Magnetic circular dichroism of UCl$_6^-$ in the ligand-to-metal charge-transfer spectral region$^+$

Frédéric Gendron,$^a$, Valerie E. Fleischauer,$^b$ Thomas J. Duignan,$^b$a Brian L. Scott,$^c$ Matthias W. Lölbe,$^c$ Samantha K. Cary,$^c$ Stosh A. Kozimor,$^d$ and Jochen Autschbach$^b$,$^c$*$^d$

We present a combined $ab$ initio theoretical and experimental study of the magnetic circular dichroism (MCD) spectrum of the octahedral UCl$_6^-$ complex ion in the UV-Vis spectral region. The ground state is an orbitally non-degenerate doublet $E_{5/2u}$ and the MCD is a $C$-term spectrum caused by spin–orbit coupling. Calculations of the electronic spectrum at various levels of theory indicate that differential dynamic electron correlation has a strong influence on the energies of the dipole-allowed transitions and the envelope of the MCD spectrum. The experimentally observed bands are assigned to dipole-allowed ligand-to-metal charge transfer into the 5f shell, and 5f to 6d transitions. Charge transfer excitations into the U 6d shell appear at much higher energies. The MCD-allowed transitions can be assigned via their signs of the $C$-terms: Under $O_h$ double group symmetry, $E_{5/2u}$ $\rightarrow$ $E_{5/2g}$ transitions have negative $C$-terms whereas $E_{5/2u}$ $\rightarrow$ $F_{7/2g}$ transitions have positive $C$-terms if the ground state $g$-factor is negative, as is the case for UCl$_6^-$. 

1 Introduction

Magnetic circular dichroism (MCD) spectroscopy probes the differential absorption of left- vs. right-hand circularly polarized light induced by a static magnetic field in the propagation direction of the light beam. The absorption is usually associated with electronic transitions. Unlike conventional electronic CD, which only occurs in chiral systems or via chiral induction, MCD can be observed for non-chiral systems. In particular in combination with theoretical calculations, MCD spectroscopy is a powerful tool to investigate the electronic structure of molecules. MCD experiments have been extensively used to characterize transition metal complexes,$^{1-7}$ metallic clusters,$^8$ mesogenic organic materials,$^9$ active sites in biological systems,$^{10-15}$ and to study the magneto-optical properties of lanthanide-based materials.$^{16,17}$ Compared to regular absorption spectroscopy, MCD provides information on the magnetic properties of the ground state (GS), similar to electron paramagnetic resonance (EPR) spectroscopy, as well as information about the electric and magnetic properties of excited states (ESs). MCD spectra tend to reveal more information than absorption spectra, especially in regions with overlapping absorption bands,$^{18}$ because the MCD intensities of different transitions may have different signs. Due to the different selection rules of MCD and absorption spectroscopies, the two techniques may also provide complementary information.

The theory underlying MCD was developed by Buckingham and Stephens$^{16,20}$ and further elaborated by Piepho and Schatz.$^{21}$ The MCD intensities are attributed to three mechanisms characterized by the so-called $A$-, $B$- and $C$-terms. The $A$-term corresponds to transitions into excited states subject to Zeeman splitting by the applied magnetic field. This term is temperature independent and gives rise to a derivative shape of the signal in the MCD spectrum. The $B$-term, also temperature independent, arises from a mixing of zero-field states caused by the magnetic field. Finally, for systems with a degenerate ground state, the $C$-term arises from the splitting of the ground state degeneracy by the magnetic field. This splitting leads to a difference in the thermal population of the ground state components. Therefore, the $C$-term is temperature-dependent. Furthermore, $C$-terms represent the dominant MCD mechanism for paramagnetic systems at low temperature.

Using this formalism, a number of computational methods for MCD have been developed. A relatively large number of
applications were performed using time-dependent Kohn–Sham theory (KST) for the calculations of the A- and B-terms,23–25 or a combination thereof,26 while Coriani et al. used wavefunction methods to calculate A- and B-terms of organic molecules.37 C-Terms of transition metal complexes were also investigated with KST calculations.28,29 However, the known problems of KST with approximate functionals to treat many open-shell systems limit the applicability of this approach. Furthermore, modeling C-term properly require inclusion of spin–orbit (SO) coupling18,29,30 which is a relativistic effect. In particular, for systems without orbitally degenerate ground states, consideration of SO coupling is essential in order to rationalize any observed temperature-dependent (i.e. C-term) MCD, as this contribution to the spectrum would be zero otherwise.21 Wavefunction based C-term calculations were performed by Bolvin for the bimetallic mixed-valence Creutz–Taube complex.11 In this case, C-terms were calculated using multi-reference wavefunction methods, with SO coupling included via state-interaction (see Section 2.2 for details). Based on a somewhat related multi-reference configuration interaction approach, Ganyushin and Neese implemented all MCD terms and were able to calculate the MCD spectra of organic radicals and the iron complex [Fe(CN)6]3– successfully.32 This approach was subsequently applied to rationalize the MCD spectra of more challenging iron complexes.33,34

To our knowledge, ab initio computational MCD simulations for actinide complexes have so far not been attempted. Moreover, scarce experimental MCD studies of actinide complexes have been reported, despite the potential utility of the technique, as demonstrated in its numerous applications to transition metal spectra. Early actinide applications of MCD date to the 1970s and include the resolution of the vibronic lines of U4+ doped into Cs2ZrCl6,14 studies of the uranyl nitrates (di-, tri-, and tetranitrates),35 and MCD studies of UO2.36 Denning and co-workers reported the first detailed application of MCD spectroscopy in actinide chemistry in their studies of Cs2UO2Cl4, CsUO2(NO3)3 and NaUO2(CH3CO2)3.37,38 Combined with single crystal polarized absorption studies, the MCD spectra enabled the identification and detailed assignment of seven electronic states in all complexes. While subsequent applications of MCD to 5f systems are rare, notable examples include studies of the Dsh and Dsh complexes Cs2UO2F5 and [NBu4][UO2(NO3)3]39 respectively, as well as MCD studies of uranyl chloride complexes in non-aqueous solvents.40 In all these cases, the MCD spectra display A- and B-terms as expected for singlet ground states. C-Term MCD spectroscopy of actinide complexes is exceedingly rare and has so far been limited to pioneering studies of NpO2Cl42– and NpO2(NO3)32– by Denning et al.41,42 Among other useful information about the electronic structure, the MCD spectra provide the excited state EPR g-factors, which we studied recently for the Np systems by ab initio calculations.43 Herein, we report a combined theoretical and experimental study of the MCD C-term spectrum of the uranium(V) complex ion UCln5–, with measurements performed on solid [PPPh4]UCln.

