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# The ground state and electronic spectrum of CUO: a mystery

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Results are presented from a theoretical study of the lower electronic states of the CUO molecule. Multiconfigurational wave functions have been used with dynamic correlation added using second order perturbation theory. Extended basis sets have been used, which for uranium were contracted including scalar relativistic effects. Spin-orbit interaction has been included using the state-interaction approach. The results predict that the ground state of linear CUO is  $\Phi_2$  with the closed shell  $\Sigma_0^+$  state 0.5 eV higher in energy. This is in agreement with matrix isolation spectroscopy, which predicts  $\Phi_2$  as the ground state when the matrix contains noble gas atoms heavier than Ne. In an Ne matrix, the experiments indicate, however, that CUO is in the  $\Sigma_0^+$  state. The change of ground state due to the change of the matrix surrounding CUO cannot be explained by the results obtained in this work and remains a mystery.

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## 1 Introduction

In a recent article in *Science*, Li and co-workers reported that the CUO molecule "exhibits very different stretching frequencies in a solid argon matrix compared to that in a solid neon matrix".<sup>1</sup> The reported frequencies were 872.2 (U–O) and 1047.3 (U–C) in Ne while they are 804.3 and 852.5 in Ar. The same shifts are obtained with heavier noble gas matrices and also if 1% of Ar is mixed into a Ne matrix. These large shifts cannot be explained as simple matrix effects. Li *et al.* performed DFT calculations using the Amsterdam density functional (ADF) code but without including spin-orbit coupling. They studied two states, one closed shell state and a triplet state corresponding to excitation from the HOMO to a  $5f\phi$  orbital on uranium. For free CUO they found the closed shell to be the ground state but with the triplet state only about 0.03 eV higher in energy. However, when they added one argon atom to the system the triplet state became the ground state, 0.02 eV below the singlet. Computed frequencies for the two states were in reasonable agreement with the measured values in Ne and Ar matrices, respectively. The somewhat unexpected conclusion was that, when the CUO molecule is bound in a noble gas matrix, its ground state shifts from a singlet closed shell, when Ne is used, to a triplet state in Ar matrices. Later, the same group has given strong indications that uranium will bind four Ar atoms in the first coordination shell.<sup>2</sup>

However, even if, seemingly, the DFT calculations give theoretical support to this conclusion, one worries about the small energy differences. Spin-orbit coupling in the triplet state can certainly be expected to be larger than a few hundredths of an eV. If this is the case, the triplet state would be the ground state also for the isolated molecule. We therefore decided to study the problem using

*ab initio* methods where the effect of spin-orbit coupling can be included. Linear triatomic molecules with the general structure XUY (X,Y = C,N,O) have earlier been studied and their vibrational frequencies have been computed.<sup>3</sup> The method used in these studies was multiconfigurational SCF theory (CASSCF)<sup>4</sup> with dynamic electron correlation included using second order perturbation theory.<sup>5,6</sup> Good agreement was obtained for the vibrational frequencies. All the studied molecules were either U(vi) with a closed shell structure or U(v) with one electron outside the closed shell. Because the vibrational frequencies agreed well with experiment, it may be concluded that the electronic state assumed to be the ground state was correct. The ability of the present approach to predict the correct ground state for this type of molecules was further tested in a study of the ground state and the lower excited states of the OUO molecules.<sup>7</sup> The calculation also included spin-orbit coupling using the new state interaction method developed by Malmqvist *et al.*<sup>8</sup> It was found that the ground state was  $^3\Phi_u(\Omega = 2)$  with the electronic configuration (5f)(7s) outside the closed shell. The lowest gerade state,  $^3H_g(\Omega = 4)$  was found 0.5 eV higher in energy with a considerably larger bond distance (1.88 compared to 1.75 for the  $^3\Phi_u$  state). The computed vibrational frequency for the ground state was  $923\text{ cm}^{-1}$  to be compared to the experimental value  $915\text{ cm}^{-1}$ .<sup>9</sup> A lower frequency was obtained for the  $^3H_g$  state. We concluded that the correct ground state had been predicted. Pierloot has recently studied the electronic spectrum of the uranyl ion in the crystal Cs<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> using the same CASSCF/CASPT2/SO method as here.<sup>10</sup> Excellent agreement with experiment was obtained. We have given these examples in order to illustrate that the CASSCF/CASPT2/SO approach is capable of predicting the properties of XUY systems with high accuracy. The present study will show one case where it is seemingly not so. Our earlier studies of the CUO molecule has assumed the ground state to be  $^1\Sigma^+$ , a closed shell. However, from the results of the present more detailed study it is concluded that the free CUO molecules has a  $^3\Phi(\Omega = 2)$  ground state corresponding to the oxidation state U(v) instead of U(vi). This result is not in agreement with the experimental results of Li *et al.*<sup>1</sup> if one assumes that the molecule in an Ne matrix will have the same electronic structure as a free CUO molecule, while the structure changes in a matrix of heavier noble gas atoms.

