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On the nature of copper binding to benzene

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Abstract: Adsorption of copper atom on benzene surface has been studied at the *ab initio* MP2 and CCSD(T) theory levels. CCSD(T)/CBS binding energies of the copper atom adsorbed on hollow, top, and bridge positions are 16.77, 19.27 and 21.08 kJ/mol, respectively. Adsorption at the bridge position represents the most stable structure of the Cu-benzene complex with charge transfer from benzene to the copper atom playing a key role.

Keywords: Cu-benzene complex, correlation method, charge-transfer, benchmark CCSD(T)/CBS

Introduction

Weak van der Waals interaction between metal atoms and aromatic molecules is interesting from several points of view. One of the aspects is the absorption of aromatic molecules on metal surface. This is very important for understanding processes in surface science, heterogenous catalysis (Ago et al., 2012; Nieminen et al., 2008; Syomin et al., 2001), or molecular electronics (Cho et al., 2011; Cho, Choi and Kim, 2011; Heath and Ratner, 2003). On the other hand, interaction of graphene with metal atoms leads to formation of hybrid systems with application in sensing, catalysis, nanoelectronics, or hydrogen storage (Baby et al., 2010; Hong et al., 2010; Li et al., 2010a, 2010b; Scheuermann et al., 2009; Shan et al., 2010; Xiong et al., 2010, Singla et al., 2021). Hydrogen storage utilizes two different mechanisms (Malček and Bučinský, 2020): dissociation of molecular hydrogen by the host material and chemisorption of atomic hydrogen; and physisorption of molecular hydrogen on host material by weak van der Waals forces.

Theoretical calculations can provide essential information on the interaction between various metals and aromatic molecules or graphene surface. The description of this interaction is complicated due to the electronic structure of metals, which is affected by relativistic effects (Bučinský et al., 2011) and static and dynamic correlation requiring computational and time demanding methods to compute even simple systems.

Our previous study focused on interactions in Ag-benzene and Au-benzene complexes (Granatier et al., 2011). Charge transfer from benzene to the gold atom plays an important role in Au-benzene complexes. On the other hand, silver interacts with benzene by dispersion force. Thus, the silver atom preferred adsorption site is the center of the benzene ring, while the most stable structure of the Au-benzene complex is achieved by adsorption of the gold atom on the direct carbon atom or C—C bond.

In previous similar theoretical works (Bilić et al., 2006; Caputo et al., 2007; Chan, Neaton and Cohen, 2008; Giovannetti et al., 2008; Khomyakov et al., 2009; Manadé et. al., 2015), the interaction of paramagnetic copper with the carbon surface was calculated mostly at the DFT level. As copper is expected to be adsorbed on the carbon surface by a weak van der Waals bond, the DFT method may not provide correct description of this interaction. Therefore, high accuracy wave function theory (WFT) methods such as correlation MP2 and CCSD(T) were used in this study. The high computational demand of these methods allowed only simple systems to be calculated. As adsorption of the copper atom on a benzene molecule represents a very simple model for the description of copper atom adsorption on graphene surface, MP2 and CCSD(T) methods can be applied to obtain benchmark data and compare them with results calculated at the DFT theory level. The Cu-benzene complex was studied to provide better understanding of the nature of the bond between copper and the carbon surface.

Computational methods

Benchmark calculations of the Cu-benzene complex were performed using the spin-adapted CCSD(T) method with restricted closed-/open-shell reference function (Heckert et al., 2006; Neogrády and Urban, 1995; Urban, Neogrády and Hubač, 1997; Watts, Gauss and Bartlett, 1993) and the less demanding MP2 method (Møller and Plesset, 1934). The $3p^6 3d^{10} 4s^1$ shell of the copper atom and all electrons in benzene except for $1s^2$ electrons of the carbon atoms were explicitly correlated in correlation MP2 and CCSD(T) calculations.

Relativistic effects have been included using the scalar one-component Douglas-Kroll-Hess approximation (Douglas and Kroll, 1974; Hess and Chandra, 1987). All relativistic MP2 and CCSD(T) calculations were performed with two various types of relativistic all-electron basis sets. Both used basis sets provide high accuracy results for molecular properties such as ionization potential, electron affinity, electrical moments, or polarizabilities and are useful in calculations of binding energies of noncovalent interacting Cu-benzene complexes. The aug-cc-pVXZ-DK basis sets (Balabanov and Peterson, 2005, 2006; Dunning, 1989; Kendall, Dunning and Harrison, 1992) represent the first basis set type and are useful for benchmark calculations. The ANO-RCC basis set (Roos et al., 2004, 2005) was used to understand the interaction between the copper atom and the benzene molecule and for comparison with previous results (Granatier et al., 2011). The advantage of this basis set is that it is available for various degrees of contraction. CCSD(T) calculations were performed using ANO-RCC-VDZP and ANO-RCC-VTZP basis sets, and the MP2 binding energies were also computed using the ANO-RCC-VQZP basis set.