Of particular interest are the contributions of the 5f orbitals to covalent ligand–metal bonding, which has been of great interest for a long time.44–47 Most of the previous studies were focused on the ligand-field (LF) states arising from the 5f0 configurations. With the help of experimental techniques such as near infra-red (NIR) absorption spectroscopy and EPR measurements, in combination with crystal-field or molecular orbital models, it has been shown that the absorption spectrum in the LF spectral regions of UXn5– complexes are strongly influenced by covalent interactions between the 5f and the ligand orbitals of σ and π character.48–52 Computational studies have shown that the 5f orbitals of t1u and t2u symmetry can form bonding and antibonding combinations with ligand orbitals of corresponding symmetry. The magnitude of the 5f-ligand mixing in these orbitals influences the magnetic properties of the complexes.53–57

In contrast to the comparatively well-studied LF states, there is an almost complete lack of information about the nature of the electronic ESs in the UV-Vis spectral region of these complexes. In this region, the spectra are thought to be dominated by charge-transfer (CT) transitions, in particular ligand-to-metal CT (LMCT). An early attempt of characterizing the CT spectrum was made by Ryan on the uranium(V) series UXn5– (X = F, Cl, Br).58 The lowest CT bands were found at ca. 25 300 and 17 400 cm−1 for X = Cl and Br, respectively. However, due to the very broad absorption bands in the CT region, displaying multiple and overlapping transitions, the spectrum could not readily be resolved and an assignment was virtually impossible.

The current study represents the first combined experimental and theoretical investigation of the MCD spectrum of an actinide complex in the charge-transfer spectral region, performed for the complex UCln5–. The combination of our experimental MCD spectrum and multi-reference electronic structure calculations allows us to assign the spectrum up to ca. 40 000 wavenumbers. It is shown that the electronic transitions in this region of the spectrum correspond mainly to ligand-to-metal charge transfer (LMCT), principally from the chloride 3p orbitals of t1g symmetry in the O6 point group to vacant uranium 5f orbitals of t1u and t2u symmetry. The sign of the MCD intensities is directly related to the symmetry of the transitions. Furthermore, 5f to 6d transitions are shown to contribute to the MCD spectrum.

2 Experimental, theoretical, and computational details

2.1 Experimental methods

2.1.1 General considerations. The 238U isotope is a low specific-activity α-emitting radionuclide and its use presents a hazard to human health. The experimental component of this research was conducted in a radiological facility with appropriate analyses of these hazards and implementation of controls for the safe handling and manipulation of these toxic and radioactive materials.
All procedures were performed with rigorous exclusion of air and moisture using Schlenk and glovebox techniques under an atmosphere of argon. All glassware was dried at 150 °C for at least 12 h. Acetonitrile (anhydrous, Fischer) was dried over CaH₂, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. UC₄ was prepared as previously described from UO₃ and hexachloropropene. Elemental analyses were carried out by the Midwest MicroLab, LLC in Indianapolis, IN.

2.1.2 Synthesis of tetraphenylphosphonium uranium(vi) hexachloride, (PPh₄)UCl₆

Method A. On a Schlenk line under argon, UO₂Cl₂H₂O (0.900 g, 2.51 mmol) was dissolved in thionyl chloride (5 mL) and stirred, followed by the addition of PPh₄Cl (0.942 g, 2.51 mmol) dissolved in thionyl chloride (5 mL). The orange solution was heated to reflux at 90 °C overnight, over which time a color change to dark red/orange, and finally, a lighter orange was observed. After cooling to room temperature, the solvent was removed in vacuo yielding an orange solid, and the flask was sealed and transferred to a glove box. The solid was taken into 5 mL of acetonitrile, transferred to a scintillation vial, heated to 50 °C to dissolve all of the solid, and allowed to crystalize at ambient temperature. After 5 days, orange crystals were present and could be isolated in 73% yield as (PPh₄)UCl₆, which was characterized by single crystal X-ray diffraction.

Method B. In an argon filled glovebox, PPh₄Cl (0.524 g, 1.40 mmol) was dissolved in thionyl chloride (5 mL) and was added to a 20 mL scintillation vial containing UO₃ (0.400 g, 1.40 mmol) also dissolved in thionyl chloride (5 mL). The solution was allowed to stir for a few minutes, after which a color change to deep red was observed. The solution was allowed to cool to room temperature and dark red crystals grew over the course of several days. The mixture was heated to 91 °C and refluxed for 3 days, cooled to 21 °C, and the solvent was removed in vacuo. The resulting yellow powder was washed with diethyl ether and dissolved in acetonitrile heated to 91 °C, followed by slow cooling. After 3 days, orange crystals and green crystals were present in the solution. The orange crystals were picked out with tweezers and identified as (PPh₄)UCl₆ (0.463 g, 0.588 mmol, 42%) that were suitable for single crystal X-ray diffraction measurements. Anal. calcd for C₃₄H₂₅Cl₆U: C, 36.59; H, 2.56. Found, C, 36.66; H, 2.66.

