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The electronic spectrum of CUONg₄ (Ng = Ne, Ar, Kr, Xe): New insights in the interaction of the CUO molecule with noble gas matrices

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The electronic spectrum of the CUO molecule was investigated with the IHFSCC-SD (intermediate Hamiltonian Fock-space coupled cluster with singles and doubles) method and with TD-DFT (time-dependent density functional theory) employing the PBE and PBE0 exchange–correlation functionals. The importance of both spin–orbit coupling and correlation effects on the low-lying excited-states of this molecule are analyzed and discussed. Noble gas matrix effects on the energy ordering and vibrational frequencies of the lowest electronic states of the CUO molecule were investigated with density functional theory (DFT) and TD-DFT in a supermolecular as well as a frozen density embedding (FDE) subsystem approach. This data is used to test the suitability of the FDE approach to model the influence of different matrices on the vertical electronic transitions of this molecule. The most suitable potential was chosen to perform relativistic wave function theory in density functional theory calculations to study the vertical electronic spectra of the CUO and CUONg₄ with the IHFSCC-SD method. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742765>]

I. INTRODUCTION

The chemistry of uranium remains fascinating and challenging, with implications that go beyond the use of fissionable ²³⁵U in nuclear energy, with e.g., a growing interest in possible applications in catalysis.^{1,2} This is due to uranium's wide range of oxidation states (+6, +5, +4 and +3) and coordination geometries.^{3–6} These features arise from the availability of the spatially rather different 5*f*-, 6*d*-, 7*s*-, and 7*p*-orbitals that are energetically close and do participate in the chemical bonding.

Many uranium complexes contain the uranyl (UO₂²⁺) species, perhaps the best studied of its molecular oxides due to its predominance in the aqueous chemistry of uranium. For this ion (but also for non-oxide isoelectronic species such as NUN) the uranium metal center forms strong triple bonds with the axial ligands.^{3,7–14} The high stability and linear structure of these U(VI) species are well explained by the “pushing from below” model proposed by Tatsumi and Hoffmann.¹⁵ In the linear structure the strong interaction between the semi-core uranium 6*p*-orbitals and the oxygen 2*p*-orbitals brings the energy of the σ_u HOMO (highest occupied molecular orbital) close to that of the 5*f*-orbitals of the uranium leading to a significant 5*f* participation in this orbital.¹⁶ The accompanying lowering of the energy leaves a large HOMO-LUMO gap for the cation, making uranyl an archetypical closed-shell species. For other isoelectronic species such as NUO⁺ or CUO the picture is slightly different since the bonds are not equal, even though both can still be regarded as triple bonds. To the diminishing electronegativity of N and C with respect to O there corresponds a decreasing HOMO-LUMO gap, as seen in various theoretical studies^{13,17} as a marked decrease of ionization potentials and the lowest electronic excitation

energies on going from UO₂²⁺ to NUN, NUO⁺, and up to CUO.^{18,19}

For CUO in particular, the HOMO has a predominantly U–C bonding character with the U–O bond lying at significantly lower energy.¹⁷ Moreover, a point is reached where low-lying triplet excited states are so close to the ground-state that some theoretical approaches predict them to be the electronic ground-state.^{12,17} This suggests that even weakly bound equatorial ligands can play an important role in establishing the precise ordering of states in the lower part of the spectrum. This agrees with the findings in the extensive experimental studies of CUO trapped in noble gas matrices that spurred the interest of theoreticians in this molecule. Tague *et al.*²⁰ excited uranium atoms in excess of CO by laser ablation and found that uranium can insert in the triple CO bond and form the CUO molecule. The experimentally measured U–C and U–O stretching vibrations are 853 cm^{−1} and 804 cm^{−1} in an argon matrix, but when the same experiment was carried out by Zhou *et al.*²¹ in a solid neon matrix, they found the U–C and U–O frequencies at 1047 cm^{−1} and 872 cm^{−1}. Later on, a similar experiment was carried out for krypton and xenon matrices as well. Again, a large red shift (≈ 70 and ≈ 200 cm^{−1} for the U–O and U–C stretching modes, respectively) was observed, relative to the data obtained in the neon matrix.^{22–24} This large red shift in the vibrational spectra suggest that the ground-state of CUO depends on the noble gas environment, with the weakly interacting neon atoms the system favors a singlet ground-state while the stronger interaction in the heavier noble gas matrices, i.e., argon, krypton, or xenon,^{23,25,26} produces a triplet ground-state in which also a nonbonding uranium 5*f_φ* or 5*f_δ* is occupied (or a mixture thereof if spin–orbit coupling is accounted for¹⁷). Direct

validation for this hypothesis could come from electronic spectroscopy on CUO in these matrices. Such data are available for other uranium compounds^{27,28} in noble gas matrices, but to the best of our knowledge CUO has not yet been studied in this manner. One thus has to rely on theoretical predictions for the electronic spectra. In the theoretical treatment one needs to accurately describe not only electron correlation but also, because of the heavy atoms involved (U, Xe), both scalar and spin-orbit relativistic effects.

These requirements pose significant challenges²⁹ to calculations, especially because the electronic states may have a marked multi-reference character. Suitable methodologies are, for instance, the relativistic formulations^{30–32} of the Fock-space coupled cluster singles and doubles (FSCC-SD (Refs. 33–35)) method, or the spin-orbit complete active space second-order perturbation theory (SO-CASPT2 (Refs. 36 and 37)). The recent work of Infante *et al.*,³⁸ who employed the spin-orbit coupling restricted active space second order perturbation (SOC-RASPT2 (Ref. 39)) method to investigate the UO_2Ar_4 species, can be considered to be at the limit of what is currently feasible employing wave function based approaches. Since the CUO species has less symmetry, an all-atom treatment is still out of reach. The Fock-space based approaches are less affected by active space limitations, but are computationally more expensive than the PT2 ones and at present are also not able to tackle a full seven atom model (both experimental and theoretical studies suggest coordination of four noble gas atoms in the equatorial plane perpendicular to the CUO unit^{23,25,26}).