Benchmark binding energies were evaluated at the approximate CCSD(T)/CBS theory level, where the difference between CCSD(T) and MP2 binding energies calculated in the small basis set is added to the MP2/CBS biding energy (Jurečka and Hobza, 2002). MP2 binding energy in the complete basis sets was obtained using the Halkier's extrapolation scheme (Halkier et al., 1998) from MP2 calculations in finite basis sets. While the less demanding and well-parallelizable MP2 calculations are performed in large basis sets, the highly demanding CCSD(T) calculations are computed in small basis sets which allows for faster completion of the basis set for the difference between the correlation CCSD(T) and MP2 energies convergences compared with the MP2 and CCSD(T) correlation energies themselves. CCSD(T)/CBS binding energies and equilibrium distance between the copper atom and benzene surface were obtained employing the aug-cc-pVXZ-DK and ANO-RCC-VXZP basis sets. Although the ANO-RCC basis set does not meet the requirements for extrapolation to an infinite basis set, it provides results comparable to standard extrapolation techniques (Granatier, 2017). On the other hand, the aug-cc-pVXZ-DK basis sets are standardly used to evaluate energies in the complete basis set.

All calculated WFT binding energies were treated for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise correction (Boys and Bernardi, 1970). MP2 as well as CCSD(T) binding energies were calculated using the OpenMolcas program package (Fdez Galván et al., 2019).

DFT calculations were performed with an empirical D3 correction term describing the dispersion energy (Grimme et al., 2010). According to the suggestions of the authors, TPSS (Tao et al., 2003) and PBE (Perdew, Burke and Ernzerhof, 1996, 1997) functionals with the def2-QZVP basis set (Weigend and Ahlrichs, 2005) were used. DFT-D3 calculations were done using the ORCA program package (Neese, 2012).

The structure of benzene was optimized at the MP2/cc-pVTZ level and was taken from our previous papers with C—C and C—H bond lengths equal to 1.394 Å and 1.082 Å, respectively (Granatier et al., 2011, 2013; Lazar et al., 2014). The geometry of benzene was assumed to be frozen in all subsequent WFT calculations. The copper metal atom was modeled as being adsorbed at one of three different positions: (h) the 'hollow' site above the center of the aromatic ring, (t) a 'top' site directly above a C atom, and (b) a 'bridge' site above the midpoint of a C—C bond. Each bonding position leads to a different nature of the bond. Bond lengths of the studied complexes correspond to the distance between the metal atom and the plane of the benzene ring.

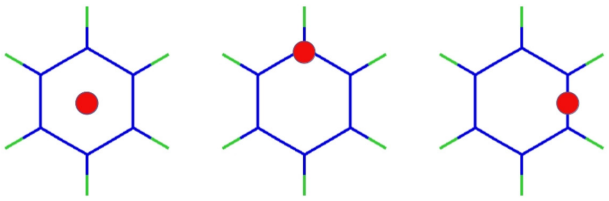

Fig. 1. Benzene molecule; three potential sites for metal atom adsorption: a) hollow, b) top, and c) bridge.

Results

All relativistic MP2 and CCSD(T) binding energies and the corresponding equilibrium distances calculated with ANO-RCC-VXZP (X = T, Q) and aug-cc-pVXZ-DK (X = D, T) basis sets are collected in Tab. 1. The relativistic BSSE corrected MP2/ANO-RCC-VTZP and CCSD(T)/ANO-RCC-VTZP potential energy curves for Cu-benzene with copper adsorbed at the hollow, top, and bridge positions are collected in Fig. 2.

