# Predicting the electronic structure and magnetic properties of $UO_2^+$, $UO_2(CO)_5^+$ and $UO_2(Ar)_5^+$ using wavefunction based methods

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## A B S T R A C T

The electronic structure and magnetic properties of $UO_2^+$, and two complexes, $UO_2(CO)_5^+$ and $UO_2(Ar)_5^+$ in $D_{5h}$ symmetry are studied with a combination of relativistic theoretical methods: *ab-initio* wavefunction calculations, density functional theory (DFT), and crystal-field (*CF*) models with parameters extracted from the *ab-initio* calculations. The model Hamiltonian techniques are employed to describe theoretically the state interaction and the "competition" between Crystal field (*CF*) and spin–orbit coupling (*SO*), this is important besides for a correct description of the sign of the *g*-factors using also a symmetry criteria.

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## 1. Introduction

The coordination chemistry of actinides elements has important implications for the energetic and environmental problems, but the electronic structure and bonding in these kind of systems are really challenging in both experimental as well as theoretical field [1–3]. In aqueous solution uranium exist as the uranyl cation $UO_2^{2+}$, which has a closed shell $^1\Sigma_g^+$ electronic ground state. Recent spectroscopy experiments have isolated uranium and its oxides in rare gas matrices in order to probe the intrinsic structure and bonding in these systems, which have been complemented with further computational works [4–9]. Selected complexes has been investigated to explore salvation and coordination, however, the number of complexes studied is limited. Metal carbonyls provide classic examples of ligand bonding, and infrared spectroscopy is a sensitive indicator for the electronic structure and geometries of these systems. Recently was reported the production of gas phase $U^+$ and $UO_2^+$ carbonyl cations and their study with infrared spectroscopy in the $C−O$ stretching region [10–12]. These kind of molecules are obtained in general by laser vaporization of a depleted metal and their characterization needs many spectroscopic techniques like mass and infrared spectroscopy [13]. From a pure academical point of view these carbonyl complexes are good systems to study the well known 18-electron rule and particularly, for the case of actinides, often the 22-electrons rule [14–17].

The $UO_2^+$ has an odd number of electrons, then this cation cannot form 22-electrons carbonyls, but they closely approach this electron count. The odd number of electrons is also attractive to study the magnetic properties which are also very special and interesting in these kind of molecules. In these kind of molecules, where always the electronic states are Kramers doublets (or quartets and sextets in the case of cubic or icosahedral molecules). The magnetic properties are characterized predominantly by the splitting of states by a magnetic field. This interaction can be described by means of a phenomenological model Hamiltonian made use of rationalize experimental data.

A vast number of actinides compounds afford open shell $5f^n$ configurations of the metal center. The corresponding electronic ground and excited states may exhibit electron paramagnetism, which can be studied experimentally by electron paramagnetic resonance (EPR), paramagnetic NMR (pNMR), and other techniques. The magnetic properties of transition metal complexes are mainly caused by the spin magnetic moment, since the orbital angular momentum is often quenched by the ligand field. For lanthanide complexes, due to the semi-core character of the $4f$ orbitals, magnetic properties can usually be rationalized via perturbations of the free ion by the crystal field (*CF*) of the ligands. Finally for actinide (An) complexes, the $5f$ shell interacts much stronger with the environment, being involved in the chemical bonding.Tipically the spin–orbit (*SO*) interaction for the actinide valence shells and *CF* effects are of the same order of magnitude, This makes particularly interesting the theoretical description of actinide compounds [18–22]. It is noted that *SO* coupling is a relativistic effect [18,23,24]. In heavy metal complexes, otherwise to light atoms, the

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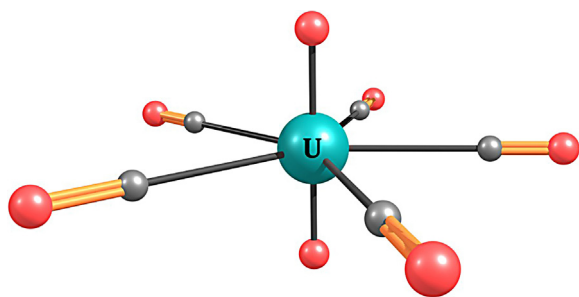*E-mail addresses:* dayan.paez@unab.cl, d.paezhernandez@yahoo.es

**Fig. 1.** Molecular model used for $UO_2(CO)_5^+$.

relativistic effects increases rapidly with the nuclear charge of the metal. Therefore, *SO* coupling and scalar relativistic effects are crucial in theoretical studies of actinides systems.