## 2 The ground and lower excited states of the CUO molecule

A series of calculations have been performed in order to understand the ordering of the electronic states in CUO and their properties. They were all performed using the complete active space SCF method<sup>4</sup> with dynamic electron correlation added using second order perturbation theory (CASPT2).<sup>5,6,11</sup> The earlier studies of XUY compounds<sup>3</sup> had shown that an adequate description of the closed shell state, which was assumed to be the ground state, could be obtained with an active space comprising 12 electrons in 12 orbitals. Thus, for each of the six bonding orbitals one antibonding orbital was added (four  $\sigma$ - and eight (4+4)  $\pi$ -orbitals). This active space has been used here in the preliminary calculations with added  $\delta$ - and  $\phi$ -orbitals to describe the excited states. However, in the final calculations with full inclusion of spin-orbit coupling, this active space becomes too large and it was therefore reduced to six electrons in six orbitals (two  $\sigma$ - and four (2+2)  $\pi$ -orbitals). The lowest  $\sigma$ - and  $\pi$ -orbitals were moved to the inactive space and the corresponding weakly occupied orbitals were included only at the CASPT2 level of theory. With the addition of the  $\delta$ - and  $\phi$ -orbitals the active space thus has 6 electrons in 10 orbitals. Test calculations showed that the energy separation between the lower excited states were not affected by the restriction of the active space.

The CASPT2 calculations included in the correlation treatment all valence electrons plus the 5d, 6s, and 6p electrons of uranium. In the largest calculations, the multistate option was used. All calculations to be discussed below were performed with the MOLCAS-5 quantum chemistry software.<sup>12</sup>

### 2.1 A preliminary study using ECP

A preliminary study was performed on the closed shell state,  $^1\Sigma^+$ , and the  $^3\Phi$  state using the Stuttgart relativistic ECP (energy-consistent pseudopotential) basis set<sup>13</sup> for uranium and the ANO-L (atomic natural orbital, large) basis set of the MOLCAS library for C and O, contracted to

**Table 1** Geometry, vibrational frequencies ( $\text{cm}^{-1}$ ) and relative energy (eV) for the  $^1\Sigma^+$  and  $^3\Phi$  states of CUO. Results obtained at the CASPT2 level of theory

	$r_{\text{CU}}$	$r_{\text{OU}}$	$\nu_{\text{CU}}^a$	$\nu_{\text{OU}}^a$	$\Delta E$
Calculation 1					
$^1\Sigma^+$	1.772	1.808	1077(1047)	870(872)	—
$^3\Phi$	1.889	1.842	858(853)	796(804)	0.09
Calculation 2					
$^1\Sigma^+$	1.770	1.795	1021(1047)	871(872)	—
$^3\Phi$	1.871	1.818	824(853)	764(804)	-0.11

<sup>a</sup> Experimental values within parenthesis, from ref. 1.

4s3p2d. The geometry was optimized at the CASPT2 level of theory for both states using a two-dimensional grid. The results are presented in Table 1 under the heading ‘‘Calculation 1’’.

The results shows unambiguously that the conclusions made by Li *et al.* were correct. The computed frequencies for the  $^1\Sigma^+$  state agree well with the results obtained in a Ne matrix while those obtained for the  $^3\Phi$  state are very similar to the frequencies measured with a heavier noble gas host. The adiabatic energy difference is computed to be 0.09 eV. Li *et al.* obtained 0.02 eV at the DFT level. Both numbers are small and, with the expected error bars, there is no reason to question the interpretation made in the *Science* article. However, none of these calculations included spin-orbit coupling, which certainly will stabilize the  $^3\Phi$  state relative to  $^1\Sigma^+$ .