2.1.3 MCD spectroscopy. The (PPh₄)UCl₆ sample for MCD spectroscopy was prepared in an inert atmosphere glove box equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glove box. EPR samples were prepared in a 4 mm OD suprasil quartz EPR tube from Wilmad Labglass. X-Band EPR spectra was recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat. The instrumental parameters employed for all samples were as follows: 1 mW power; time constant 41 ms; modulation amplitude 4 G; 9.38 GHz; modulation frequency 100 kHz.

2.2 Computational details

2.2.1 Kohn–Sham calculations. Kohn–Sham theory (KST) density functional and time-dependent KST (TDKST) calculations were carried out with the Turbomole package, version 5.7. A 60-electron quasi-relativistic effective core potential (ECP) along with a matching ECP60MWB-SEG valence basis set was used to replace the uranium core and mimic relativistic valence-shell effects. For the Cl atoms, the calculations employed a split-valence basis set with one set of polarization functions, def2-SV(P). The TDKST calculations were performed with several functionals, ranging from the PBE66,67 (Perdew–Burke–Ernzerhof) non-hybrid generalized gradient approximation (GGA) functional, the B3LYP68 (Becke, three-parameter Lee–Yang–Parr) hybrid functional with 20% exact exchange (ex), a hybrid version of PBE (PBE0)69,70 with 25% ex, and ex only (i.e., Hartree–Fock theory). The calculations were performed with O₃ symmetry.

2.2.2 Wavefunction calculations. The ab initio wavefunction based calculations were carried out with a developer's version of the Molcas package (pre 8.0). The second-order Douglas–Kroll–Hess scalar relativistic Hamiltonian was employed in the calculations without spin–orbit (SO) coupling, along with all-electron ANO-RCC Gaussian-type basis sets contracted to TZP quality (U = 26s23p17d13f5g3h/9s8p6d4f2g1h; Cl = 17s12p5d2g/5s4p2d1f). The computations used state averaged CASSCF (Complete Active Space Self Consistent Field) and RASSCF (Restricted Active Space Self Consistent Field) wave functions. Dynamical electron correlation was treated using CASPT2 (Complete Active Space Perturbation Theory at 2nd order). The CASPT2 calculations were performed using the multi-state approach with a real shift of 0.2 in order to avoid intruder states in the wave functions. Spin–orbit (SO) coupling was treated by state interactions between the CASSCF/CASPT2 wave functions, using the Restricted Active Space State Interaction (RASSI) program. For brevity, the spin-free scalar relativistic (SR, i.e. not including SO coupling) and the calculations with SO coupling are referred to in the following as SCF-SR, PT2-SR, SCF-SO and PT2-SO, respectively. The electronic g-factors were calculated according to ref. 76 as implemented in the RASSI module of Molcas. A local modification of Molcas was used to generate natural orbitals (NOs), natural spin orbitals (NSOs) and the orbital \( m^r (r) \) and spin \( m^s (r) \) magnetizations from the sample to ±0.001 K. All MCD spectra were baseline-corrected against zero-field scans.
SO wave functions. For degenerate states, the state components were chosen to diagonalize the $z$ component of the Zeeman operator, and the orbitals and magnetizations of the state component with the most positive $\langle S_z \rangle$ were visualized. Iso-surfaces of the orbitals and magnetizations were created and visualized with the graphical user interface of the Amsterdam Density Functional suite. Simulated Gaussian-broadened SR and SO absorption spectra were generated using an open-source software.

The wavefunction calculations were performed using $C_1$ symmetry, to target gerade vs. ungerade states, with a combination of RAS and CAS active spaces. A ‘ras1’ space corresponding to 18 electrons in 9 orbitals was used to represent the occupied ligand based orbitals. This active space consists of the 9 highest-energy doubly occupied orbitals of $a_g$ symmetry and are shown in Fig. 1(a). Under octahedral symmetry, these orbitals belong to the $e_g, a_{1g}, t_{2g}$ and $t_{1g}$ species. In combination with this RAS space, a ‘ras2’ principal active space was used to represent the seven 5f orbitals of the central $U^{5+}$ ion. These orbitals are shown in Fig. 1(b) and are labeled $5f_{a2u}, 5f_{t_{1u}}$, and $5f_{t_{2u}}$. In order to reduce the computational cost associated with such a large active space, only single excitations from the ras1 space into the ras2 space were considered, corresponding to the dipole-allowed ligand to metal charge transfer (LMCT) excited states. For the present work, state-averaged RAS and CAS calculations were performed for 441 SR doublet states of $A_g$ symmetry, 189 SR quartet states of $A_g$ symmetry and for the seven SR 5f doublet states of $A_u$ symmetry. For a reasonable description of the SO coupling at the metal site, the mixing of a large number of electronic states is required. Here because of computational limits, the RASSI procedure was performed with the first 165 doublet states and first 150 quartet states of $A_g$ symmetry and the 7 doublet states of $A_u$ symmetry.

The influence of the dipole-allowed $5f \rightarrow 6d$ transitions on the MCD spectrum of $UCl_6^-\cdot Co$ was also taken into account. The introduction of the additional 6d orbitals into the previously

![Fig. 1](image-url) Isosurfaces ($\pm 0.03$ a.u.) of selected natural orbitals of the GS of $UCl_6^-$. (a) Ligand based orbitals of gerade symmetry comprising the ras1 space in the LMCT calculations, and (b) 5f orbitals of ungerade symmetry comprising the ras2 space (RAS(19,16)SCF calculation). (c) 6d orbitals of gerade symmetry comprising the ras3 space (RAS(1,12)SCF calculation).
described CAS/RAS combination leads to a poor quality of the spectra resulting from the state-averaged calculations due to the too large number of states of different nature. Therefore, the 5f → 6d transitions were calculated separately with an active space corresponding to the ras2 space of the seven 5f orbitals and a ras3 space with the five vacant 6d orbitals, allowing one particle in the ras3 space. The energies of the calculated 5f → 6d transitions and the corresponding simulated MCD spectrum are given in Table S2 and Fig. S4 of the ESI,† respectively. The C-terms were then combined with those calculated for the LMCT transitions to generate the full MCD spectra. The computational strategy to add separately calculated 5f → 6d transitions to the spectra, versus state-averaged calculations with an active space comprising ligand + 5f + 6d orbitals, can be assessed by a comparison of the corresponding MCD spectra shown in Fig. S8 and S9 of the ESI.†