This leaves as alternative the use of so-called embedding approaches in which interactions from the environment are modeled in a simplified manner.⁴⁰ Since both the molecule of interest and the environment consist of neutral molecules, and because the dipole moments of the two states of interest of CUO do not differ much (3.5 D in the singlet state and 2.4 D in the excited triplet state²⁴), the most important factor is probably a combination of Pauli repulsion and weak coordination from the equatorial ligands. Most embedding methods are not able to capture such subtle effects as they are usually designed to describe primarily electrostatic interactions. A method that should in principle be able to capture both Pauli repulsion and (to lesser extent) weak coordination bonds is the so-called WFT-in-DFT (wave function theory in density functional theory) embedding, first proposed by Carter and co-workers,^{41–43} for studying the electronic spectra of impurities on solids and surfaces.^{44,45} In this method, one divides the system of interest in an active part (for which the spectra are to be calculated with a given wave function method) and an environment that is described by DFT. This type of approach has been applied successfully in describing the effect of chloride-actinyl interactions on the f - f spectra of the NpO_2^{2+} cation.⁴⁶ The WFT-in-DFT frozen density embedding (FDE) scheme is theoretically well-defined and suitable for extension to coupled subsystems⁴⁷ and can provide an enormous reduction of both computational cost and the complexity of the data that is to be analyzed. We therefore think it is of interest to use the CUO noble gas interaction as another test case for the feasibility of the approach in describing uranium coordination chemistry. As we will use the method in

its uncoupled formulation, we need to ascertain that there is no coupling between the electronic excitations on CUO with those of the environment,⁴⁸ something that can be explored at DFT level. In addition, we will use a monomer expansion of the wave function which will also limit the possibilities to describe donation from the noble gas orbitals into the CUO orbitals. This system therefore constitutes a stringent test for the applicability of this simplest form of WFT-in-DFT embedding, but one in which there is a fair chance of success given the fact that DFT-in-DFT typically works well for such weak interactions.^{49–54}

In this work our initial goal was to investigate the use of WFT-in-DFT embedding for determining the electronic structure of the model CUONg_4 ($\text{Ng}=\text{Ne, Ar, Kr, and Xe}$) systems, with particular emphasis on the still debated issue of whether or not there is a change in the nature of the ground-state (between singlet and triplet) for the different noble gas ligands. While carrying out the TD-DFT calculations that were used to validate the embedding procedure, we obtained new insights in the effect of including exact exchange in the TD-DFT description of this molecule that are worthwhile to report as well. These will be discussed in Sec. III A.

II. COMPUTATIONAL DETAILS

Our investigations required three types of calculations: geometry optimization and calculation of vibrational frequencies for the two possible ground-states of the CUO molecule, TD-DFT calculations of the isolated, embedded, and supermolecular species, and IHFSCC-SD calculation of the isolated and embedded species. For the latter two we also need to discuss the generation of the embedding potential that was used. We will partition the section on computational details accordingly.

A. Geometry optimization and harmonic frequencies

We performed spin-free DFT geometry optimization and analytical frequency calculations with the TURBOMOLE 5.10 package^{55–57} employing the PBE0 exchange–correlation (xc) functional^{58,59} in conjunction with the def-TZVP (triple- ζ valence polarization) basis sets.⁶⁰ For the heavy elements (uranium and xenon) small-core effective potentials were utilized.^{61,62}

Geometries and structures were obtained for the $^1\Sigma^+, ^3\Phi$ states of CUO and the 1A_1 ($^1\Sigma^+$) and 3E ($^3\Phi$) states for the CUONg_4 ($\text{Ng}=\text{Ne, Ar, Kr, Xe}$) models. All the DFT calculations were performed in C_{2v} point group symmetry with the multiple grid option m5, that is, a coarser grid during SCF iterations and a more precise grid at the final SCF iteration and the gradient evaluation, as implemented in the TURBOMOLE 5.10 program package.

B. Time-dependent density functional theory and time-dependent Hartree–Fock

All-electron spin-free TD-DFT (Refs. 63 and 64) calculations were carried out with the ADF2010 package^{65–67} in C_{2v} point group symmetry with the PBE (Ref. 68) and PBE0

(Refs. 58 and 59) xc functional and the TZ2P (triple- ζ double polarization) basis sets from the ADF repository.⁶⁹ Scalar relativistic effects were incorporated through the ZORA (zeroth-order regular approximation) Hamiltonian.⁷⁰ The spin-free TD-DFT vertical excitation energies were obtained at the optimized geometries within the adiabatic local density approximation (ALDA), in which the local (in time and space) functional derivative of the LDA functional is used in the TD-DFT kernel. The exact (not fitted) density was used to evaluate all xc contributions, with the numerical integration accuracy option set to a value of 10.

For every molecule we determined the 30 lowest-lying (singlet and triplet) states, which was sufficient to characterize the 22 transitions corresponding to excitations from the $25a_1(f_\sigma\{U\} + p_\sigma\{C\})$ and $12b_1/b_2(f_\pi\{U\})$ orbitals to the $26a_1(f_\sigma\{U\} + s_\sigma\{C\} + p_\sigma\{C\})$, $13b_1/b_2(f_\phi\{U\})$, $27a_1/5a_2(f_\delta\{U\})$ and $28a_1/6a_2(f_\delta\{U\})$ orbitals of the CUO molecule and the same kind of orbitals for the CUONg₄ model systems. In addition we carried out time-dependent Hartree-Fock (TD-HF) calculations with the same basis set and setup as for the TD-DFT runs.

C. Frozen density embedding

DFT-in-DFT (Refs. 71–75) calculations were performed with the ADF2010 (Refs. 65–67) package, using a development version of the PYADF (Ref. 76) scripting framework. The same settings as specified above for the supermolecular Kohn–Sham (KS) runs were employed for the DFT part.

