RELIABILITY OF DFT METHODS FOR DESCRIPTION OF Cu SITES AND THEIR INTERACTION WITH NO IN ZEOLITES

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Received May 4, 1998
Accepted June 15, 1998

Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

The reliability of various DFT functionals for description of Cu sites and their interaction with NO in zeolites is tested. The dissociation energies of $Cu^{n+}H_2O$ and $Cu^{n+}NO$ systems calculated with various DFT functionals are compared with those obtained at the MP2 and CCSD(T) levels of theory. It is concluded that hybrid density functional (B3LYP) gives reliable description of studied systems, while LDA seriously overestimates dissociation energies.

Key words: Catalysis on zeolites; Copper ligands; NO decomposition; B3LYP; CCSDCT; *Ab initio* calculations.

Cu-Exchanged zeolites, particularly CuZSM-5, became widely studied systems experimentally and theoretically since a high activity of these systems for both decomposition of NO (refs[1–5]) and selective catalytic reduction[6,7] (SCR) has been discovered. EPR and XANES studies[2,8–10] have shown that Cu is incorporated into the ZSM-5 as Cu^{2+} and upon heating the CuZSM-5 undergoes autoreduction[9,11,12]. Based on the results of EPR, IR, and photoluminescence spectroscopy[13], four distinguished Cu sites with different reducibility and activity in SCR and NO decomposition were assigned. It has been suggested that the Cu^{2+} cations with higher capability of reduction and higher activity for NO decomposition and SCR are those which are located in the lower charge density region of zeolite framework (single Al site).

Recently, many theoretical studies of Cu coordination in the zeolite matrices appeared in the literature. The Cu interaction with zeolite and Cu interaction with small molecules (CO or NO) was studied on systems where the zeolite is modeled either by water ligands[14–17] or by more realistic zeolite models (five-member or six-member rings of zeolite)[18–22]. It has been found that for Cu^0 and Cu^+ oxidation states the water-ligand model can provide a description consistent with that obtained using more realistic zeolite clusters. Good agreement was found for the binding of Cu^{2+} in higher coordination environment. For low coordination of Cu^{2+} the qualitative differences between the results obtained with the water-ligand and larger cluster model were found. Water-ligand models and small zeolite clusters were used also for calculations of IR frequency shifts of the adsorbed CO and NO molecules[15–17]. It should be noted, that the models used in theoretical studies mentioned above are rather small and that they may not provide sufficient representation of zeolite structure. In addition, many of these studies employed calculations at local density approximation (LDA) level, which is not expected to provide sufficiently reliable description of such systems.

It is our long term goal to verify the experimental interpretation of EPR, IR, and photoluminescence spectroscopy experiments by means of reliable models of modern computational chemistry. In particular, we plan to study coordination of copper cations in the zeolite framework and the interaction of Cu-exchanged zeolites with NO employing embedding model[23] where significant part of zeolite framework ("cluster") is treated quantum mechanically and the surrounding environment is treated with the empirical potentials. Due to the size of the model describing the active site in zeolites, the DFT method appears to be the most suitable compromise between accuracy and tractability. However, the level of accuracy of this method depends on the correlation and exchange functionals used. Despite a number of studies of the interaction of Cu^{n+} (n = 0, 1, and 2) with zeolites using DFT functionals, no systematic study of the reliability of these functionals for description of the nature of Cu site in zeolites has been done.

In this contribution, the reliability of DFT functionals and moderately large basis set is tested against the more accurate methods (CCSD(T) in particular) and larger basis sets. The results presented here serve as a guide for selection of the optimal (considering the level of accuracy and computational cost) method and basis set for investigation of the nature of Cu active sites and their interaction with NO in zeolites. In order to test the reliability of various DFT functionals, calculations on small systems, in particular, $Cu^{n+}H_2O$, CuNO, and $Cu^{n+}NO$, where $n = 1$ and 2, were carried out and results are reported below.