Correct description of the Cu-benzene complex requires the use of correlation methods. The ROHF binding energy curves are repulsive for all three structures, but the inclusion of electron correlation leads to the appearance of an energy minimum. However, the correlation MP2 and CCSD(T) methods provide a different picture of the inter-

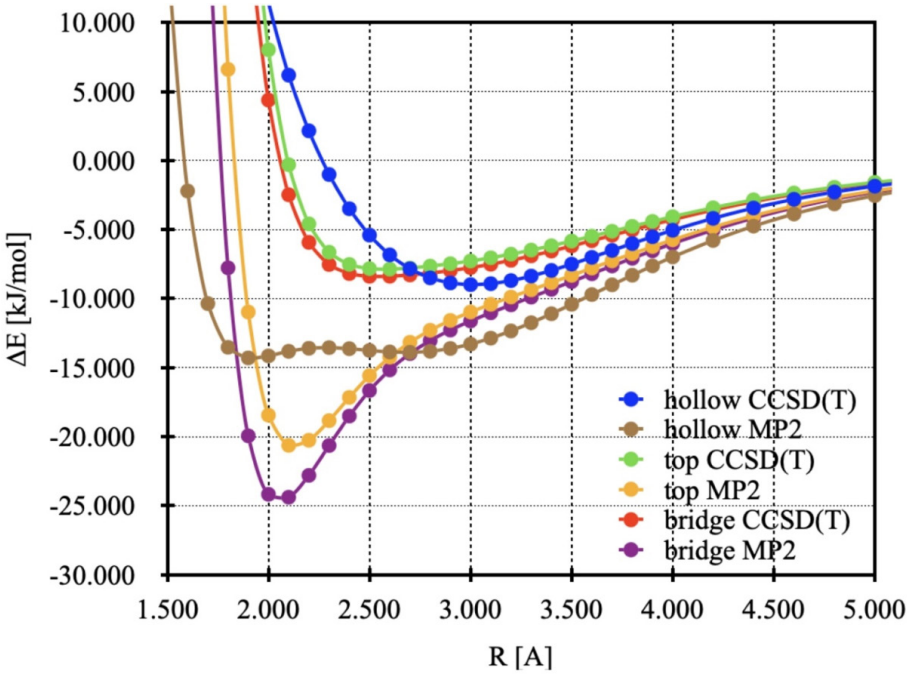

Fig. 2. DKH relativistic BSSE corrected CCSD(T)/ANO-RCC-VTZP and MP2/ANO-RCC-VQZP potential energy curves for Cu-benzene complex with copper adsorbed at the hollow, top, and bridge positions. The MP2 curve shows a double minimum. This minimum has no physical meaning and is the result of BSSE correction together with the properties of the ANO-type basis set.

Tab. 1. Extrapolated binding energies, Δ*E* [kJ/mol], and optimal bond lengths, R (in terms of the shortest distance between the copper atom and the benzene surface) [Å], for Cu-benzene complex calculated at the DKH-MP2 and DKH-CCSD(T) theory level. All binding energies are BSSE corrected.

		hollow	top	bridge
MP2/ANO-RCC-VTZP	ΔE [kJ/mol]	10.26	12.75	15.36
	R [Å]	3.00	2.20	2.12
CCSD(T)/ANO-RCC-VTZP	ΔE [kJ/mol]	8.99	7.87	8.40
	R [Å]	3.01	2.57	2.54
MP2/ANO-RCC-VQZP	ΔE [kJ/mol]	14.31	20.71	24.62
	R [Å]	1.92	2.13	2.05
MP2/aug-cc-pVDZ-DK	ΔE [kJ/mol]	12.32	13.34	15.26
	R [Å]	2.97	2.27	2.19
CCSD(T)/aug-cc-pVDZ-DK	ΔE [kJ/mol]	11.70	10.57	11.34
	R [Å]	2.93	2.56	2.55
MP2/aug-cc-pVTZ-DK	ΔE [kJ/mol]	14.13	20.52	24.17
	R [Å]	2.73	2.14	2.07

action between the copper atom and the benzene molecule. The Cu-benzene complex with copper atom adsorbed at the bridge position represents the most stable structure. The MP2/ANO-RCC-VTZP and MP2/ANO-RCC-VQZP binding energies are 15.36 and 24.62 kJ/mol, respectively. The binding energy of copper positioned above the carbon atom (top position) is by about 16 % lower. The hollow position of the benzene molecule represents the least stable site determined at the MP2 theory level. Binding energy calculated with ANO-RCC-VTZP and ANO-RCC-VQZP basis set is lower by about 32 % and 42 %, respectively. Distances between the copper atom and benzene plane estimated by the MP2/ANO-RCC-VTZP method are 3.00 Å, 2.20 Å, and 2.12 Å for hollow, top, and bridge adsorption sites, respectively. The larger ANO-RCC-VQZP basis set provides similar results for the top and bridge positions, but the bond distance is by about 1.1 Å shorter above the benzene ring.