In the FDE setup the total electronic density of the CUO complexes (CUONg₄, Ng=Ne, Ar, Kr, Xe) was partitioned into the density of CUO and a Ng₄ environment and subsequently updated in nine freeze-and-thaw cycles⁷⁵ to allow for polarization of both the environment and the active system. We utilized the monomolecular basis set expansion, in which only basis functions belonging to the currently active system are used. This expansion introduces an additional approximation with respect to the supermolecular calculations which is typically small for the cases with limited overlap between the embedded subsystem and the environment.⁷⁷ Since the PBE0 xc functional is orbital-dependent it cannot be used to provide an xc contribution to the embedding potential. We chose to use the PBE (Ref. 68) xc for this contribution, following earlier work on orbital-dependent functionals.^{46,78–80} For the kinetic energy component of the embedding potential we tested out a number of different functionals: the Thomas–Fermi^{81–83} functional, the NDSF functional of Wesolowski and co-workers⁸⁴ (which contains a TF component but was developed especially for FDE), the PW91K (Ref. 85) functional, and PW91K with the long-distance correction proposed by Jacob and Visscher⁷⁸ (PW91K-CJCORR). This procedure yielded converged embedding potentials that were subsequently used in WFT-in-DFT calculations as well as DFT-in-DFT calculations to allow for comparison with supermolecular results.

These FDE TD-DFT calculations were carried out in the uncoupled approach⁸⁶ in which the response of the environment to the electronic excitation is neglected and in which

charge-transfer excitations are not taken into account. The validity of the first approximation was investigated by performing exploratory calculations with the coupled excitation framework of Neugebauer⁸⁷ from which we found that these couplings are indeed negligibly small.

D. Wave function theory

The WFT-in-DFT calculations were done using the FDE-implementation⁴⁶ in the DIRAC10 (Ref. 88) relativistic quantum chemical package.

The IHFSCC-SD (intermediate Hamiltonian Fock-space coupled cluster with singles and doubles^{30–32}) method with a Dirac–Coulomb (DC) Hamiltonian, where $\langle SS|SS \rangle$ integrals have been approximated by a point charge model,⁸⁹ was used. The valence double- ζ basis set of Dyall⁹⁰ (dyall.v2z) for the uranium atom and the augmented correlation consistent polarized valence double- ζ basis sets of Dunning⁹¹ (aug-cc-pVDZ) for oxygen and carbon atoms were employed.

In the Fock-space coupled cluster^{34,40,92,93} method a diagonalization of an effective Hamiltonian yields amplitudes and eigenvalues of the set of states that is related to a closed-shell reference system (sector $(0h, 0p)$) by electron annihilation (h), creation (p), or both.^{94–98}

For CUO, the conventional approach would be to obtain the excitation energies that we are interested in by selecting the appropriate active space for a sector $(1h, 1p)$ (“one hole, one particle”) calculation of the Fock-space. This procedure does, however, lead to convergence problems while determining the “one particle” (electron affinity or sector $(0h, 1p)$ of Fock-space) amplitudes that are required as input for the sector $(1h, 1p)$ calculation. These problems could be traced back to the presence of a number of low-lying Rydberg orbitals, that appear at lower energies than the local orbitals of interest (i.e., those that are involved in the lowest electronic transitions) in the CUO molecule. These problems with Rydberg orbitals were not encountered in the earlier work of Infante and Visscher¹⁷ due to lack of very diffuse functions in their basis. Since we are now interested in the interaction with the environment, augmented basis sets are clearly preferable, so we need to find a way around this problem. This can be done by calculating the electronic spectrum via sector $(0h, 2p)$ of Fock-space, i.e., starting from the CUO²⁺ as a reference system and calculating excitation energies as differences between the second electron affinities that are obtained in this sector. With this choice of reference system, the local orbitals are all below the diffuse orbitals and fully converged results can be obtained.

For the systems we investigated, all spinors with energies $\epsilon \in [-3.00; 80.00]$ a.u. were correlated, which correspond to 11 occupied (22 electrons) and about 350 virtual spinors. This corresponds to slightly larger active spaces with respect to those employed in our earlier work on the UO₂²⁺, NUN, and NUO⁺ molecules,^{18,99} and significantly enlarged the valence active space in comparison with the previous work of Infante and Visscher.¹⁷ A detailed description of the active spaces for each particular molecule is given in the supplementary material.¹¹⁰

III. RESULTS AND DISCUSSION

We start with a brief discussion of the electronic structure of the CUO molecule, for which we obtained TD-DFT results with functionals that were not yet applied to this molecule. In order to focus on the essential physical aspects at play, in the discussion that follows we will employ a spin-free model in which the question of ordering of the lowest electronic states reduces to the discussion of a gap between a closed-shell singlet and an open-shell triplet state. We may thereby take over some of the knowledge gained in non relativistic calculations on light molecules to the current species.

A. Electronic structure of the CUO molecule

The relative energies of the singlet σ^2 and triplet $\sigma^1\phi^1$ states of the CUO compound have been intensively debated for a number of years as the different electronic structure methods that have been used did not give a consistent picture. While disagreeing on the precise energy difference, all methods give qualitatively the same picture with respect to the bond length and vibrational frequency difference between these two states. The $\sigma^1\phi^1$ ($^3\Phi$) state has longer U–O and in particular U–C bond lengths than the σ^2 ($^1\Sigma^+$) state. This is easily explained by the transfer of an electron from a bonding U–C orbital to the non-bonding $5f_\phi$ -orbital of the uranium atom. Inclusion of spin-orbit coupling (SOC) gives the same qualitative picture with some admixture of the $^3\Delta_2$ state into the lower $^3\Phi_2$ state that lowers this state relative to the $^1\Sigma_0^+$ state which is in first order not affected by SOC.

