laboratory data (see for example ref 25). The constant $k_1(Z_a)$ can be set equal to zero if one is interested mainly in the region near equilibrium.

To complete our definition, we recall that the bond order B_{ab} for the atoms a and b in a m-atom molecule is

$$B_{ab} = \sum_{i\in a}\sum_{j\in b}(P_{ij}S_{ij})(P_{ji}S_{ji}) \quad (5)$$

where $a = 1, ..., m$ and $b = 1, ..., m$ and where

$$P_{ij} = 2\sum_k c_{ik}c_{kj} \quad (6)$$

are the density matrix elements, with c_{ik} being the scf coefficients and S_{ij} the overlap integrals.

Below, in sections 2 and 3, we report a study on He_2, Ne_2, Ar_2, HeNe, HeAr, NeAr, C_6H_6−He, C_6H_6−Ne, and C_6H_6−Ar to obtain the van der Waals parameters, eq 4, used for the computations on naphthalene systems.

2. He_2, HeNe, HeAr, Ne_2, NeAr, and Ar_2

The van der Waals interactions for the noble gas diatomics have been the subject of intense studies, and the relative potential energy curves are well determined.[25−29] As discussed in ref 13, the He_2, Ne_2, and Ar_2 minima and equilibrium internuclear distances are well reproduced by the HF-CC approach. The $k_2(Z_a)$ parameters in eq 4, used in this work for the determination of the van der Waals potential in He_2, Ne_2, and Ar_2, have the values 21.2045, 102.9269, and 132.4, respectively. However, for Ar_2, the computed HF-CC minimum is shifted to larger distance (by 0.15 bohr) relative to laboratory data (see ref 25); the correct value is obtained with $k_2(Ar_a) = 100.0$ and $k_3(Ar_a) = 1684.0$. In Figure 1, we report the HF-CC potential energy curves for He_2, Ne_2, and Ar_2 obtained with the above constants; the HF-CC computed values are indicated with open circles, and the experimental determined minima are indicated with a full circle. One can verify that not only the energy minima, but also the internuclear distances, are in good agreement with the laboratory data.[25−27] The same constants are used to compute the van der Waals interaction energies for the mixed systems He−Ne, He−Ar, and Ne−Ar, and the corresponding potential energy curves are given in Figure 1. Again, we note that the overall agreement between HF-CC computations at the energy minima and laboratory data[28,29] is satisfactory; note, in addition, that the above computations verify the transferability of the $k_2(Z_a)$ and $k_3(Z_a)$ parameters.

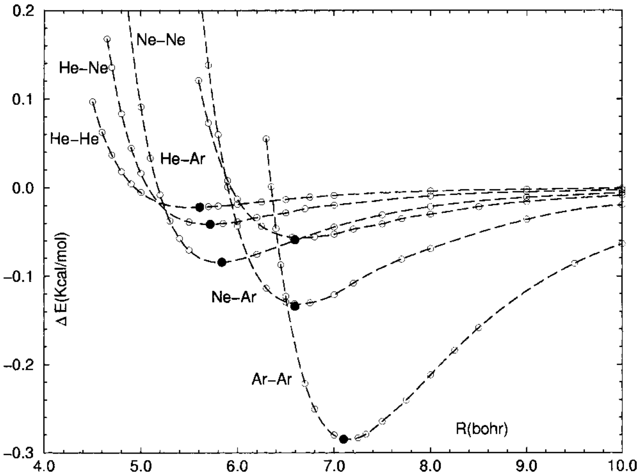

Figure 1. HF-CC van der Waals potential. Open circles for HF-CC computations, full circles for experimental values.