METHODS

Two basis sets denoted as B1 and B2 were used in these calculations. In the basis set denoted as B1, O, N, and H atoms are described using correlation-consistent valence triple-zeta-plus-polarization functions[24]. For Cu atoms, 1s, 2s, and 2p electrons are described using the energy-adjusted relativistic effective core pseudopotential and valence electrons are described using basis set[25] of the form (2111111s/22111p/2211d). In the basis set denoted as B2, all-electron valence triple-zeta-plus-polarization (TZP) basis set is used for description of all atoms except hydrogen which is described using valence double-zeta-plus-polarization (DZP) basis set. For the N,O/Cu/H atoms the (10s,6p)/(14s,10p,5d)/(4s) basis sets optimized by Schafer *et al.*[26] contracted to

{511111,411}/{62111111,331111,311}/{31} were used. Polarization functions with the exponents 1.2, 1.0, and 0.8 were added to the basis set of O, N, and H atoms, respectively. The effect of polarization functions on Cu atom for both types of basis set was tested by augmentation of both basis sets by f functions (exponents 3.1235 and 1.3375, ref.[27]).

The local and gradient-corrected hybrid functionals were used for obtaining equilibrium geometries and interaction energies of the species considered in the present study. The LDA calculations made use of the exchange functional of Dirac[28] and the correlation functional of Vosko, Wilk, and Nusair[29] (VWN). The gradient-corrected DFT calculations made use of Becke[30] and hybrid Becke[31] exchange functionals and of correlation functionals of Lee, Yang, and Parr[32] (LYP), and of Perdew and Wang[33] (PW91). The results obtained with various DFT functionals were compared with those obtained using MP2 (refs[34,35]) and CCSD(T) (ref.[36]) methods.

The geometry optimizations were carried out using various density functionals, namely LDA, B3LYP, B3PW91, and at the MP2 level. Due to the very similar geometrical parameters obtained at the B3LYP and B3PW91 levels, only those obtained at the B3LYP level are reported. Dissociation energies obtained at the various levels of theory are discussed at the geometries obtained with the B3LYP functional.

DFT and MP2 calculations were carried out using Gaussian94 program package[37] while CCSD(T) calculations were performed using Molpro96 program[38].

RESULTS AND DISCUSSION

This section is divided into two parts. In the first part we discuss the interaction of Cu^{n+} (n = 1, 2) with H_2O molecule and the second part deals with the interaction of Cu^{n+} (n = 0, 1, and 2) with NO molecule.

Interaction of Cu^{n+} with H_2O

It should be noted that $Cu^{2+}H_2O$ structure considered in this study is only a local minimum, dissociation to the Cu^+ and H_2O^+ ions is an exothermic process. The geometries of the lowest states of $Cu^{n+}H_2O$ (n = 1, 2) systems were optimized at the MP2, LDA, BLYP, B3LYP, and B3PW91 levels. Geometrical parameters are defined in Fig. 1a and representative set of calculated parameters is summarized in Table I. Results obtained for the $^1A'$ state of Cu^+H_2O system at the MP2 and B3LYP levels (employing ECP basis set denoted B1) are in very good agreement, giving r(Cu–O) distance 1.94 and 1.92 Å, respectively. Very similar results were also obtained at the BLYP and B3PW91 levels of theory. On the other hand, LDA calculations employing the same basis set give somewhat different results with r(Cu–O) distance 1.83 Å and angle $\xi = 34°$ while at the MP2 and B3LYP levels this angle is 0 and 9°, respectively. (Angle ξ describes the deviation from C_{2v} structure, $\xi = 0°$.) Calculations on the $^2A'$ state of $Cu^{2+}(H_2O)$ ion reveal that the equilibrium structure is even less sensitive to the choice of method used for geometry optimization (Table I) than in case of singly charged species. The effect of basis set was also investigated. It was found that both basis sets considered in this study give very similar results. In addition, augmentation of basis set by up to three