Roos *et al.*¹² performed CASPT2 calculations with *a posteriori* included SOC and predicted the $^3\Phi_2$ to be the ground-state of CUO. Later on, Infante and Visscher¹⁷ applied a relativistic coupled cluster with singles doubles and perturbative triples—CCSD(T) method—as well as the Fock-space coupled cluster with singles and doubles—FSCC-SD—method. They found a strong stabilization of the $^1\Sigma_0^+$ state by the dynamic correlation effects and concluded that this state should be the ground-state for an isolated molecule. This supports the explanation that was put forward to explain the experimental findings. Recently Yang *et al.*¹³ published SOC configuration interaction with singles and doubles (CISD (Ref. 100)) calculations that are in qualitative agreement with these coupled cluster results. They determined the $^1\Sigma_0^+$ state to be the lowest state in both $^1\Sigma_0^+$ and Φ_2 optimized

geometries. Noticeable is the large discrepancy (amounting to about 1 eV) between the different electronic structure methods employed so far. From the results of Infante and Visscher it appears that adding dynamical correlation, by correlating more electrons or improving the basis set, favors the more compact $^1\Sigma_0^+$ state, thus yielding a larger gap. It is therefore of interest to see what a DFT treatment of electron correlation gives.

Taking the $^1\Sigma_0^+$ as the reference state we chose the DFT-optimized structure of this state, with U–O and U–C bonds of 1.779 and 1.733 Å, respectively, for spin-free vertical excitation calculations. In the following discussion we will focus on excitations from the σ (HOMO) orbital to the virtual σ , δ , and ϕ molecular orbitals. These transitions give rise to the $^{1,3}\Sigma$, $^{1,3}\Delta$, and $^{1,3}\Phi$ excited-states. While the δ - and ϕ -orbitals also play an important role in some molecules isoelectronic to the UO_2^{2+} such as NUN and NUO⁺, CUO is special in having also a relatively low-lying σ virtual orbital. In most studies this orbital has been ignored, but we will see that it can play a role in some of the calculations.

In agreement with ΔSCF calculations with the same functionals that place the $^3\Phi$ below the reference $^1\Sigma^+$ state, TD-DFT calculations with the PBE (Ref. 68) and PBE0 (Refs. 58 and 59) xc functionals indicate a negative excitation energy for this triplet state. As states with negative excitation energies are not calculated by the standard TD-DFT algorithm,⁶⁴ we added a very small admixture of Hartree–Fock (HF = 0.1%) exchange to the PBE xc functional to force the program to use the algorithm for hybrid functionals. As shown in Table I this admixture does not affect the energies of remaining states, but indicates a singlet-triplet gap of –0.13 eV. As found elsewhere (see e.g.,¹⁰¹ for a recent discussion), such artificially low triplet states are more likely to occur when the fraction of exact exchange is larger. With 25% of exact exchange (the PBE0 xc functional) the $^3\Phi$ state lies 0.20 eV below the $^1\Sigma^+$ state and the separation increases to 0.55 eV for the 100% of exact exchange in the TD-HF method. At the same time the exchange splitting between the $^3\Phi$ and $^1\Phi$ increases dramatically from 0.23 eV (PBE) to 1.96 eV (TD-HF). Concerning the trend noted previously in the WFT calculations, in which an improvement of the description of dynamical correlation lowered the $^1\Sigma$ relative to the $^3\Phi$ state, we find qualitative agreement by defining TD-HF as the most uncorrelated method and TD-DFT with PBE as the most correlated method.

TABLE I. Spin-free vertical excited-states of the CUO molecule with respect to the $^1\Sigma^+$ ground-state (in eV): a comparison of different methods.

Symmetry	TD-DFT(PBE)			TD-HF	CASPT2 ^a	CCSD ^b	CCSD(T)		IHFSCC-SD
	HF=0%	HF=0.1%	HF=25%				Ref. 17	Ref. 108	
$^3\Sigma^+$	0.80	0.80	1.03	1.68	...	...	...	...	0.88
$^3\Phi$	...	–0.13	–0.20	–0.55	0.09	0.77	0.83	0.68	1.34
$^3\Delta$	0.41	0.41	0.46	2.35	0.54	...	...	...	1.36
$^1\Sigma^+$	1.47	1.48	1.77	2.85	...	...	...	...	1.50
$^1\Delta$	0.71	0.71	0.98	2.83	0.72	...	...	...	1.53
$^1\Phi$	0.10	0.10	0.50	1.41	0.59	...	...	...	1.67

^aRef. 12.

^bRef. 17.

TABLE II. Spin-orbit vertical excited-states of the CUO molecule with respect to the $^1\Sigma_0^+$ ground-state (in eV): a comparison of different methods.

State ^a	IHFSCC-SD(22e)	CCSD(T)(34e) ^b	CASPT2(12e) ^c	SO-CISD(24e) ^d
$^3\Sigma_1^+$	0.81	...	...	...
$^3\Phi_2$	0.94	0.60	-0.36	0.30
$^3\Phi_3$	1.01	...	-0.15	0.57
$^3\Delta_1$	1.22	...	0.19	0.58
$^3\Delta_2$	1.28	...	0.31	...

^aSubscripts denote Ω -values and superscripts spin multiplicity.^bRef. 17.^cRef. 12.^dRef. 13.

For the WFT-based methods we note that the spin-free CASPT2 calculations of Roos *et al.*¹² predict the $^3\Phi$ state slightly above the singlet state by 0.09 eV, but this is not enough for this state to remain the lowest when SOC is accounted for. Since dynamical correlation is only included up to the second-order in perturbation theory, one can again fit these results in a trend leading from HF (predicting the $^3\Phi$ state to be the ground-state by 0.5 eV) to the coupled cluster methods that predict a $^1\Sigma_0^+$ ground-state. This trend is even stronger when including our new IHFSCC-SD (Refs. 30–32) data that were obtained using a larger basis set and active space than was feasible earlier.¹⁷ From these calculations we obtain the $^3\Phi$ state at even more than 1.3 eV above the closed-shell $^1\Sigma^+$ state, with an open-shell $^3\Sigma^+$ state being the first excited-state at 0.88 eV.

We believe that the new DFT and CC results are interesting because they clearly illustrate the difficulties in finding a proper description of the balance between exchange and correlation (in a DFT picture) and static and dynamic correlation (in a WFT picture) for actinides. The model xc hole used in the DFT approach will have to provide an equally good description of the strong angular correlation found in the radially localized ϕ -orbitals as well as for the qualitatively dif-

ferent correlation in the σ bonding orbital. This is difficult to achieve on basis of information from only the electron density and its gradient, while adding exchange in a hybrid approach has a limited value as this brings along the large error in the HF description. For the WFT methods the challenge is equally large as an electron in the ϕ -orbital will have a stronger interaction with the semicore electrons than an electron in a more extended σ -orbital, requiring a well-balanced basis set and a substantial number of electrons to be correlated. We plan to study these aspects in more detail in another publication.