3. Van der Waals Interaction Energies of He, Ne, and Ar with Benzene

The van der Waals interaction energies of He, Ne, and Ar with C_6H_6 have been analyzed in a number of papers;[1−8] the energetically most favorable approach of a noble gas atom to the benzene molecule is found to be along a line perpendicular to the C_6H_6 molecular plane and passing through the center of the ring. However, different from the case of the systems He_2, HeNe, HeAr, Ne_2, NeAr, and Ar_2, the available laboratory and computer simulation data for the C_6H_6 interactions energies are still under investigation,[9] and for the equilibrium geometry, one is confronted with a somewhat extended range of internuclear distances and values for the energy. For C_6H_6−Ar, there is a recent and accurate ab initio study[2] with extensive mapping of the van der Waals potential energy surface. Nevertheless, it is somewhat difficult to select a consistent set of targets for the fitting of the needed van der Waals parameters $k_2(H)$ and $k_2(C)$ for the H and C atoms, respectively. With the values $k_2(H) = 0.0$ and $k_2(C) = 30.0$ for the H and C atoms, we obtain the potential energy curves labeled A given in Figure 2; in the figure, we report the literature's range of values both for the energy minima (vertical bar) and for the internuclear distances (horizontal bar); as in Figure 1, the open circles indicate the computed HF-CC values. The HF-CC computed van der Waals interactions are 0.22_{73} kcal/mol at 6.16_5 bohr for C_6H_6−He, 0.46_{16} kcal/mol at 6.50_1 bohr for C_6H_6−Ne, and 1.12_{43} kcal/mol at 6.73_3 bohr for C_6H_6−Ar. With the above notation, we

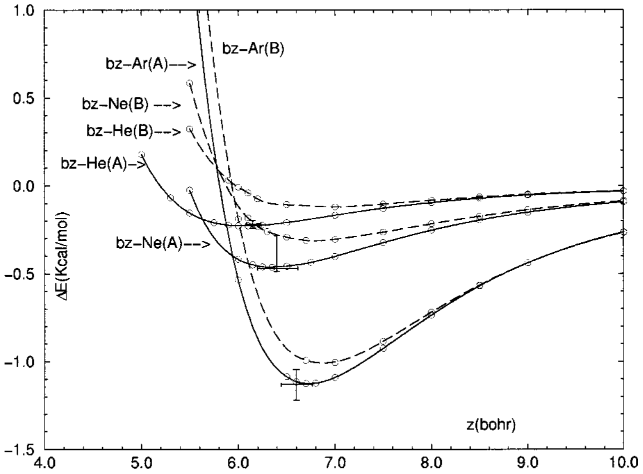

Figure 2. Van der Waals potentials for He, Ne, and Ar approaching C_6H_6 along lines perpendicular to the molecular plane.

indicate that no more than the first two decimal figures are assumed reliable on the basis of the data reported in Figure 1. Equilibrium distances and energy minima from literature data[1,3,9] for C_6H_6−He are in the ranges 6.085−6.236 bohr and 0.1973−0.2398 kcal/mol; for C_6H_6−Ne, the ranges are from 6.198 to 6.614 bohr and from 0.4312 to 0.4866 kcal/mol, and for C_6H_6−Ar, the ranges are from 6.690 to 6.727 bohr and from 1.0446 to 1.2176 kcal/mol. We conclude that the agreement of the HF-CC computation with the literature data is reasonable.

We have used the above parameters also to compute the van der Waals potential for the rare gas atom placed on a line perpendicular to the molecular plane and crossing the midpoint of a C−C bond. As expected, the interaction decreases relative to approach A; these new potential energy curves are labeled with the letter B, as shown in Figure 2.

The HF and the HF-CC total molecular energies for C_6H_6 are −230.7739 and −232.2385 hartrees, respectively, with corresponding atomization energies of 1035.16 kcal/mol for HF and 1360.93 kcal/mol for HF-CC, to be compared with the laboratory value[12] of 1360.85 kcal/mol (see ref 12 for the zero point energy and thermal corrections); the basis set superposition error for the rare gas complexes is very small and about 0.001 kcal/mol. Note that in a strict respect of the spirit of the HF-CC assumptions, the computation of the atomization energy assumes that (1) we have computed “the Hartree-Fock energy”, i.e., the Hartree-Fock limit energy, and (2) the HF-CC adds the full correlation energy correction to the HF energy. Actually our HF energy −230.7739 hartree for C_6H_6 is not at its HF limit value, as noted in the introductory section. Indeed, we have computed the HF energy for C_6H_6 with a larger basis set, with additional d and f polarization functions (see ref 12) obtaining an HF atomization of 1042.08 kcal/mol, thus a value 6.04 kcal/mol larger than the 1035.16 kcal/mol reported above. The 1360.93 kcal/mol value given above for the HF-CC atomization energy includes a correction of 6.04 kcal/mol—namely, it is corrected for “basis set deficiencies”.