## 2.2 Addition of spin-orbit coupling

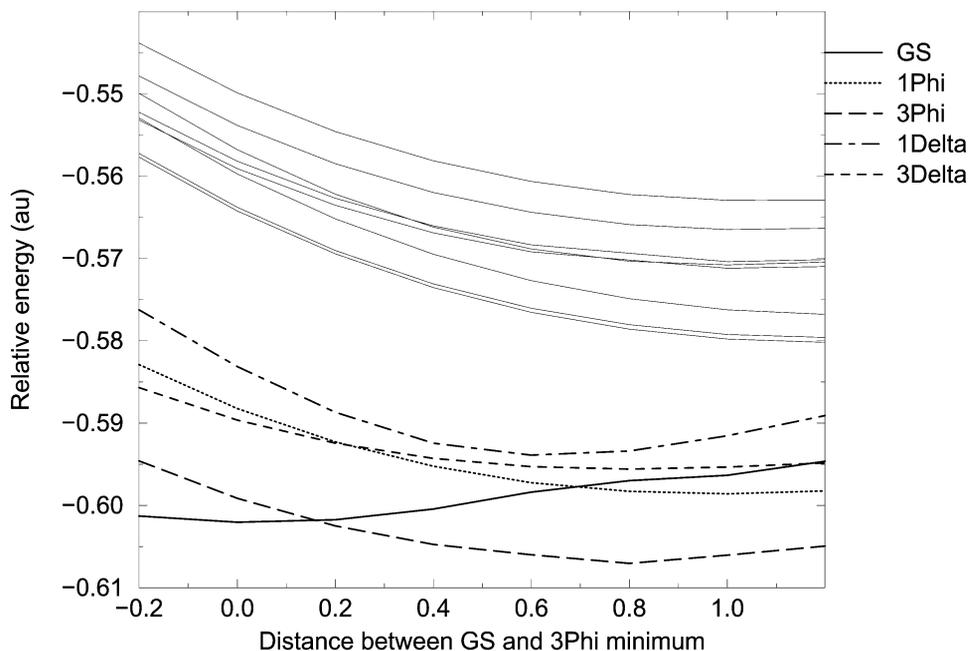
As a first attempt to estimate the effects of spin-orbit coupling, the zero-order splitting of the  $^3\Phi$  state was computed using the newly developed RASSI-SO (restricted active space state interaction-spin-orbit) code in MOLCAS.<sup>8</sup> So far, such calculations can only be performed using an all-electron basis set. The R-ECP was therefore replaced by a relativistically contracted ANO basis set contracted: 9s8p7d5f2g.<sup>14</sup> The energy separation at the CASPT2 level of theory was now 0.02 eV, still placing the  $^1\Sigma^+$  state below  $^3\Phi$ . However the spin-orbit splitting of the  $^3\Phi$  state was computed to be 0.35 eV, thus exchanging the ordering of the states. The  $^3\Phi$  state is now the lowest state at both geometries, which is at variance with the experimental results. Is it possible to perform a calculation at a higher level of theory?

## 2.3 The lower excited states of CUO

The above calculations were performed with a limited basis set and the inclusion of spin-orbit coupling was only carried out at the lowest possible level of theory. In order to make any firmer conclusions, it is necessary to remove as much of these uncertainties as possible. It was therefore decided to repeat the above calculations using a larger basis set and including in the calculation a larger number of electronic states. The basis set was increased to 10s9p7d5f3g2h for uranium and 5s4p2d1f for C and O, based on the same primitive sets. The active space consisted of six electrons in ten orbitals as described above.

First the geometries and the vibrational frequencies of the  $^1\Sigma^+$  and the  $^3\Phi$  state were determined at the CASPT2 level of theory. The results are presented in Table 1 under the heading ‘‘Calculation 2’’. Computed bond distances are now somewhat shorter, in particular for the  $^3\Phi$  state. This is most likely a result of the larger basis set. The frequencies are smaller compared to the earlier results. The  $^3\Phi$  state is found 0.08 eV above the  $^1\Sigma^+$  state at the equilibrium geometry of this state. The adiabatic energy difference is, however, negative placing the  $^3\Phi$  state 0.11 eV below the singlet state. These more accurate calculations thus favor the triplet state compared to the R-ECP results reported above.