Coming back to the main topic of this paper, we also analyzed the influence of the spin-orbit coupling on the transitions. The results are listed in Table II in which we kept the major LS-designation but added the Ω values, which is the only proper quantum number after inclusion of SOC. Besides the relativistic splitting of all the triplet states, there is no qualitative difference with the spin-free transition energies.

B. The CUONg₄ models

In this section we investigate how the interaction with the environment affects the lowest electronic states. We focus on the $^1\Sigma^+$ and $^3\Phi$ states, but also consider the fate of the $^3\Sigma^+$ state when the system is confined in a matrix.

1. Geometries and vibrational frequencies

Table III lists all the geometries and vibrational frequencies obtained in this work. We observe a slight increase of the U–C and U–O bond distances due to the environment that becomes stronger when we attach heavier, more polarizable, noble gas (Ng) atoms. The four attached noble gas atoms move slightly out of the equatorial plane with a C–U–Ng angle slightly larger than 90° in the singlet states and slightly smaller than 90° in the triplet states of the CUOXe₄ complex.

TABLE III. Optimized structures and vibrational spectra calculated using DFT with PBE0 xc functional in the C_{2v} point group symmetry. Bond distances are given in Å, angles in degrees, and frequencies in cm^{-1} . Reference theoretical studies are presented in round brackets and experimental data in square brackets.

System	d(U–C)	d(U–O)	d(U–Ng)	$\angle$ CUNg	ν_{UC}	ν_{UO}
CUO($^1\Sigma^+$)	1.733 (1.714 ^a , 1.770 ^b , 1.757 ^c , 1.738 ^d)	1.779 (1.759 ^a , 1.795 ^b , 1.798 ^c , 1.785 ^d)			1175 (1269 ^a , 1089 ^c , 1183 ^f , 1182 ^d)	927 (960 ^a , 870 ^d , 917 ^e , 922 ^f)
CUONe ₄ ($^1\Sigma^+$)	1.734 (1.769 ^c)	1.782 (1.805 ^c)	3.315	99.7	1170 (983 ^c) [1047 ^c]	923 (847 ^c) [872 ^c]
CUOAr ₄ ($^1\Sigma^+$)	1.738 (1.774 ^c)	1.788 (1.811 ^c)	3.416	95.8	1156 (963 ^c)	913 (840 ^c)
CUOKr ₄ ($^1\Sigma^+$)	1.741 (1.775 ^c)	1.790 (1.812 ^c)	3.455	94.5	1145 (947 ^c)	908 (839 ^c)
CUOXe ₄ ($^1\Sigma^+$)	1.747 (1.782 ^c)	1.793 (1.813 ^c)	3.554	92.4	1127 (942 ^c)	901 (839 ^c)
CUO($^3\Phi$)	1.836 (1.814 ^a , 1.871 ^b , 1.857 ^c)	1.808 (1.789 ^a , 1.818 ^b , 1.825 ^c)			948 (893 ^c)	879 (828 ^c)
CUONe ₄ ($^3\Phi$)	1.840 (1.862 ^c)	1.811 (1.828 ^c)	3.147	91.7	942 (884 ^c)	872 (819 ^c)
CUOAr ₄ ($^3\Phi$)	1.845 (1.868 ^f , 1.871 ^c)	1.815 (1.843 ^f , 1.833 ^c)	3.309	90.4	932 (881 ^f , 869 ^c) [835 ^f , 853 ^c]	868 (824 ^f , 814 ^c) [793 ^f , 804 ^c]
CUOKr ₄ ($^3\Phi$)	1.848 (1.873 ^f , 1.874 ^c)	1.817 (1.839 ^f , 1.835 ^c)	3.374	89.9	926 (876 ^f , 864 ^c) [832 ^f , 842 ^c]	864 (822 ^f , 810 ^c) [790 ^f , 797 ^c]
CUOXe ₄ ($^3\Phi$)	1.853 (1.875 ^f , 1.879 ^c)	1.818 (1.833 ^f , 1.836 ^c)	3.514	88.6	917 (870 ^f , 860 ^c) [830 ^f]	860 (819 ^f , 808 ^c) [789 ^f]

^aMRSOCISD (Ref. 13).^bSO-CASPT2 (Ref. 12).^cDFT/PW91 (Ref. 23).^dDFT/PW91 (Ref. 26).^eDFT/PBE0 (Ref. 109).^fDFT/PBE0 (Ref. 102).

FIG. 1. Total bonding energies of the CUONg_4 complexes with respect to the $1\Sigma^+$ (solid line) and 3Φ (dashed line) states of the CUO system (DFT calculations in ADF).

The weakening of the U–C and (to less extent) U–O bond in the triplet state is most clearly visible in the U–C and U–O stretch vibrations. For the bare molecule the U–C stretch is lower by 227 cm^{-1} in the triplet state than in the singlet

FIG. 2. CUONe_4 orbitals involved in the lowest-lying electronic transitions visualized with an isosurface value of 0.03 in the ADFGUI.¹⁰⁷

state. Compared to this difference the matrix effects are much weaker with a shift of $31\text{ (48)}\text{ cm}^{-1}$ of the U–C stretch for the singlet (triplet) state in the model for the xenon matrix. The experimentally observed shift of 238 cm^{-1} of the U–C stretch upon going from neon to argon does therefore best match with the 195 cm^{-1} difference between the vibration of the singlet state in the neon model and the triplet state in the argon model. This is already discussed in detail by Andrews *et al.*²³ who obtained slightly different values but a qualitatively similar trend with the PW91K functional. The new data with hybrid functionals provides further support for their interpretation. Note that only trends can be reliably compared, for a more complete comparison with the experimental values it might be necessary to include more than just four noble gases around the CUO to model the matrix. Moreover, it might be necessary to consider also anharmonic effects.¹⁰²