We conclude that our computations yield realistic energy values also for the six C_6H_6 component atoms, for the rare gas atoms, and for the C_6H_6 atomization energy; this feature is important since it allows comparing total energies for different molecular systems. Note that past literature of quantum chemical

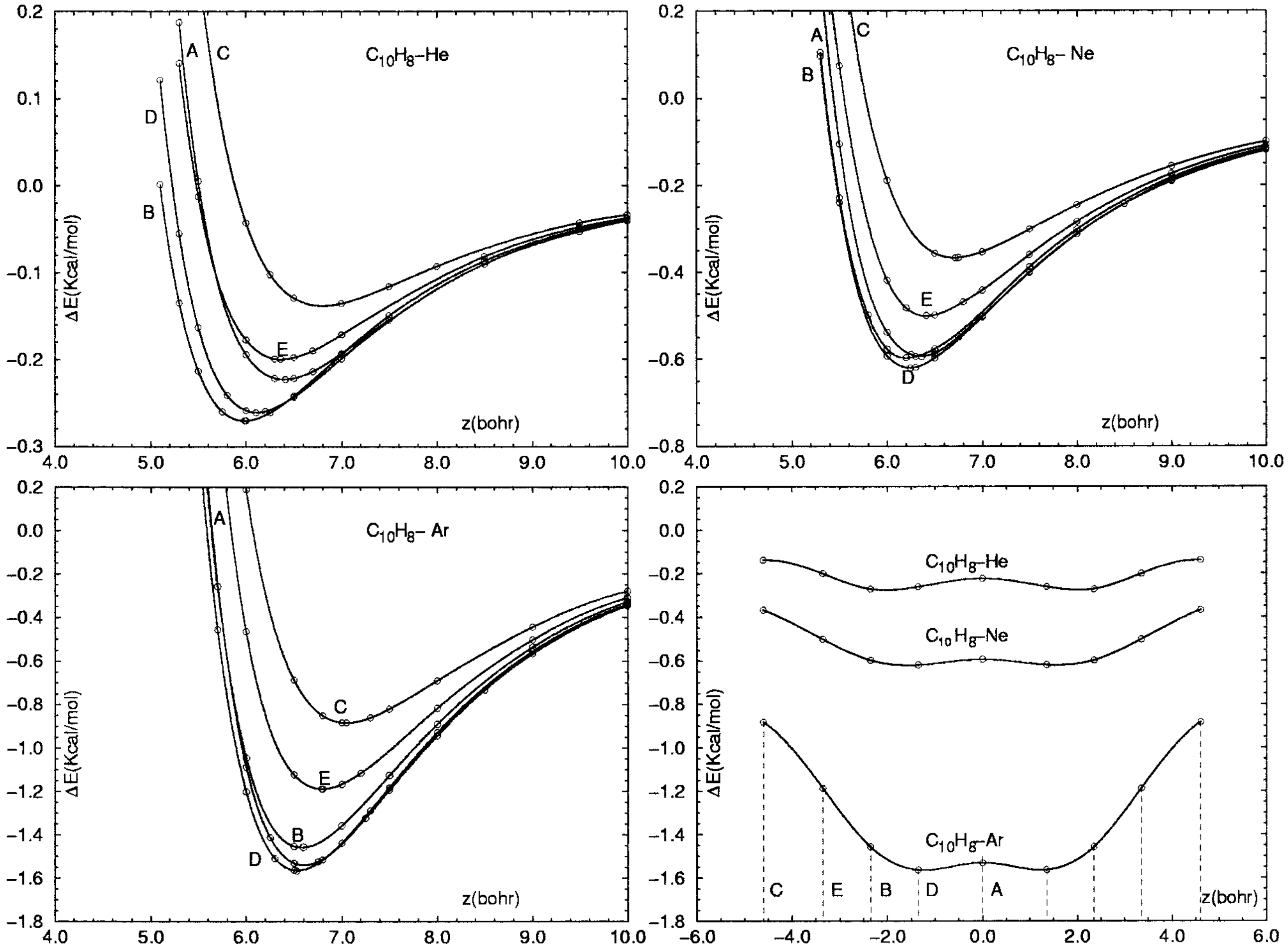

Figure 3. Van der Waals interaction energies for naphthalene along lines A, B, C, D, and E and shallow double minima (see text).