TABLE I
Geometrical parameters of Cu^+H_2O and $Cu^{2+}H_2O$ systems optimized at various levels of theory: r_1 and r_2 are the Cu–O and O–H bond lengths (in Å), respectively, α is the H–O–H angle, and ξ is the angle between C_2 axes of water molecule and Cu–O bond

Method	Cu^+H_2O				$Cu^{2+}H_2O$			
	r_1	r_2	α	ξ	r_1	r_2	α	ξ
LDA/B1	1.834	0.978	108.4	33.3	1.848	1.011	108.3	20.1
B3LYP/B1	1.925	0.966	109.0	0	1.868	0.992	107.9	37.8
B3LYP/B2	1.938	0.975	107.2	0	1.902	1.004	106.5	32.3
MP2/B1	1.936	0.964	107.4	8.7	1.830	0.979	109.2	0
MP2[a]	1.929	0.962	107.4	–	–	–	–	–
MP2[b]	1.971	–	–	–	1.860	–	–	–
BLYP[c]	1.940	0.985	106.9	–	–	–	–	–
LDA[d]	1.888	–	–	–	1.906	–	–	–

[a] Ref.[39], calculations employing 6-311+G(2d,2p) basis set for H and O and augmented Wachters basis set for Cu. [b] Ref.[40], calculations employing 6-311+G(d,p) basis set for H and O and modified Wachters basis set for Cu. [c] Ref.[17], calculations employing 6-31G* basis set on H and O and Wachters basis set on Cu. [d] Ref.[15], calculations employing DZP basis set (with 3 d functions on Cu).

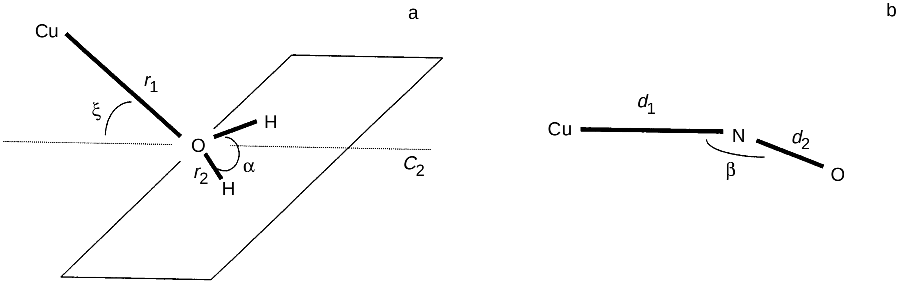

FIG. 1
Definition of geometrical parameters of $Cu^{n+}H_2O$ (a) and $Cu^{n+}NO$ (b); r_1 and r_2 are the Cu–O and O–H bond lengths, α is the angle H–O–H, and ξ is the angle between C_2 axes of water molecule and Cu–O bond; d_1 and d_2 are the Cu–N and N–O bond lengths and β is the angle Cu–N–O

polarization f functions on Cu atom has no effect on the resulting geometries. The geometrical parameters obtained by other authors[15,17,39,40] are also summarized in Table I. These are in agreement with geometrical parameters obtained in this study.

As we mentioned above, the only geometrical parameter which is sensitive to the level of theory employed is the angle ξ describing the deviation from C_{2v} structure. However, it should be noted that even at the levels of theory where C_s geometry is found to be a minimum, the C_{2v} structure is only a few tenths of kcal/mol above C_s structure for Cu^+H_2O and 1–2 kcal/mol above C_s structure for $Cu^{2+}H_2O$. Thus, it is possible that the zero-vibrational level lies above the energy of C_{2v} structure. In other words, this out-of-plane vibrational mode follows a rather shallow potential. This indicates that the Cu^{n+}–H_2O interactions is essentially electrostatic, in agreement with the qualitative analyses based on simple MO picture.