2. Ground-state DFT study

To simplify the comparison between the CUO and CUONg_4 complexes, we will use (idealized) C_{4v} point group symbols, with in parenthesis the $C_{\infty v}$ designations to indicate the parentage of the states or orbitals. We define the zero of our energy scale as the $1A_1(1\Sigma^+)$ state of CUO with a cage of four Ng atoms at infinite distance and plot in Figure 1 the variation of the binding energy of the $1A_1(1\Sigma^+)$ and the $3E(3\Phi)$ states as a function of Ng type. This interaction with the cage is indeed slightly more pronounced in the triplet state with the largest difference occurring when moving from neon to argon, but the difference is only 0.04 eV. This can only change the order of two states if they are already very nearly degenerate. As discussed already in the section of TD-DFT, the PBE0 functional places the triplet slightly below the singlet already for the bare CUO molecule and considering optimized structures for the triplet state reinforces that conclusion.

3. Excitation energies from TD-DFT

To understand the trends in excitation energies, it is instructive to look at the changes in the valence orbital energies of CUO induced by the attachment of the Ng atoms. We consider the closed-shell singlet calculation in which we have as HOMO a bonding U–C σ -orbital, as LUMO a nonbonding σ -orbital, and at higher energy a ϕ - and two δ -orbitals. These orbitals are depicted in Figure 2. When adding the Ng atoms the two δ -orbitals are split by the ligand field into $27a_1$ and $5a_2$, and the $28a_1$ - and $6a_2$ -orbitals, respectively. In Figure 3(a) we plot the energy difference of all relevant virtual orbitals relative to the HOMO to get a first indication of the effect of the environment on excitation energies. The diffuse non-bonding σ -orbital, which is the LUMO in bare CUO and CUONe_4 , is pushed up by the repulsive interaction with the closed-shell ligands and rises in the argon system above the ϕ -orbitals, and in krypton and xenon also above the lower δ -orbital $27a_1$. This indicates that this orbital is indeed of less interest in explaining the electronic structure of the molecule in the matrix.

Spin-free excitation energies are listed in Table IV, with the negative transition energies indicating a triplet ground-state. In agreement with the ΔSCF calculations, we find small

FIG. 3. Lowest-lying valence orbital energies of the CUO ($^1\Sigma^+$) and the CUONg_4 (1A_1) complexes from the supermolecular and DFT-in-DFT/PBE0 calculations using different kinetic energy functionals in ADF. Orbital energies are given relative to the energy of HOMO for all the compounds.

effects on the transition energies, except for the large effect on the $b\ ^3A_1$ ($^3\Sigma^+$) and $d\ ^1A_1$ ($^1\Sigma^+$) states that correspond to excitation to the diffuse σ -orbital. These transitions rapidly shift to higher energies when adding the noble gas cage. Other changes in the electronic spectrum introduced by the noble gas environment are relatively small for the lowest-lying excitations (difference less than 0.1 eV). Those results are shown in supermolecular case, where the differences in the electronic transitions between the bare CUO and the CUONg_4 complexes are plotted. We note a relatively large difference between the Ne and Ar cage, but as already seen in the orbital energy differences, an overall surprisingly small effect of the matrix given the experimental findings.

C. DFT-in-DFT electronic structure of the CUONg_4 compounds

1. The quality of embedding potential

We now investigate whether the subtle effect on the environment can be represented by an FDE embedding potential.

Two criteria may be used to quantify the quality of the FDE-approach: (1) the reproduction of the ground-state density of the complex and (2) the error in the calculated transition energies. These errors can be evaluated exactly in DFT and are supposed to carry over to the WFT description.

To assess the first error we compare the electron density calculated within the DFT-in-DFT framework to the supermolecular density. This criterion tests the accuracy of the approximation used for the non-additive parts of the kinetic energy and xc functionals. For the latter we restrict ourselves to the PBE functional to remain as close as possible to the PBE0 hybrid functional used in the supermolecular calculation. For the repulsive kinetic energy contribution to the embedding potential that models the Pauli repulsion of the Ng cage, we used the simplest local Thomas–Fermi (TF) (Refs. 81–83) and the often more robust⁷⁷ gradient-corrected functional PW91K.⁸⁵ Since underestimation of the Pauli repulsion may give rise to unphysical transfer of electron density from the active center to the environment subsystem—the so called “electron leak” problem,^{52,78,103} we also considered the NDS

TABLE IV. Spin-free vertical excitation energies of the $\text{CUO}({}^1\Sigma^+)$ and $\text{CUONg}_4({}^1A_1)$ from the KS/TD-DFT/PBE0 approach (in eV).

Symmetry ^a	CUO	CUONe ₄	CUOAr ₄	CUOKr ₄	CUOXe ₄
$a^3E({}^3\Phi)$	-0.204	-0.222	-0.233	-0.253	-0.231
$a^3A_1({}^3\Delta)$	0.464	0.431	0.384	0.211	0.368
$a^3A_2({}^3\Delta)$	0.464	0.440	0.399	0.259	0.385
$a^1E({}^1\Phi)$	0.504	0.472	0.434	0.333	0.411
$a^1A_1({}^1\Delta)$	0.983	0.951	0.915	0.839	0.891
$a^1A_2({}^1\Delta)$	0.983	0.978	0.960	0.892	0.949
$b^3A_1({}^3\Sigma^+)$	1.029	1.245	1.598	1.930	1.826
$c^3A_1({}^3\Gamma)$	1.317	1.289	1.274	1.234	1.281
$b^3A_2({}^3\Gamma)$	1.317	1.289	1.275	1.236	1.284
$d^3A_1({}^3\Delta)$	1.324	1.296	1.281	1.245	1.289
$c^3A_2({}^3\Delta)$	1.324	1.296	1.281	1.243	1.289
$b^1A_1({}^1\Gamma)$	1.484	1.455	1.438	1.405	1.441
$b^1A_2({}^1\Gamma)$	1.484	1.455	1.438	1.404	1.440
$c^1A_1({}^1\Delta)$	1.726	1.693	1.666	1.653	1.620
$c^1A_2({}^1\Delta)$	1.726	1.710	1.698	1.671	1.692
$b^3E({}^3\Phi)$	1.773	1.748	1.736	1.698	1.745
$c^3E({}^3\Phi)$	1.775	1.765	1.761	1.737	1.773
$d^1A_1({}^1\Sigma^+)$	1.771	1.938	2.156	2.323	2.248

^aWe use the C_{4v} point group symmetry notation with $C_{\infty v}$ irreps indicated in parenthesis.