The CCSD(T) approach provides a different order of preferred adsorption sites, but the calculated CCSD(T)/ANO-RCC-VTZP binding energies for all three Cu adsorption positions are similar, i.e. 8.99, 7.87, and 8.40 kJ/mol for the hollow, top, and bridge positions, respectively. The bond distance between the copper atom and benzene plane is 2.93 Å for the most stable hollow position; equilibrium distances for the top and bridge positions are by about 0.4 Å shorter.

The relativistic aug-cc-pVXZ-DK basis set provided similar results. The CCSD(T) method also prefers the hollow position. Compared to the CCSD(T)/ANO-RCC-VTZP, the CCSD(T)/aug-cc-pVDZ-DK binding energies are by about 3 kJ/mol higher. For the hollow, top, and bridge positions, the binding energies correspond to 11.70, 10.75, and 11.34 kJ/mol, respectively. While the CCSD(T) approach prefers the hollow position, the MP2 method indicates the bridge position as the most stable Cu-benzene complex while adsorption above the center of the benzene ring corresponds to the least stable configuration.

Determination of the most stable position is very important, however, both correlation methods calculated in the finite basis set give different results. Therefore, the calculated results were extrapolated to the complete basis set (CBS).

The evaluated MP2/CBS and CCSD(T)/CBS binding energies and equilibrium distances are collected in Tab. 2. The DFT-D3 approach was fitted to the results in the complete basis set. Therefore, Tab. 2. also contains the DFT-D3 data.

Benchmark CCSD(T)/CBS results (labeled as CCSD(T)/[avTQ-avT]) were obtained by adding the correction term (difference of CCSD(T) and MP2 binding energies) calculated with the aug-cc-pVTZ-DK basis set to the MP2/CBS binding energy, evaluated by the Halkier's method of binding energies extrapolation at the MP2/aug-cc-pVTZ-DK and MP2/aug-cc-pVQZ-DK theory level (labeled as MP2/[avTQ]). Benchmark CCSD(T)/[avTQ-avT] binding energies for the hollow, top, and bridge positions are 16.77, 19.27, and 21.08 kJ/mol, respectively. The corresponding equilibrium distances are 2.57, 2.28, and 2.25 Å for (h), (t), and (b) positions, respectively. Computing of the correction term in the smaller aug-cc-pVDZ-DK basis set led to a decrease in the computing demand without accuracy loss. The same order of energies was obtained by direct extrapolation of CCSD(T)/aug-cc-pVDZ-DK and CCSD(T)/aug-cc-pVTZ-DK binding energies (labeled as CCSD(T)/[avDT]) to complete basis set. Binding energies of the Cu-benzene complex are 14.56, 16.99, and 18.49 kJ/mol for the (h), (t), and (b) structure, respectively.

The MP2/CBS overestimates the binding energies and decreases the bond distance between the cop-

Tab. 2. Extrapolated DKH-MP2/CBS, DKH-CCSD(T)/CBS and DFT-D3 binding energies, ΔE [kJ/mol], and optimal bond lengths, R (in terms of the shortest distance between the copper atom and the benzene surface) [Å], for Cu-benzene complex. Results were evaluated from aug-cc-PVXZ-DK (X = D, T, Q) or ANO-RCC-VXZP (X = D, T, Q) data. Basis sets used in the Halkier's extrapolation scheme are shown in square parentheses. Indication after the dash labels the basis for calculating the correction term. Binding energies calculated by the WFT methods were BSSE corrected.

		hollow	top	bridge
MP2/[avTQ]	ΔE [kJ/mol]	23.74	26.70	31.49
	R_e [Å]	1.82	2.09	2.02
CCSD(T)/[avDT]	ΔE [kJ/mol]	14.56	16.99	18.49
	R_e [Å]	2.66	2.31	2.27
CCSD(T)/[avTQ-T]	ΔE [kJ/mol]	16.77	19.27	21.08
	R_e [Å]	2.57	2.28	2.25
MP2/[TQ]	ΔE [kJ/mol]	22.77	25.94	30.61
	R_e [Å]	1.83	2.10	2.03
CCSD(T)/[DT]	ΔE [kJ/mol]	12.26	12.89	13.81
	R_e [Å]	2.81	2.38	2.34
CCSD(T)/[TQ-T]	ΔE [kJ/mol]	15.59	17.45	18.98
	R_e [Å]	2.64	2.30	2.25
DFT-D3/TPSS	ΔE [kJ/mol]	27.75	34.32	35.39
	R_e [Å]	2.45	2.18	2.15
DFT-D3/PBE	ΔE [kJ/mol]	23.61	34.46	34.74
	R_e [Å]	2.49	2.18	2.16

per atom and benzene plane, especially for the (t) position. For example, while the energy difference between top and hollow positions is overestimated by about 20 % in comparison with the reference CCSD(T)/[avTQ-avT] results, the energy gap between the preferred bridge and top position is larger by about 100 %. The bond distance is shorter by about 0.2 Å for the top and bridge position, but the equilibrium distance in the hollow structure is shorter by about 0.7 Å.