The dissociation energies of $Cu^{n+}H_2O$ are summarized in Table II. For Cu^+H_2O system, where the experimental dissociation energy is available, the CCSD(T)/B1+2f cal-

TABLE II
Dissociation energies of the Cu^+H_2O and $Cu^{2+}H_2O$ systems (in kcal/mol) at the B3LYP/B1 optimized geometries[a]. Unless stated otherwise, energies are reported without ZPE and BSSE corrections

Method	Cu^+H_2O	$Cu^{2+}H_2O$
LDA/B1[b]	61.2	158.6
B3LYP/B1	45.7	122.4
B3LYP/B2	43.8	120.3
MP2/B1	40.3	104.0
CCSD(T)/B1	38.3	104.2
CCSD(T)/B1+2f	41.4	108.0
CCSD(T)/B1+2f+ZPE[c]	39.1	–
CCSD(T)[d]	37.2	–
MP2[d]	38.9	–
MP2[e]	37.7	99.7
BLYP[f]	52.5	–
LDA[g]	52.3	139.5
BP86[g]	39.4	126.0
Experiment[h]	38.4	–

[a] In case of $Cu^{2+}H_2O$ system we refer to dissociation towards Cu^{2+} and H_2O. [b] Geometry optimized at the LDA level. [c] ZPE corrections calculated at HF/B1 level of theory. [d] Ref.[39], calculations employing 6-311+G(2d,2p) basis set for H and O and augmented Wachters basis set for Cu. [e] Ref.[40], calculations employing 6-311+G(d,p) basis set for H and O and modified Wachters basis set for Cu. [f] Ref.[17], calculations employing 6-31G* basis set on H and O and Wachters basis set on Cu. [g] Ref.[15], calculations employing DZP basis set (with 3 d functions on Cu). [h] Ref.[41].

culation gives dissociation energy in excellent agreement with experiment[41]. The augmentation of basis set with the third f function and with one g function does not change the interaction energies by more than few tenths of kcal/mol. CCSD(T) calculations employing B1 basis set (which does not include any polarization function on Cu) give dissociation energy by about 3 kcal/mol too low. On the other hand, f functions have only small effect (less than 1 kcal/mol) on DFT dissociation energies. MP2 calculations tend to slightly overestimate the Cu^+H_2O dissociation energy (by 2 kcal/mol) while the $Cu^{2+}H_2O$ dissociation energy is in excellent agreement with the CCSD(T) value. The LDA dissociation energies are seriously overestimated for both systems. The calculations employing more sophisticated density functionals, *e.g*. B3LYP, give dissociation energies for Cu^+H_2O and $Cu^{2+}H_2O$ which are slightly overestimated. Comparing CCSD(T)/B1+2f and B3LYP/B1 (where f functions on Cu are not important) this overestimate is 11.9 and 13.3% for singly and doubly charged ion, respectively. However, B3LYP and B3PW91 dissociation energies are considerably better than those obtained at LDA level which are about 50% too large. The gradient corrected BLYP functional gives the results of intermediate quality, thus, the reliability of DFT functionals improves in the series local density approximation, gradient corrected functionals (BLYP), and hybrid functionals (B3LYP and B3PW91). The basis set superposition error (BSSE) for Cu^+H_2O calculated with B1 basis set at the B3LYP and MP2 levels is 2.5 and 3.3 kcal/mol, respectively.

Our CCSD(T) and MP2 results for Cu^+H_2O dissociation energy, obtained with ECP, agree with all-electron basis sets CCSD(T) and MP2 calculations reported by Hoyau and Ohanessian[39]. Both CCSD(T) results are in agreement with experiment. The MP2 dissociation energies of Cu^+H_2O and $Cu^{2+}H_2O$ reported by Magnusson and Moriarty[40] appear to be slightly underestimated probably due to the insufficiency of basis set used on Cu atom. Overestimation of dissociation energy in the calculations using DFT methods discussed above was also found by other authors: In agreement with our results the B3LYP hybrid functional was found to give reliable dissociation energies[39], while the BLYP (ref.[17]) and LDA (ref.[15]) results are significantly overestimated (Table II). The LDA and BP86 dissociation energies reported by Schneider *et al.*[15] do not follow the trend observed by other authors: LDA energies of Schneider *et al.* are 9 and 19 kcal/mol smaller than dissociation energies reported in this work and also BP86 dissociation energies of Schneider *et al.* are surprisingly small; for Cu^+H_2O system these are even smaller than B3LYP dissociation energies. This unexpected agreement with CCSD(T) results (and experiment) could be due to some fortuitous error cancellation in method and basis set used by Schneider *et al.*