The LMCT transitions from the ligand valence orbitals of a_u symmetry into the vacant uranium 6d orbitals were also investigated. As seen in Table S3 (ESI†), the lowest LMCT transitions arising from ligand orbitals of a_u symmetry are calculated above 60 × 10^3 cm⁻¹ at the PT2-SR and PT2-SO level. Since these transitions are far higher in energy than the lowest LMCTs arising from the a_u ligand orbitals symmetry (see Tables 3 and 5) they are not discussed further.

The experimental structure of UCl_6^- in [PPh_4]UCl_6 is of C_i symmetry with U–Cl bond lengths of 2.5146, 2.5141 and 2.5047 Å. In order to simplify the assignment of the excited states, the wave-function calculations, as well as the KST calculations, were carried out on a perfectly octahedral structure with averaged U–Cl bond lengths of 2.511 Å. As seen in Table S3 (ESI†), the energies of the LF states remain almost identical between the two structures. Furthermore, the calculated MCD spectra are found to be similar between the two structures (see Fig. S3, ESI†).

### 2.3 Magnetic circular dichroism

MCD is the difference in absorption of left and right circularly polarized (CP) light propagating parallel to a magnetic field with amplitude B. We use the sign conventions and the Gaussian units adopted by Piepho & Schatz.† The differential absorbance at energy E for a transition between two electronic states |M⟩ and |N⟩ is given by

\[
\frac{\Delta A}{E} = \frac{\Delta \kappa \ell}{E} = \frac{\pi^2}{n_e} \epsilon \mu_B B \left[ A \left( -\frac{\partial f(E)}{\partial E} \right) + \left( B + \frac{C}{k_B T} \right) f(E) \right] \tag{1}
\]

with the MCD A-, B- and C-terms

\[
A = \frac{1}{g_M} \sum_{mn} \left( \langle N| \hat{L}_x + 2 \hat{S}_z |N \rangle - \langle M| \hat{L}_x + 2 \hat{S}_z |M \rangle \right) \times \left( \langle M|\hat{d}_{-1}|N \rangle^2 - \langle M|\hat{d}_{+1}|N \rangle^2 \right) \tag{2a}
\]

\[
B = \frac{2}{g_M} \text{Re} \sum_{mn} \frac{\sum_{K} \langle K| \hat{L}_x + 2 \hat{S}_z |K \rangle}{W_K - W_N} \sum_{\kappa} \langle K| \hat{d}_{\kappa} |N \rangle \langle M| \hat{d}_{-1} |M \rangle \times \left( \langle M|\hat{d}_{-1}|N \rangle^2 - \langle M|\hat{d}_{+1}|N \rangle^2 \right) \tag{2b}
\]

\[
C = \frac{1}{g_M} \sum_{mn} \langle M| \hat{L}_x + 2 \hat{S}_z |M \rangle \times \left( \langle M|\hat{d}_{-1}|N \rangle^2 - \langle M|\hat{d}_{+1}|N \rangle^2 \right) \tag{2c}
\]

The indices m, n and κ count the components of degenerate states, E is the photon energy, and f(E) is a normalized line shape function, usually taken to be a Gaussian centered at the excitation energy. We assume that the MCD is strictly linear in B, and therefore the wavefunctions and energies entering the various terms in eqn (1) are not magnetic field dependent. The definition given above is for an electromagnetic wave propagating in the z direction, and the components of degenerate states must be chosen such that they diagonalize the dimensionless operator \( \hat{L}_x + 2 \hat{S}_z \). The constant \( \gamma \) is defined as

\[
\gamma = \frac{2N_A \pi^3 \log e}{250hc} \tag{3}
\]

In eqn (1), \( z = (n_e^2 + 2)/3 \), and \( z^2/n_e \) is a local field correction for a medium with refractive index n_e. We will omit this term in the following and assume \( n_e = 1 \). Further, \( \kappa \) is the path length through the absorbing medium, \( \hat{d}_{\pm} \) are two of the irreducible spherical components of the electric dipole operator, \( \mu_B = e\hbar/(2m_e c) \) is the Bohr magneton, \( \mu_z = -\mu_B(\hat{L}_z / 2 + \hat{S}_z) \) is a component of the magnetic dipole operator, \( k_B \) is the Boltzmann constant, T is the absolute temperature, and \( g_M \) is the degeneracy of state M. In eqn (1), the differential absorbance is dimensionless and \( \Delta \epsilon \) is in the usual units of mol⁻¹ cm⁻¹.

For a system with a degenerate ground state, in particular at the low temperatures employed in the present measurements, the MCD spectrum is completely dominated by the C-terms. The MCD C-term spectrum for UCl_6^- was calculated from the state energies and matrix elements of the electric dipole and the spin and orbital angular momentum operator components, obtained from the CAS and RAS calculations. Instead of eqn (2c), the following expression was used for the C_u-term for a wave propagating in direction \( u \in \{x, y, z\} \) of the laboratory coordinate frame, and the magnetic field pointing in the same direction:

\[
C_u = -\frac{i}{g_M} \sum_{mn} \langle M|m'|L_u + 2S_u|M \rangle \left( \langle M|\hat{d}_{+1}|N \rangle \times \langle N|\hat{d}_{-1}|M \rangle \right) \tag{4}
\]
Here, $\mathbf{d}$ is the electric dipole moment vector operator. Further, $\times$ indicates the vector cross product. The $u$-component of the resulting vector is used to calculate $C_u$. The isotropic $C$-term is given as

$$C = \frac{1}{3} \sum_u C_u$$

For an octahedral molecule such as $\text{UCl}_6^-$, the three $C_u$ and $C$ are equivalent. Eqn (4) is preferable over (2c) in computations because in (4) it is not required that the Zeeman operator is diagonal in the basis of the state components. However, we confirmed that numerical codes using both versions give identical spectra.