High oxidation states are of particular relevance in actinide chemistry, especially for earlier actinides. Of outstanding importance are the rather stable actinyl ions, $AnO_2^{n+}$, and complexes thereof. The present work is concerned with relativistic quantum chemical studies of the electronic structure and magnetic properties of uranium (V) cation, $UO_2^+$, and its corresponding $D_{5h}$ system with carbonyl ligands, $[UO_2(CO)_5]^+$, as depicted in Fig. 1. The high symmetry allows a description by a model Hamiltonian with only a few *CF* parameters. At the same time the different ligand field cause sizable changes of the magnetic behavior, as known from experimental data. Also the studied is extended to another similar molecules where the equatorial ligands are noble gases. The existence of a direct bonding interaction between uranium and noble-gas was reported by J. Li and coworkers in 2002 in the matrix-isolated *CUO* molecule from the reaction of laser ablated *U* atoms with *CO* and isolated in solid noble-gas matrices [25–29]. These authors had demonstrated that *CUO* form complexes with four or more noble-gas atoms. The existence of these molecules was an starting point to predict the existence of similar systems with $UO_2^+$ cation which were obtained recently by X. Wang and coworkers [25]. Density Functional Theory (DFT) calculations of the $UO_2(N_g)_n^+$ indicate that all the ground states are derived from the $UO_2^+$ $^2\Phi_u$ state. Even though the states derived form the $^2\Delta_u$ state of $UO_2^+$ are only some hundreds of cm$^{-1}$ higher in energy, the *SO* coupling will favor $^2\Phi_u$ as the ground state [30,25]. The DFT calculations also shown that the $U–N_g$ bonding energies in $UO_2^+$ molecules are twice stronger than in *CUO* complexes, because of the combination of electron-donation and ion induced dipole interactions [25]. It means that these molecular systems are sufficient stable to try to predict their magnetic properties and evaluate the effect of the ligands on that.

*f*-Elements compounds often exhibit very large *g*-factors deviation from $g_e$, and they may afford pronounced magnetic anisotropy. Both these effects are caused by an orbital contribution to the magnetic moment, which can result from a spatial degeneracy of an open shell, or by the *SO* interaction, or by a combination of these factors. There have not been many first-principles quantum-chemical calculations of *g*-factors in open-shell actinides complexes. However, such calculations can gain invaluable insight on how structure and bonding affects the magnetic properties of the complexes. Prior studies have focused, for instance, on the octahedral $5f^1$ $AnX_n^{-6}$ ($X =$ halide) series and selected $5f^3$ $An(III)$ complexes. A relative simplicity of the electronic structure and the octahedral symmetry renders the $5f^1$ series $AnX_n^{-6}$ ideal for benchmark calculations [31,32]. Due to the high symmetry, *g* is isotropic for these complexes. The *g*-factors for $AnX_n^{-6}$ were first calculated within a Dirac scattered wave formalism using a DFT framework [33–35]. More recently we have studied the series with complete active space (CAS) ab-initio wavefunction methods, using methods described in the

Computational Details where *SO* coupling is introduced at the wavefunction level in form of a state interaction. Recently, a strategy has also been devised whereby *SO* coupling is treated variationally in CAS calculations [32,31,36,37].

Turning back, the aim of the present study is calculate the *g*-factors for a series of $UO_2^+$ complexes with high symmetry ($D_{5h}$) to apply the well known model Hamiltonian techniques developed before for these kind of molecular systems and compare them with similar reported cases to proof the predictable value of the wavefunction based methods (MCSCF). Previously a similar analysis for $D_{3h}$ and $D_{4h}$ symmetries has been reported and now the effect of *CF* and *SO* coupling is analyzed for $D_{5h}$ case which is a systematic study of the magnetic properties in a higher symmetrical actinides compounds.

## 2. Molecular models and computational details

The structure optimizations were performed at the DFT level with the 2012 version of the Amsterdam Density Functional (ADF) code [38]. The open metal shell was treated with fractional orbital occupations resembling an 'average of configurations' (AOC) [39]. Two different occupations were used, in the first case the unpaired electron was distributed equitably in the seven *f* orbitals, it means in the orbitals with $\sigma$, $\pi$, $\delta$ and $\phi$ symmetries. For brevity, here and in the following sections we often use the $D_{\infty h}$ symmetry orbital classification ($\sigma$, $\pi$, $\delta$, $\phi$) also for the 5*f* orbitals of these complexes. In the second case the unpaired electron was only distributed in the non-bonding $\delta$ and $\phi$ orbitals, it means an occupation like $\delta^{0.5}\phi^{0.5}$. With ADF, the optimizations utilized the scalar relativistic form of the all-electron zeroth-order regular approximation (ZORA) Hamiltonian [40], with different Generalized Gradient Approximation (GGA) [41–44] and hybrid functionals [45], and a triple-zeta doubly polarized all-electron Slater type basis (TZ2P) from the ADF basis set library [46].

All the wavefunction based calculations were performed with the ORCA program package [47]. We employed in the present work the multiconfigurational wave function obtained from the state average complete active space self consistent field (SA-CASSCF) [48,49]. Calculations were done with the scalar relativistic many-electron Hamiltonian, which takes into account the bonding static and dynamic correlation effects. The scalar relativistic effects are taken into account by means of the second order Douglas–Kroll–Hess transformation [50]. The spin–orbit coupling (SOC) and spin–spin coupling (SSC) were calculated very accurately using a wave function obtained from a multiconfigurational calculation of a multireference type such as MRCI [51–53]. The SOC and SSC along with Zeeman interaction can be included by means of the quasi-degenerate perturbation theory. In this approach the SOC, SSC and the Zeeman operator are calculated in the basis of pre-selected solution of the Born-Oppenheimer Hamiltonian [51,52,54,55]. For the correlated calculations basis set of Def2-TZVP quality for all the atoms with the corresponding auxiliary basis sets have been used.

## 3. Results and discussion

### 3.1. Electronic structure

The structure of $UO_2(CO)_5^+$ has been optimized using DFT and different occupations schemes like has been described in the previous section. Table 1 collects the principal optimized bond lengths. For selected functionals, the equilibrium $U–O_{yl}$ distance is not particularly sensitive to the fractional occupation pattern. The distance difference between both occupation schemes not exceed the 0.004 Å and the same occur when the integer occupation $\phi^1\delta^0$ is