Interaction of Cu^{n+} with NO

Both Cu–NO and Cu–ON "end-on" structures were considered. It was found that Cu–NO structure is more stable for both ions and for neutral complex considered in this study.

This is in agreement with the results of Hrusak and coworkers who studied neutral and singly charged species[42]. Thus, we will not consider Cu–ON structures in further discussion.

The geometries of the energy lowest states of $Cu^{n+}NO$ ($n = 0$, 1, and 2) have been optimized at the DFT level and are summarized in Table III. However, in case of $Cu^{2+}NO$ system only the triplet state has been found to be stable. The lowest singlet state of $Cu^{2+}NO$ is about 70–80 kcal/mol lower in energy (depending on the level of theory used) at the geometry of triplet, however, this state is not stable with respect to the dissociation into Cu^+ and NO^+ ions. Therefore, only the triplet state will be considered in further discussion. Even if NO and Cu^{2+} do not bind in the singlet state in the gas phase and the structure found for $Cu^{2+}NO$ triplet corresponds to local minimum only, it is still important to test the reliability of DFT for description of this interaction. The positive charge on copper in the zeolite is compensated by negative charges around Al atoms in "T" positions, thus, the electron affinity of copper is lowered. Indeed, NO binding to the Cu^{2+} in zeolite has been suggested[13].

Very similar geometrical parameters have been obtained at the B3PW91/B1 and B3LYP/B1 levels of theory. Somewhat different parameters were obtained at the LDA/B1 level, in particular Cu–N bond length is more than 0.1 Å shorter for neutral and for singly charged species. Augmentation of the basis set with f polarization functions on Cu atom was shown to have very small effect on the optimized geometrical parameters. Very similar geometrical parameters for Cu^+NO has been obtained by Thomas *et al*. at the B3LYP level[43], while somewhat larger bond lengths were found by Hrusak *et al*. who used CCSD and small basis set[42].

The dissociation energies of $Cu^{n+}NO$ are summarized in Table IV. From these data it is apparent that LDA severely overestimates binding energies in all cases. On the other hand, results obtained with B3LYP functional are in reasonable agreement with CCSD(T)/B1+2f results, with B3LYP dissociation energies being larger than CCSD(T)

TABLE III

Geometrical parameters of $Cu^{n+}NO$ ($n = 0$, 1, and 2) optimized at the B3LYP/B1 level of theory: d_1 and d_2 are the Cu–N and N–O bond lengths (in Å), respectively, and β is the angle Cu–N–O

System	d_1	d_2	β
CuNO ($^1A'$)	1.916	1.172	118.5
Cu^+NO ($^2A'$)	1.928	1.132	131.4
$Cu^{2+}NO$ ($^3B_1$)	1.895	1.129	180.0

by 4.9, 6.8, and 5.0 kcal/mol for neutral, singly, and doubly charged systems, respectively.

For the neutral CuNO complex it was found that at the CCSD(T) level using geometries optimized with a small basis set the lowest singlet state is about 7–8 kcal/mol below the lowest triplet[42]. Using the MP4 method we have found singlet below triplet by 8.2 kcal/mol, however, at the B3PW91 level of theory both states have nearly the same energies (with triplet 1.8 kcal/mol below singlet). The CCSD(T)/B1+2f dissociation energies are about 6 kcal/mol larger than those reported in ref.[42]. This discrepancy could be attributed to different geometries used in these studies (we have found Cu–N distance 1.916 Å while Hrusak *et al.*[42] found Cu–N distance 2.110 Å).