In Section 3, the isotropic MCD intensities are given in the form of ‘stick spectra’ which represent the $C$-terms in units of Debye$^2$ centered at the excitation wavenumber. The simulated spectra were obtained from a superposition of the $C$-term spectra corresponding to eqn (1), with $f(E)$ being a normalized Gaussian function, representing $A/\sigma$ in 1 mol$^{-1}$ cm$^{-1}$ T$^{-1}$. Multiplication by 0.3298 gives the molar ellipticity per Gauss, i.e. $[\theta]/B$ in units of deg cm$^2$ dmol$^{-1}$ G$^{-1}$. All calculated quantities were initially obtained in dimensionless Hartree atomic units (a.u.). The conversion from au to Debye$^2$ for the $C$-terms is 6.4605. The spectra were generated on an energy scale in au, which was subsequently converted to wavenumbers. With $E$ and $C/(k_B T)$ in atomic units, the numerical conversion to Gaussian units in eqn (1) for a field of 1 Tesla is approximately 0.0014803, as given previously by Seth et al.$^{25}$ If not stated otherwise, the Gaussian broadening used a half width at 1/e peak height of $\Delta = 9.375 \text{ cm}^{-1} \sqrt{\nu}$ converted to au, where $\nu$ is the numerical wavenumber of the excitation in cm$^{-1}$. This broadening corresponds to a full width at half peak height of $2 \ln 2 \Delta \approx 1.386 \Delta$.

### 3 Results and discussion

#### 3.1 Electronic LMCT spectrum according to Kohn–Sham calculations

The electronic structure and the LMCT spectrum of $\text{UCl}_6^-$ were first investigated at the SR level with TDKST, using different functionals as detailed in Section 2.2.1. A KS molecular orbital (MO) diagram of $\text{UCl}_6^-$ calculated with B3LYP is shown in Fig. 2. The nature of the ground state (GS) of this complex was previously described with the help of molecular orbital models$^{56,52}$ and with orbital interaction diagrams,$^{54,81,82}$ and therefore, only the principal features are summarized here. Under the $O_h$ symmetry, the seven uranium 5f atomic orbitals (AOs) are split into a non-degenerate $a_{2u}$ orbital, and three-fold degenerate sets of $t_{1u}$ and $t_{2u}$ orbitals. The KS frontier orbitals are qualitatively the same as the natural orbitals from the SCF-SR calculations. As seen in Fig. 1, the 5f $a_{2u}$ orbital is non-bonding in character and corresponds to the highest singly occupied molecular orbital (SOMO) of $\text{UCl}_6^-$.

The eighteen chloride 3p AOs form two sets of symmetry-adapted orbitals. A first set corresponds to linear combinations of the six Cl 3p$_\sigma$ orbitals ($\sigma$ and $\pi$ refer here to the local rotational symmetry about the U–Cl bonds) and span the $a_{1g}$, $e_g$, and $t_{1u}$ irreducible representations (irreps). The second set corresponds to linear combinations of the twelve Cl 3p$_\pi$ AOs, spanning the $t_{1g}$, $t_{2g}$, $t_{1u}$ and $t_{3u}$ irreps. By symmetry, the ligand based $t_{1g}$ and $t_{3u}$ orbitals can form bonding and anti-bonding combinations with the 5f orbitals of corresponding symmetry. The resulting anti-bonding combinations correspond to the lowest unoccupied molecular orbitals (LUMOs) of $\text{UCl}_6^-$. The $t_{1u}$ orbitals are $U$–Cl $\pi$–$\pi$ mixed in character, while the $t_{2u}$ orbitals are of $U$–Cl $\pi$ character (see Fig. 1). The $e_g$ and $t_{2g}$ ligand AO combinations can mix with the uranium 6d orbitals of corresponding symmetry. The bonding combinations are doubly occupied and shown in Fig. 1. In agreement with previous KST calculations,$^{54}$ the highest occupied ligand-centered orbitals are the non-bonding $t_{1g}$ orbitals, lying just below the metal-centered SOMO $a_{2u}$.

The TDKST calculated absorption spectra of $\text{UCl}_6^-$ are shown in Fig. 2 for the different functionals investigated. The energies, oscillator strengths, and assignments of the principal excitations are given in Table 1. The reader is reminded that under the $O_h$ symmetry the 5f $\rightarrow$ 5f transitions are electric-dipole forbidden, and therefore no allowed electronic excitations were calculated in the near infra-red (IR) region. These transitions were observed experimentally,$^{58}$ however, their intensities arise from vibronic coupling, a treatment of which is beyond the scope of the present work.