In order to include spin-orbit coupling, the calculations were extended to include all states that can be formed by exciting from the highest occupied  $\sigma$ - or  $\pi$ -orbitals to the 5f $\phi$  and 5f $\delta$  orbitals. This gives rise to the following 15 electronic states:  $^1\Sigma^+$ ,  $^3\Pi$ ,  $^1\Pi$ ,  $2 \times ^3\Delta$ ,  $2 \times ^1\Delta$ ,  $2 \times ^3\Phi$ ,  $2 \times ^1\Phi$ ,  $^3\Gamma$ , and  $^1\Gamma$ . The corresponding number of component states for the spin-orbit Hamiltonian is 49.



**Fig. 1** The MS-CASPT2 relative energies (in au) for the lower electronic states of CUO plotted along a line connecting the minimum of the  ${}^1\Sigma^+$  ( $x = 0.0$ ) and  ${}^3\Phi$  states ( $x = 1.0$ ). The corresponding minimum geometries are given in Table 1, calculation 2.

State average CASSCF calculations (in  $C_{2v}$  symmetry) followed by multi-state (MS) CASPT2 calculations<sup>15</sup> were carried out along a line connecting the minima of the  ${}^1\Sigma^+$  and  ${}^3\Phi$  states, respectively. The resulting MS-CASPT2 curves (without spin-orbit coupling) are shown in Fig. 1. The  $x$ -axis in the figure (and also in Fig. 2) represents a linear interpolation between the two minima.

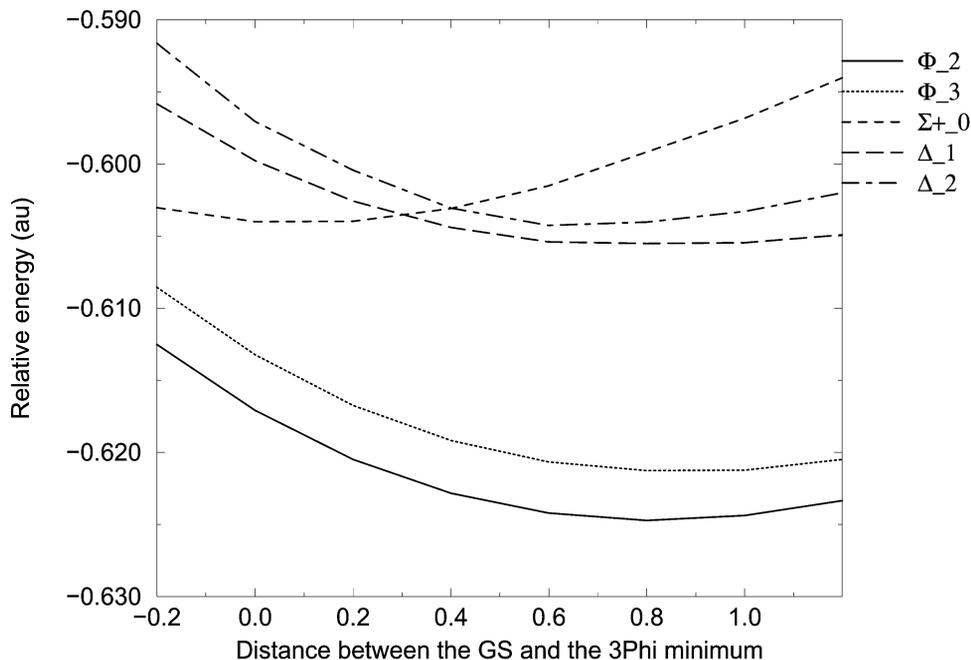
The figure illustrates the closeness in energy of the lower electronic states. Actually, close to the  ${}^3\Phi$  minimum ( $x = 1.0$ ) there are five electronic states within an energy range of 0.4 eV. We notice that the closed shell state is only the third state at this geometry. Both  ${}^3\Phi$  and  ${}^1\Phi$  are lower in energy. We can expect considerable spin-orbit coupling between these states.