(Ref. 84) functional and the zero-overlap correction of Jacob and Visscher⁷⁸ that eliminate such problems. We used the error measures defined by Bernard *et al.*:¹⁰⁴ integrated absolute errors in the electron density, the integrated root mean square errors in the electron density, and the magnitude of the errors in the dipole moment. While the former two strictly depend on the absolute size of the error in the electron density, the latter also provides information on its spatial redistribution. The size of the errors is taken relative to the sum of fragment density obtained by simply superimposing the density of the cage and the density of the bare CUO molecule.

The simple TF potential provides a reasonable description and has even the smallest errors measures for the complex with xenon (see Table V). For the neon cage PW91K provides the best description, while for the other two cases, argon and krypton, no unambiguously best functional can be selected. In correcting for charge-leak artifacts, the Jacob and Visscher⁷⁸ correction reduces the embedding potential too much, underestimating the interaction between CUO and the cage. This can have an adverse effect on the dipole moment, when compared to its parent functional, PW91K. For the NDS (Ref. 84) kinetic energy functional that is based on the TF

FIG. 4. Contributions to the total embedding potential from the electrostatic, non-additive xc and non-additive kinetic energy—TF to the left and NDS to the right—components along the Ng–U–Ng axis in the $\text{CUONg}_4({}^1A_1)$ complexes (in hartree).

FIG. 5. Contributions to the total embedding potential from the electrostatic, non-additive xc and non-additive kinetic energy—PW91K to the left and PW91K-CJCORR to the right—components along the Ng–U–Ng axis in the CUONg₄(¹A₁) complexes (in hartree).

functional we see an improvement relative to TF for the Ar and Kr complexes but a slightly worse performance for the Ne and Xe complexes.

The best overall performance for the two cases that are of most interest, neon and argon, is therefore obtained with the PW91K kinetic energy functional. More interesting than these errors in the density is, however, the effect on the valence orbital energies of the DFT-in-DFT CUONg₄ complexes. These results are indicative of the errors that can be expected in the supermolecular spectra. This data are given in Figures 3(b)–3(d). From the figures we observe that the effect of the cage is generally underestimated by the FDE approach: while in KS/DFT the 26a₁-orbital is the LUMO only for the CUO and CUONe₄ molecules, with FDE it is, e.g., always found as LUMO for CUOXe₄. Even more troublesome is the fact that the order of the 26a₁- and 13b₁/b₂-orbitals is reversed (crossing of the blue dashed lines between Ar and Kr) for the heavier noble gas cages. To check whether these artifacts are due to the freeze-and-thaw procedure we also did some test calculations in which the density of unperturbed Ng atoms was used to represent the density of the cage, but this gave the same picture.

More insight can be obtained by analyzing the three separate components of the potential: the electrostatic (Coulomb and nuclear), and the non-additive xc and kinetic energy components. In Figures 4 and 5 these are plotted along the Ne–U–Ne and Ar–U–Ar lines in an idealized geometry (with the Ng all exactly in the equatorial plane). In all pictures we see that it is the balance between the large attractive electrostatic and the repulsive kinetic energy components that determines the potential. This balance is more difficult to obtain when the electrostatic terms become larger, as is the case for the heavier Ng atoms. The exact potential should furthermore reflect the shell structure of the atoms that also becomes more pronounced for the heavier atoms. For the uncorrected TF and PW91K potentials the shell structure mainly arises from the compensation of the monotonously negative Coulomb potential by the monotonously positive kinetic energy component, while for the NDS approach the switching function that is used to interpolate between two functional forms also introduces oscillations in the kinetic energy component for the heavier Ng atoms. The Jacob and Visscher correction⁷⁸ operates on the full potential and reduces this in the vicinity of the nuclei to obey an exact limit for non-overlapping systems.

TABLE V. Integrated errors in the electron density: Δ^{abs} (absolute) and Δ^{rms} (root mean square), magnitude of the error in the dipole moment $|\Delta_{\mu}|$ for the sum of fragments, and the DFT-in-DFT/PBE0 calculations with a different approximate non-additive kinetic energy functionals. The most accurate values are marked in boldface.

System		$\Delta^{abs} \times 10^{-3}$	$\Delta^{rms} \times 10^{-3}$	$ \Delta_{\mu} (\text{D})$
$^1\text{CUONe}_4$	Sum of fragments	1.35	0.99	0.183
	FDE (Thomas–Fermi)	4.57	0.03	0.029
	FDE (NDS)	4.84	0.03	0.033
	FDE (PW91K)	2.32	0.02	0.010
	FDE (PW91K-CJCORR)	6.23	0.04	0.171
$^1\text{CUOAr}_4$	Sum of fragments	2.76	1.39	0.354
	FDE (Thomas–Fermi)	1.42	1.39	0.146
	FDE (NDS)	1.40	0.06	0.139
	FDE (PW91K)	1.39	0.07	0.261
	FDE (PW91K-CJCORR)	1.66	0.09	0.370
$^1\text{CUOKr}_4$	Sum of fragments	2.71	1.23	0.225
	FDE (Thomas–Fermi)	1.08	0.06	0.089
	FDE (NDS)	1.10	0.06	0.115
	FDE (PW91K)	1.03	0.06	0.188
	FDE (PW91K-CJCORR)	1.33	0.85	0.348
$^1\text{CUOXe}_4$	Sum of fragments	2.27	0.11	0.205
	FDE (Thomas–Fermi)	1.36	0.07	0.178
	FDE (NDS)	1.41	0.07	0.222
	FDE (PW91K)	1.40	0.08	0.302
	FDE (PW91K-CJCORR)	1.40	0.08	0.307

For the current system this leads to an almost complete reduction of the potential which explains the too small orbital energy shifts for this approach.