The first dipole-allowed electronic excitation corresponds to a ligand-to-metal charge transfer (LMCT) from the ligand-centered $t_{1g}$ orbitals to the uranium based $t_{1u}$ 5f orbitals. This excitation is calculated at $22 \times 10^3$ cm$^{-1}$ with the functional PBE, and is blue shifted to 27 and $29 \times 10^3$ cm$^{-1}$ when using the hybrid functionals B3LYP and PBE0, respectively. As expected from the orbital diagram in Fig. 2, in the same region of the spectrum a second LMCT is calculated and corresponds to $t_{1g} \rightarrow t_{2u}$ transitions. The oscillator strengths of these first two sets of excitations are relatively small ($f < 0.02$ with B3LYP) and give rise to the first absorption band in the TDKST spectra. A more intense second absorption band is also assigned to LMCT excitations. The underlying electronic excitations of this band correspond to transitions from the $t_{1g}$ orbitals into the vacant 5f orbitals $t_{1u}$ and $t_{3u}$. Overall, in the electronic absorption spectrum between 25 and $35 \times 10^3$ cm$^{-1}$, the calculated LMCTs correspond to transitions from the Cl 3p orbitals of $\pi$ character into the metal 5f orbitals. Experimentally, the absorption spectrum was not completely assigned. However, Ryan tentatively estimated that the lowest LMCT transition was centered around $25.3 \times 10^3$ cm$^{-1}$, which is in the range of the lowest KST LMCT. For comparison, Kaltsoyannis and Bursten placed the first charge transfer at $21.7 \times 10^3$ cm$^{-1}$ by using the Slater transition state approach in combination with relativistic Xz calculations.$^{81}$

Excitations out of the Cl 3p $\sigma$ orbitals are calculated at much higher energies. For instance, an intense peak at $41 \times 10^3$ cm$^{-1}$ corresponding to $e_g \rightarrow t_{1u}$ is calculated with PBE, while an intense $a_{1g} \rightarrow t_{1u}$ excitation is calculated at $45 \times 10^3$ cm$^{-1}$ with...
Fig. 2 TDKST absorption spectra (left) and B3LYP molecular orbital diagram (right) of UCl$_6^{2-}$. Electronic transitions with oscillator strengths larger than 0.015 are shown in form of ‘stick spectra’.

Table 1 Principal LMCT energies ($\Delta E$, cm$^{-1}$) and oscillator strengths ($f$) calculated using TDKST$^a$

<table>
<thead>
<tr>
<th>PBE</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>Assignment</th>
<th>B3LYP</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>Assignment</th>
<th>PBE0</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 940</td>
<td>0.014</td>
<td>$t_{2g}(z') \rightarrow t_{1u}(z')$</td>
<td>27 092</td>
<td>0.011</td>
<td>$t_{2g}(z) \rightarrow t_{1u}(z)$</td>
<td>28 607</td>
<td>0.015</td>
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<td>0.019</td>
<td>$t_{2g}(z) \rightarrow t_{1u}(z)$</td>
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<tr>
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<td>42 164</td>
<td>0.012</td>
<td>$c_g(\beta) \rightarrow t_{1u}(\beta)$</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Only the oscillator strengths larger than 0.010 are given. $\Delta E$ is the energy of the state compared to the GS.

the hybrid PBE0. Interestingly, in the region above $35 \times 10^3$ cm$^{-1}$, the most intense excitation calculated with the hybrid functional B3LYP at $43 \times 10^3$ cm$^{-1}$ corresponds to a metal-to-metal transition from the singly occupied 5f orbital $a_{2u}$ into the vacant 6d $t_{2g}$ orbitals. In the wavefunction calculations (vide infra), metal 5f $\rightarrow$ 6d transitions appear at very high energies in the SCF calculations, but move into the experimentally accessible spectral range when dynamic correlation is included.

We note that an overestimation of CT excitation energies by TDKS and hybrid functionals with low to moderate fractions of eX is rather uncommon. The observed trend of PBE being overall – potentially closer to experiment and hybrid functionals yielding too high excitation energies has previously been noted for $\pi$ to $\pi^*$ excitations in organic dyes that afford significant differential electron correlation between the two states.$^{3,14}$ Differential correlation must play a role as well in the spectrum of UCl$_6^{2-}$, because the LMCT excited states (ESs) have two electrons in the 5f shell whereas the GS has only one. This expectation is supported by the substantial shifts between the SCF and PT2 spectra discussed below. Compared to the hybrid TDKS calculations, the PBE spectrum affords too much structure and a ‘tail’ stretching to very low energies. The hybrid DFT spectra likely produce an overall better envelope of the LMCT spectrum, albeit blue-shifted.

3.2 SR wavefunction calculations

The electronic states of UCl$_6^{2-}$ were calculated with wavefunction theory at the SCF-SR and PT2-SR levels. The calculated energies of the ligand-field states are collected in Table 2 and compared to results obtained in previous computational studies. In agreement with the KST calculations, the GS is the orbitally non-degenerate $^2A_{2u}$ where the unpaired orbital is the non-bonding $5f_{a_{2u}}$ shown in Fig. 1(b). The two excited LF states are of symmetry $^4T_{2u}$ and $^2T_{1u}$, where the unpaired electron is shared among the antibonding $t_{2g}$ and $t_{1u}$ orbitals, respectively. The introduction of dynamic correlation with CASPT2 leads to a
slight destabilization of the ligand-field excited states. Our calculated energies and the SCF vs. PT2 trend are in line with previous computational studies, some of which used a similar active space but a different U–Cl bond length. These variations do not appear to lead to significant changes on the electronic structure. Notter & Bolvin also investigated the influence of larger active spaces that included some ligand-centered orbitals. The CAS(7,10) active space, for instance, included three doubly occupied ligand 3p combinations. For the LF part of the electronic spectrum, the inclusion of ligand-centered orbitals is evidently not critical.

The LMCT absorption spectra of UCl$_6^-$ calculated at the SCF-SR and PT2-SR level are shown in Fig. 3. The energies and the assignments of the most intense excitations are given in Table 3. As discussed already, the SR GS of UCl$_6^-$ is $^2$A$_{2u}$, and therefore only transitions to excited states of symmetry $^2$T$_{2g}$ are dipole-allowed. Transitions into any of the excited SR Quartet states are spin-forbidden. We remind the reader that the electric dipole operator in O$_h$ symmetry belongs to the T$_{1u}$ species, and $^2$A$_{2u}$ $\otimes$ T$_{1u}$ $\rightarrow$ T$_{2g}$.