The MP2/CBS results obtained using the ANO-RCC-VTZP and ANO-RCC-VQZP basis sets correspond to the MP2/[avTQ] results. The energy differences between MP2/[avTQ] and MP2/[TQ] are below 1 kJ/mol for all three positions.

Including the correction term when computing with the ANO-RCC-VTZP basis set leads to an increase in error; differences between CCSD(T)/[TQ-T] and benchmark CCSD(T)/[avTQ-avT]) binding energies are above 1 kJ/mol. However, it should be mentioned that compared to the aug-cc-pVTZ-DK basis set, the ANO-RCC-VTZP basis set is smaller and the calculations are less demanding.

Direct extrapolation of CCSD(T)/ANO-RCC-VDZP and CCSD(T)/ANO-RCC-VTZP binding energies to CBS led to a poorer description of the interactions in the Cu-benzene complex. This lower accuracy is caused by the low quality of the basis sets, especially the ANO-RCC-VDZP basis set which contains only polarization functions.

The DFT-D3/TPSS and DFT-D3/PBE approaches overestimate the binding energies. Compared to the reference CCSD(T)/[avTQ-avT] results, the DFT-D3 binding energies are larger by about 40—80 %. All these methods provide an order of the stability of the Cu-benzene complex corresponding to the (b), (t), and (h) positions. This is contrary to the results obtained using finite basis sets, where the adsorption of the copper atom at the hollow position was preferred.

Low binding energy for copper is indicative of non-covalent binding. Compared to our previous study (Granatier et al., 2011), the CCSD(T)/ANO-RCC-VTZP results indicate that the Cu-benzene and Ag-benzene complexes are characterized by a similar interaction model. Both, copper and silver atoms prefer the hollow position and the binding energies are very close, indicating that the copper atom is bound to benzene by a dispersion interaction. However, a more detailed analysis provides different conclusion. The ROHF and MP2 approaches suggest charge transfer from the benzene molecule to the 4s orbital of the copper atom. Compared to the silver and gold atoms, the magnitude of charge transfer in the Cu-benzene complex corresponds to the value of magnitude of charge transfer in the Au-benzene complex. Moreover, the charge transfer in the Cu-benzene complex strongly depends on the position of the adsorbed metal atom. Mulliken population analysis showed that the magnitude of charge transfer in top and bridge positions is more than twice that in hollow position. Similar dependence was observed in the Au-benzene complex. On the other hand, the Ag-benzene complex is characterized by a similar charge for all three positions.

Adsorption of metal atoms on graphene surface has been studied previously (Manadé et al., 2015), showing the most stable position of the copper atom determined at the DFT/PBE and DFT-D2/PBE theory level to correspond to the adsorption of the metal atom directly on the carbon atom (t). Preferring the (t) or (b) position indicates that charge transfer plays an important role in binding copper on the graphene surface. The binding energy of this structure is 22.19 and 51.14 kcal/mol at the DFT and DFT-D2 theory level, respectively. However, the bond distance between copper and carbon surface is 2.21 Å, which is in good agreement with our results. Compared to our DFT-D3 results, the DFT/PBE and DFT-D2/PBE strongly overestimate the bond between the copper atom and the carbon surface.

Conclusion

Decoration of graphene with metal atoms represents a way of properties modification and new materials development. This requires understanding the nature of the bond between the metal and graphene. The Cu-benzene complex is a very simple model to be studied to understand the interactions between the copper atom and the graphene surface.

Therefore, this study was focused on the interaction of copper atom with benzene molecule using accurate correlation methods. Correct description of the interactions in the Cu-benzene complex requires the use of high accuracy correlation methods and high-quality basis sets and their extrapolation to complete basis set.

The DFT-D3 method is characterized by lower demandingness and the ability to describe the van der Waals complexes. Compared to high accuracy correlation methods, the DFT-D3 method provides the correct order of stability but strongly overestimates the binding energies for all three positions.

The copper atom prefers the adsorption on the bridge position. This structure of the Cu-benzene complex is characterized by strong charge transfer from the benzene molecule to the copper atom. Analogous to the Au-benzene complex, the charge transfer plays an important role in the understanding of the interactions in the Cu-benzene complex.

Thus, the significant difference between binding energy in the Cu-benzene and Au-benzene complexes will be the subject of further study.

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