2. Excitation energies from embedded TD-DFT

As the goal of the embedding approach is to reproduce the supermolecular approach, that is the data in Table IV, we directly compare the DFT-in-DFT to the reference supermolecular excitation energies in Figure 6. As was expected from the errors seen in the orbital energies, none of the kinetic energy approximations is able to reproduce the KS/TD-DFT/PBE0 results for the heavier Ng matrices. Errors are largest in absolute magnitude for the $^1,^3A_1$ and $^1,^3A_2$ excited-states in heavier noble gases. All embedding potentials do shift the 3E state above the 1A_1 ground-state. For all excitations the effect of the environment is small and the PW91K functional provides the relatively best performance, in agreement with the density error analysis discussed above.

D. WFT-in-DFT electronic structure of the CUONg_4 compounds

Considering all the information discussed above we find that the PW91K kinetic energy functional can give a qualitative description of the neon and to a less extent argon environments, although quantitative agreement and correct trends are not reached. We decided to select this embedding potential to perform WFT-in-DFT calculations and check whether the same environment effects are found.

The SOC WFT-in-DFT excitation energies are listed in Table VI. The effect of noble gas environment on the transitions is clearly much too small to cause a ground-state change in the WFT calculations, but just sufficient, in the case of neon, to place the Φ_2 excited-state below the two $^3\Sigma^+$ states. For argon this trend is reversed, in contrast to the supermolecular DFT calculations, which is due to the larger error in the embedding potential for this system. This error is larger

FIG. 6. Accuracy of different approximate non-additive kinetic energy functionals on the spin-free vertical electronic spectra of the $\text{CUONg}_4(^1A_1)$ complexes with respect to the supermolecular (KS/TD-DFT/PBE0) reference data (in eV). Red bars correspond to CUONe_4 , green to CUOAr_4 , blue to CUOKr_4 and violet to CUOXe_4 complexes.

TABLE VI. SOC vertical excitation energies of the CUO and CUONg₄ complexes from the WFT-in-DFT: IHFSCC-SD via sector (*0h*, *2p*) for the bare CUO subsystem and embedded in the Ng₄ DFT-in-DFT/PBE0/PW91K potential.

State ^a	CUO	CUONe ₄	CUOAr ₄	CUOKr ₄	CUOXe ₄
³ Σ _{0,1} ^b	0.81	1.02	0.85	0.76	0.65
³ Φ ₂	0.94	0.84	0.89	0.93	0.97
³ Φ ₃	1.01	0.94	0.98	1.02	1.06
³ Δ ₁	1.23	1.07	1.27	1.30	1.33
³ Δ ₂	1.28	1.17	1.31	1.34	1.37
¹ Σ ₀	1.37	1.51	1.36	1.31	1.21
³ Φ ₄	1.60	1.53	1.57	1.61	1.64
³ Δ ₃	1.69	1.58	1.58	1.67	1.64
¹ Δ ₂	1.72	1.68	1.75	1.78	1.76
¹ Φ ₃	1.79	1.73	1.76	1.79	1.80

^aSubscripts denote Ω-values and superscripts spin multiplicity.

^bThe differences between ³Σ₀⁺ and ³Σ₁⁺ electronic states are less than 0.01 eV.

still when utilizing an embedding with heavier Ng atoms, and leads to meaningless results as expected on basis of the DFT-in-DFT results.

IV. CONCLUSIONS AND OUTLOOK

We have optimized geometries and calculated vibrational frequencies of the CUO and CUONg₄ complexes in the ¹Σ⁺ and ³Φ states using the PBE0 hybrid xc functional. The significant difference in characteristic U–O and U–C vibrational frequencies that was observed in experiments, is in agreement with previous work, explained by a difference of electronic ground-state (¹Σ⁺ to ³Φ) in the neon and argon matrix, respectively. The direct effect of environment is smaller than 50 cm^{−1} for the U–O and U–C stretching frequencies.

Since analysis of the vibrational spectra provides only an indirect measure for the energetic ordering of the electronic states, we also investigated this ordering directly for CUO and the CUONg₄ model compounds. The spin-free and spin-orbit IHFSCC-SD excitation energies of the CUO molecule, indicate that this molecule has a singlet ground-state, which is in line with earlier Fock-space coupled cluster studies by one of us¹⁷ and the CISD calculations of Yang *et al.*¹³ These coupled cluster energies were used to assess the accuracy of hybrid TD-DFT/PBE0 excitation energies. It turns out that both components of PBE0 xc functional—DFT and HF part—are insufficiently accurate. This issue can be related to the well-known “triplet instability” problem,^{101,105,106} caused by the large exchange splitting in the 5*f*-shell, that is strongly overestimated in Hartree–Fock theory.

Compared to the large energy splittings predicted by the WFT approaches, the low-lying excited-states show only minor perturbations due to the noble gas environment. An exception are the ^{3,1}Σ excited-states that originate from electron transfer to the diffuse virtual *f*_σ-orbital. This diffuse orbital, and the corresponding transitions, are shifted to a much higher energy by the equatorial ligands.

Since the perturbations are small, we expected that these could be captured by the FDE approach, but it turns out that none of the currently available kinetic energy function-

als is able to yield results with the desired accuracy of less than 0.1 eV. For the CUONe₄ model the PW91K kinetic energy functional provides a reasonable agreement with a supermolecular approach, but for the complexes with heavier noble gases all kinetic energy functional produce too small ligand field splittings and a qualitatively incorrect result. WFT-in-DFT calculations on the CUONg₄ systems should, however, be feasible as soon as embedding potentials improve because the analysis of the densities shows that a density partitioning into a CUO and an environment density is indeed well possible.

As a side result of our work we note the importance of further development of xc functionals that can provide qualitatively correct xc splittings for actinides. While for the UO₂²⁺, NUN, and NUO⁺ molecules good agreement between the TD-DFT and IHFSCC-SD electronic excitations can be reached, this is currently not the case for the CUO molecule.

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