TABLE 1: Total HF and HF-CC Energies (hartrees), van der Waals Potential Energy (kcal/mol), and *z* Value (bohr) for the Minima of Figure 3

approach	E(HF)	E(HF-CC)	v.d.W	z
line A for He	−386.326590	−388.780681	−0.2227	6.4110
line B for He	−386.326461	−388.780756	−0.2700	5.9849
line C for He	−386.326672	−388.780545	−0.1374	6.7879
line D for He	−386.326500	−388.780742	−0.2608	6.1030
line E for He	−386.326576	−388.780644	−0.1994	6.3628
line A for Ne	−512.011735	−514.815776	−0.5947	6.3628
line B for Ne	−512.011612	−514.815779	−0.5965	6.1975
line C for Ne	−512.011950	−514.815415	−0.3677	6.7171
line D for Ne	−512.011663	−514.815818	−0.6208	6.2447
line E for Ne	−512.011756	−514.815626	−0.5004	6.4100
line A for Ar	−910.280449	−913.422498	−1.5302	6.5045
line B for Ar	−910.280812	−913.422379	−1.4555	6.5990
line C for Ar	−910.281612	−913.421465	−0.8823	7.0477
line D for Ar	−910.280616	−913.422553	−1.5647	6.5281
line E for Ar	−910.281164	−913.421952	−1.1879	6.7879

computations for van der Waals studies has often neglected to include correlation energy.

4. Van der Waals Interaction Energies with Naphthalene

With the above van der Waals constants for He, Ne, Ar, H, and C, we are in position to explore the van der Waals interaction energy in systems larger than C_6H_6, specifically, the naphthalene complexes $C_{10}H_8$−He, $C_{10}H_8$−Ne, and $C_{10}H_8$−Ar, the main goal of this work.

In the following, we assume that the naphthalene skeleton is in the *xy* plane, with the origin of the coordinate system located on the midpoint of the central carbon−carbon bond, the one shared by the two rings, hereafter indicated as C−C central bond, and with the *x* axis containing the C−C central bond. By analogy to the van der Waals study for benzene, we have computed the van der Waals energies for rare gases approaching naphthalene along the *z* axis; this line of approach is labeled A. The corresponding potential energy curves are reported in Figure 3 for $C_{10}H_8$−He, $C_{10}H_8$−Ne, and $C_{10}H_8$−Ar. As in the previous figures, the open circles designate HF-CC computed values. The HF-CC computed van der Waals energy minima for the $C_{10}H_8$ complexes are 0.22_{25} kcal/mol for He at 6.41_{00} bohr, 0.59_{38} kcal/mol for Ne at 6.36_{28} bohr, and 1.52_{99} kcal/mol for Ar at 6.50_{45} bohr. We assume that the reliability of this computation with naphthalene is equivalent to the one reported for benzene.

We have extended the computation in order to obtain additional information on the potential energy surfaces. In the *xz* plane with $x = 0.0$, perpendicular to the $C_{10}H_8$ molecular plane, we have considered four additional linear directions of approach, each one parallel to the *z* axis; we designate as B, C, D, and E the lines with $y = 2.3545$, 4.6071, 1.3545, and 3.3545 bohr, respectively, corresponding to a line through the center of the ring, to a line bisecting the midpoint of the most external C−C bond, and to two lines equidistant and at the two sides of the line B (ring center). For each line of approach, we have computed a few positions for the rare gas atom in order to determine its energy minimum; the corresponding potential energy curves and the computed HF-CC points are given in Figure 3.

For $C_{10}H_8$−He, the computed van der Waals minima are 0.27_{00} kcal/mol at $z = 5.98_{49}$ bohr for line B, 0.13_{74} kcal/mol at $z = 6.78_{79}$ bohr for line C, 0.26_{08} kcal/mol at $z = 6.10_{30}$ bohr for line D, and 0.19_{94} kcal/mol at $z = 6.36_{28}$ bohr for line E. The van der Waals interaction energies for these line of approach are reported in Figure 3. In Table 1, we report the Hartree−Fock and the HF-CC total energies (in hartrees) and the van der Waals interaction energies (in kcal/mol), computed at the minimum positions (*z* in bohr). It appears that the deepest minimum is found for the line passing through the center of the ring (B line), thus yielding a shallow double minimum with a barrier centered above the central C−C bond (A line); see top-left and bottom-right insets of Figure 3. Further, the interaction at the midpoint of the central C−C bond (A line) is stronger than the interaction at the midpoint of the lateral C−C bond (C line).