The SCF-SR and PT2-SR absorption spectra afford three principal absorption bands in the energy range considered, similar to the TDKST calculations but with different relative intensities. The first, lowest energy, band arises mainly from two LMCTs that correspond to transitions from the ligand t$_{1g}$ orbitals into the unoccupied 5f orbitals t$_{2u}$ and t$_{1u}$, respectively. The introduction of dynamic correlation (PT2) leads to a sizable energetic stabilization of these excitations and a red-shift of the absorption spectrum as a whole, but without major changes in its shape. The second major band is also assigned to excitations

<table>
<thead>
<tr>
<th>Method</th>
<th>$^2$A$_{2u}$</th>
<th>$^2$T$_{2u}$</th>
<th>$^2$T$_{1u}$</th>
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<td>2384</td>
<td>6794</td>
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<tr>
<td>PT2-SR$^a$</td>
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<td>2486</td>
<td>7732</td>
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<tr>
<td>CCSD(T)$^b$</td>
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<td>2258</td>
<td>5565</td>
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<tr>
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<tr>
<td>SCF-SR$^d$</td>
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<tr>
<td>PT2-SR$^d$</td>
<td>0</td>
<td>2580</td>
<td>7140</td>
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</table>

$^a$ This work (U–Cl bond length 2.511 Å). $^b$ Data from ref. 54 obtained with a CAS(1,7) for CASPT2 (U–Cl bond length 2.669 Å). $^c$ Data from ref. 53 obtained with a CAS(1,7) (U–Cl bond length 2.50 Å). $^d$ Data from ref. 53 obtained with a CAS(7,10) (U–Cl bond length 2.50 Å).

<table>
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<tr>
<th>Assignment</th>
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<th>PT2-SR</th>
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<td>24 354</td>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
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<td>27 505</td>
</tr>
<tr>
<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>31 412</td>
<td>25 535</td>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
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<td>29 958</td>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
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<td>30 831</td>
</tr>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>36 141</td>
<td>30 660</td>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>37 008</td>
<td>31 419</td>
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<tr>
<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>44 226</td>
<td>36 173</td>
</tr>
<tr>
<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>45 319</td>
<td>40 826</td>
</tr>
<tr>
<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>47 509</td>
<td>42 650</td>
</tr>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
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<td>43 859</td>
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<td>43 588</td>
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<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>49 516</td>
<td>43 461</td>
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<tr>
<td>$^2$T$_{2g}$ $\rightarrow$ 5f</td>
<td>52 037</td>
<td>32 353</td>
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</table>

$^a$ Only states with oscillator strengths larger than 0.001 are given. $\Delta E$ is the energy of the state compared to the GS.
from the ligand t_{1g} orbitals. The excited states have multi-configurational character at the metal center, with occupations shared among the t_{1u} and t_{2u} 5f orbitals. Similarly to the KST calculations, electronic excitations from the t_{2g} and e_{g} ligand orbitals are calculated at much higher energy. The first set of t_{2g} → 5f excitations at the SCF-SR level correspond to the shoulder below the third major peak of the spectrum. At the PT2-SR level, this peak is strongly red shifted. The last major peak is caused by electronic transitions from the σ-type ligand orbital e_{g} into the 5f orbitals.

The 5f → 6d transitions appear at very high energy at the SCF-SR level, with the lowest of these excitations corresponding to transitions from the 5f_{2g2u} orbital into the 6d_{2g} orbitals (see Table S2 of ESI†). The dynamic correlation leads to a strong energetic stabilization of the 6d^{1} states. The calculations show that there are considerable covalent interactions between the gerade ligand AO combinations and the U 6d orbitals, and between the ungerade ligand AO combinations and the U 5f orbitals (Fig. 1). The formally 'non-bonding' U 6d and 5f orbitals therefore afford significant metal–ligand antibonding character, indicating why the 5f → 6d transitions are influenced by correlation with ligand-centered orbitals. According to the calculated PT2 data, the most important set of correlating orbitals is the t_{1g} set of Fig. 1(a). The lowest 5f_{2g2u} → 6d_{2g} transitions are calculated at 32 × 10^{3} cm\(^{-1}\) at the PT2-SR level, which is much lower compared to similar excitations calculated with B3LYP. However, we already pointed out that the hybrid DFT spectra appear to be blue-shifted. Despite a large energetic stabilization, the 5f_{2g2u} → 6d_{2g} transitions remain at very high energy ( > 60 × 10^{3} cm\(^{-1}\)) and are therefore not discussed further.

### 3.3 SO wavefunction calculations

The energies of the ligand-field states of UC\(_{6}^{−}\) calculated with SO coupling at the SCF and PT2 levels of theory are given in Table 4. The SO GS of UC\(_{6}^{−}\) is a Kramers doublet of symmetry E_{5/2u}. Due to the SO coupling, the SO GS contains a strong admixture of the SR states 2A_{2u} and 2T_{2u}. In the O\(_{h}\) double group symmetry, the SR 2A_{2u} state belongs to the E_{5/2u} irrep. The SR 2T_{2u} states split into E_{5/2u} doublets and F_{3/2u} quartets.\(^{53}\) The E_{5/2u} states of different SR parentage then mix under the influence of SO coupling. This admixture of SR states is clearly visible in the NSO spin populations of the SO GS, shown in Fig. 4, corresponding to a ratio of ca. 60/40% of SR 2A_{2u} and 2T_{2u} in the SO GS. This admixture of the SR states leads to an isotropic calculated g-factor of ~1.04 in acceptable agreement with our experimental value of g = −1.13, a previous experimental value of −1.14\(^{48}\) and previous first-principles calculations.\(^{53,82,85–87}\)

The first excited state is a four-fold degenerate state F_{3/2u} and corresponds to an admixture of the SR 2A_{2u} and 2T_{1u}. This first excited state is found separated from the GS by 3523 and 3836 cm\(^{-1}\) at the SCF-SO and PT2-SO level, respectively. This calculated energy gap is in excellent agreement with an experimental value of 3800 cm\(^{-1}\) reported by Selbin et al. using near-IR absorption spectroscopy.\(^{48}\) The order of the next LF states is E_{5/2u} F_{3/2u} and E_{1/2u}. The introduction of the dynamic correlation with CASPT2 leads to a slight destabilization of these excited LF states.