In the case of Cu^+NO ion our results are in agreement with those reported by Thomas *et al.*[43] and by Hrusak *et al.*[42]. Calculations employing gradient corrected BLYP (ref.[17]) functional overestimate the dissociation energy even more than calculations with B3LYP functional. As in the case of Cu^+H_2O, the Cu^+NO dissociation energies calculated at the BP86 level by Schneider *et al.*[15] appears to be surprisingly close to B3LYP dissociation energies reported in the present paper.

TABLE IV
Dissociation energies of the CuNO, Cu^+NO, and $Cu^{2+}NO$ systems (in kcal/mol) at the B3LYP/B1 optimized geometries[a]

Method	CuNO ($^1A'$)	Cu^+NO ($^2A'$)	$Cu^{2+}NO$ ($^3B_1$)
LDA/B1	48.6	59.9	86.4[b]
B3LYP/B2	21.1	30.8	59.4
MP2/B1	6.4	24.1	53.0
CCSD(T)/B1	14.0	20.7	51.0
CCSD(T)/B1+2f	16.2	24.0	54.4
CCSD(T)[c]	–	21.7	–
CCSD(T)[d]	10.4	19.7	–
BLYP[e]	–	40.6	–
BP86[f]	26.0	33.0	–

[a] For $Cu^{2+}NO$ system we refer to dissociation to Cu^{2+} and NO fragments. [b] Due to the convergence problems with basis set B1 this energy has been calculated with basis set B2. [c] Ref.[43], calculations with ANO basis set on Cu and cc-pVTZ basis set on N and O. [d] Ref.[42], calculations with augmented ECP DZ basis set of Hay and Wadt on Cu and DZP basis set on N and O. [e] Ref.[17], calculations employing 6-31G* basis set on H and O and Wachters basis set on Cu. [f] Ref.[15], calculations employing DZP basis set (with 3 d functions on Cu).

CONCLUSIONS

The systematic study of the reliability of various density functionals for characterization of Cu^{n+} interaction with H_2O and NO molecules has been presented. The DFT results have been compared with those obtained at the CCSD(T) level and, where available, with experimental data. The dissociation energies for

$$Cu^{n+}H_2O \rightarrow Cu^{n+} + H_2O \qquad (A)$$

$$Cu^{n+}NO \rightarrow Cu^{n+} + NO \qquad (B)$$

processes ($n = 0$, 1, and 2) calculated at DFT level are always overestimated compared to CCSD(T) results. Based on the data presented above it is apparent that LDA is not capable to provide reliable results, with dissociation energies being overestimated by about 50%. In addition, geometrical parameters obtained at the LDA level of theory do not agree with those obtained at higher level of theory. Thus, the use of LDA in geometry optimization of Cu/zeolite structures should be avoided. The gradient corrected functionals used in this study appear to be sufficient for obtaining geometrical parameters, however, they tend to significantly overestimate binding energies compared to CCSD(T). The hybrid functionals perform by far the best of all density functionals tested in this study. Nevertheless, even with the B3LYP functional the dissociation energies are somewhat overestimated compared to CCSD(T).

The results obtained with effective-core basis set are in excellent agreement with those obtained with all-electron basis set. It was found that the use of polarization functions on copper is not important for description of interaction of Cu with H_2O and NO molecules at DFT level.

Based on our results we conclude that the B3LYP provides the reliable description of Cu interaction with H_2O and NO molecules, thus, it should be adequate for description of Cu interaction with zeolite and for description of interaction of Cu active sites in zeolite with NO. The B3LYP calculations are relatively inexpensive (compared to perturbation theory or coupled clusters methods) and, thus, suitable for use in conjunction with more realistic models of zeolites.

This work was supported by the Volkswagen Stiftung (grant No. I/72937). D. N. acknowledges also support from the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. C4040704). M. D. was partially supported by the Grant Agency of the Czech Republic (grant No. 203/96/1089).

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