The barrier hight is computed as $0.27_{00}-0.22_{27} = 0.04_{73}$ kcal/mol; considering the uncertainties in the parametrization, we would propose a value of 0.05 kcal/mol with an error up to 0.01 kcal/mol. This shallow double minimum feature is expected to survive also in the $C_{10}H_8$−Ne and $C_{10}H_8$−Ar system; note, however, that on one hand, the larger size of Ne and Ar atoms relative to He, might average out the interactions at the two positions, A and B, flattening the double minimum, but on the other hand, the increased strength of the interaction from He to Ar might enhance the depth of the double minimum.

From Figure 3 and Table 1, we see that the minima for the lines B, C, D, and E for $C_{10}H_8$−Ne are at 6.19_{75} bohr with 0.59_{65} kcal/mol, 6.71_{71} bohr with 0.36_{77} kcal/mol, 6.24_{47} bohr with 0.62_{08} kcal/mol, and 6.41_{00} bohr with 0.50_{02} kcal/mol, respectively. The minima for the lines B, C, D, and E for $C_{10}H_8$−Ar are at 6.59_{90} bohr with 1.45_{55} kcal/mol, 7.04_{77} bohr with 0.88_{23} kcal/mol, 6.52_{81} bohr with 1.56_{47} kcal/mol, and 6.78_{79} bohr with 1.18_{79} kcal/mol, respectively. For the neon and argon complexes, the barrier heights are 0.02_{61} and 0.03_{45} kcal/mol, respectively.

The interaction energies of the benzene complexes are somewhat smaller than those in the corresponding naphthalene complexes; in turn, the latter are intermediate between benzene and graphite;[9] for example, for the helium complexes, we have the trend 0.22, 0.27, and 0.34 kcal/mol for benzene, naphthalene, and graphite,[9] respectively. Note that in Table 1, the HF energies correspond to repulsive interactions; the computed HF energies for the isolated systems, $C_{10}H_8$, He, Ne, and Ar, are −383.465193, −2.861608, −128.547043, and −526.817240 hartrees, respectively (this holds also for all the HF interaction energies of the geometries considered in Figure 3).

Before concluding, we add a few energy data: the HF and the HF-CC total energies for $C_{10}H_8$ are −230.7739 E_h and −232.2385 E_h respectively, and the corresponding atomization energies are 1627.51 and 2160.95 kcal/mol, respectively (see ref 12 for the zero-point energy and thermal correction) to be compared with the laboratory value of 2160.97 kcal/mol; these data differ slightly from these previously reported[13] due to improved parameter optimization and a different choice among optional features in our code. The value of 2160.95 kcal/mol for the atomization energy includes a correction for "basis set deficiencies" of 10.43 kcal/mol.

5. Conclusions

We have reported computations based on the HF-CC model, namely, with the inclusion of correlation energy, for van der Waals interaction potential energies in relatively simple (diatomic), intermediate *(*C_6H_6−X), and larger than usual *(*$C_{10}H_8$−X*)* molecular systems. For the component atoms of the van der Waals complexes, the computed HF energies are near to the HF limit and the HF-CC energies add a correlation correction close to the best available atomic data.[19] The computed atomization energies from the HF-CC model for the C_6H_6 and $C_{10}H_8$ systems[12,13] are in excellent agreement with the corresponding laboratory data. By computing the van der Waals potential energies for He_2, HeNe, HeAr, Ne_2, NeAr, Ar_2, C_6H_6−He, C_6H_6−Ne, and C_6H_6−Ar, we have provided examples on the applicability of HF-CC method to van der Waals studies and on the transferability of the van der Waals parameters needed to compute van der Waals potentials for example in large hydrocarbons. A shallow double minimum with the barrier centered over the midpoint of the central C−C bond is among the predictions of this work; we look forward laboratory data to confirm this computational suggestion.

Finally, we stress that whereas today's post-HF computations require, in general, large amount of computer time, the HF-CC method is no more expensive than Hartree-Fock computations;[12−13] indeed, all the computations reported in this work have been performed on personal computers. It seems realistic to look forward to computations of van der Waals potentials for molecular complexes notably larger than those considered in the past, thus moving this field into the large molecules arena.

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