The results after the inclusion of spin-orbit coupling is presented in Fig. 2. The total calculation includes 49 components, but only the 5 lowest states are shown in the figure. The lowest state is  $\Phi_2$  followed by  $\Phi_3$  for all geometries considered (the subscript is the value of the total angular momentum,  $\Omega$ ). We have indicated the most important spin-free angular momentum component of the wave function in the label. There is, however, considerable mixing. The wave function for the  $\Phi_2$  state has 14%  $\Delta$  character and  $\Phi_3$  is a mixture of  ${}^3\Phi$  (53%),  ${}^1\Phi$  (33%) and  ${}^3\Delta$  (10%). The  $\Sigma_0^+$  state is number three at its own minimum geometry.

The calculated energy separation between  $\Sigma_0^+$  and  $\Phi_2$  is  $-0.36$  eV at the minimum geometry of the former state and  $-0.55$  eV close to the minimum geometry of  $\Phi_2$ . These results thus predict the  $\Phi_2$  state to be the ground state of free CUO.

### 3 Discussions and conclusions

We can only conclude from the present study that the predicted ground state of the free CUO molecule is the same as the one observed in noble gas matrices, which contain Ar or heavier atoms.<sup>1</sup> The observation of another ground state ( $\Sigma_0^+$ ) in a Ne matrix has thus not been confirmed. This result is actually in agreement with the results obtained by Li *et al.*, if the effect of spin-orbit coupling is added to their calculated energies. Assuming that free CUO has a  $\Sigma_0^+$  ground state implies that the relative energies computed here are in error by more than half an eV. It is a much



**Fig. 2** The MS-CASPT2/SO relative energies (in au) for the lower electronic states of CUO plotted along a line connecting the minimum of the  $^1\Sigma^+$  ( $x = 0.0$ ) and  $^3\Phi$  states ( $x = 1.0$ ).

larger error than we have earlier experienced in studies of similar compounds. On the other hand, there is no known process, which would trap the molecule in an excited state, considering the experimental conditions under which the molecule has formed during the condensation process, which allows the Ne matrix to form around the CUO molecule in a flexible way. The CUO is smaller in the  $\Sigma_0^+$  state than in the  $\Phi_2$  state, thus favoring the former state in the Ne matrix, but the energy gain can hardly be so large as to overcome an energy difference of 0.5 eV.

It is therefore more probable that the theoretical results are wrong. There are several sources of errors, which could be discussed. Usually, the most crucial one is the basis set. However, here we have used extended basis sets for all three atoms. The basis set for uranium has been generated using an Hamiltonian that includes scalar relativistic effects, using the Douglas–Kroll–Hess approximation.<sup>16,17</sup> It is an extended basis set including up to h-type functions. Also for C and O have extended basis sets been used. The results are furthermore not very sensitive to the size of the basis sets as the calculations using smaller basis sets have shown.

The CASPT2 method gives of course only an approximate treatment of dynamic electron correlation effects. It becomes problematic in cases where intruder states appear. That is, however, not the case here. The CASPT2 correction is crucial. The CASSCF energy difference at  $x = 0.0$  is 0.4 eV, with the  $^1\Sigma^+$  state lower. The energy difference is decreased to 0.1 eV at the MS-CASPT2 level of theory. So, the CASPT2 correction is about 0.3 eV. However, this number has to be wrong by more than 0.4 eV in order to change the order of the states. That would be an error larger than we have seen in any of the earlier applications in actinide chemistry.

The method used to treat spin–orbit coupling is also approximate.<sup>8</sup> The spin-free CASSCF wave functions form the basis for the spin–orbit operator for which a one-electron model is used with the two-electron terms treated using a mean-field approximation.<sup>18,19</sup> The corresponding Hamiltonian matrix is diagonalized after shifting the diagonal elements using the MS-CASPT2 energies. The approach has worked very well in a number of applications<sup>8,20</sup> with errors much smaller than is needed to explain the present discrepancy.

To summarize, there is no obvious part of the theoretical study which can explain the difference to experiment. In addition the ADF/DFT calculations of Li *et al.* give the same result.<sup>1</sup> The

discrepancy between experiment and theory has not been explained and the problem remains unsolved.

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