The LMCT absorption spectra of UC\(_{6}^{−}\) calculated at the SCF-SO and PT2-SO levels are shown in Fig. 5. The energies and the assignments of the more intense excitations are given in Table 5. Although the SO coupling mixes SR states of different symmetry, in O\(_{h}\) the states retain the g/u parity. As shown in the state diagram of Fig. 5, only transitions from the SO GS to excited states of E_{5/2g} and F_{3/2g} symmetry are allowed. These excited states derive principally from an admixture of the SR states 2T_{1g}, 2T_{2g} and 2E_{g}, and therefore, are strongly multi-configurational in character. Furthermore, the SO coupling mixes the SR LMCT doublet states with the SR Quartet states, which strongly affects the energy of the LMCT transitions as seen by comparing Fig. 5 and Fig. S10 (ESI†). As in the SR case, the dynamic correlation from PT2 leads to a substantial red-shift of the LMCT spectrum. Given the poor resolution of the available experimental absorption spectra,\(^{58}\) we forgo a detailed analysis. It is clear from the comparison of Fig. 3 and 5 and the accompanying data tables (3, 4) that SO coupling has a major effect on the appearance of the absorption spectrum. For molecules such as UC\(_{6}^{−}\), with a truly heavy element, only the SO level of theory allows a faithful comparison with experiment.

### 3.4 MCD spectrum

It is worth reiterating that the MCD C-term spectrum of UC\(_{6}^{−}\) is entirely caused by SO coupling, because the GS is not spatially degenerate, and therefore the observed MCD classifies essentially as a relativistic effect. The MCD spectra of UC\(_{6}^{−}\) calculated at the SCF-SO and PT2-SO levels are shown in Fig. 6 in comparison with the experimental spectrum. At the SCF level, the MCD spectrum exhibits three absorption bands below 40 × 10^{3} cm\(^{-1}\) and a more intense band centered at ca. 53 × 10^{3} cm\(^{-1}\). The nature of the electronic excitations associated with these bands can be easily assigned \(via\) the sign of the calculated C-terms given in Table 5. The bands with positive MCD are dominated by transitions from the SO GS into the

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**Table 4** Calculated relative energies (cm\(^{-1}\)) and assignment (%) of the ligand-field states of UC\(_{6}^{−}\) calculated with SCF-SO and PT2-SO

<table>
<thead>
<tr>
<th>States</th>
<th>SCF-SO</th>
<th>% SCF-SR states</th>
<th>PT2-SO</th>
<th>% PT2-SR states</th>
<th>Expt.(^{a})</th>
<th>CCSDT/SO(^{b})</th>
<th>PT2-SO(^{c})</th>
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</thead>
<tbody>
<tr>
<td>E_{5/2u}</td>
<td>0</td>
<td>59 2A_{2u}, 41 2T_{2u}</td>
<td>0</td>
<td>60 2A_{2u}, 40 2T_{2u}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F_{3/2u}</td>
<td>3523</td>
<td>67 2A_{2u}, 32 2T_{1u}</td>
<td>3836</td>
<td>72 2T_{2u}, 27 2T_{1u}</td>
<td>3800</td>
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<td>72 2T_{2u}, 27 2T_{1u}</td>
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<tr>
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<td>100 2T_{1u}</td>
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<td>12490</td>
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\(^{a}\) Data from ref. 48. \(^{b}\) Data from ref. 54. \(^{c}\) Data from ref. 53 obtained with a CAS(1,7) and 7 roots.
four-fold degenerate excited states $F_{3/2g}$, while bands with negative sign are dominated by transitions into $E_{5/2g}$ Kramers doublets. The first three absorption bands calculated at the SCF-SO level correspond to LMCT transitions, while the last band arises mainly from very intense $5f \rightarrow 6d$ transitions. The agreement with the experimental spectrum is fair at best. The MCD spectrum calculated at the PT2 level is in much better agreement with the experimental spectrum in terms of
Table 5: Energy ($\Delta E$, cm$^{-1}$), oscillator strength ($f$, a.u.) and MCD $C$-terms in Debye$^a$.

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>C-Term</th>
<th>SCF-SO</th>
<th>State</th>
<th>$\Delta E$</th>
<th>$f$</th>
<th>C-Term</th>
<th>PT2-SO</th>
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<tr>
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<td>24 937</td>
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<td>25 630</td>
<td>0.0161</td>
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<td>20 477</td>
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<tr>
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<td>$F_{3/2g}$</td>
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<td>0.0164</td>
<td>0.229</td>
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<td>0.0047</td>
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<td>0.0049</td>
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</table>

$^a$ Only transitions with calculated $C$-term larger in magnitude than 0.080 Debye$^2$ are given.

the relative band positions and signs. The PT2 correlation appears to be over-correcting the energies, leading to an overall red-shifted spectrum. The lowest-energy LMCT transitions are now just above 20 $\times$ 10$^3$ cm$^{-1}$, which, however, is in good agreement with the previous relativistic X$^2$ calculations$^{31}$ mentioned in Section 3.1. The 5f $\rightarrow$ 6d transitions are now calculated at 34 $\times$ 10$^3$ cm$^{-1}$, matching the second positive band in the experimental MCD spectrum when assuming an overall red-shifted calculated spectrum. The second positive MCD band in the experimental spectrum is therefore assigned to 5f $\rightarrow$ 6d transitions, whereas the remaining bands are assigned as LMCT. When only SR doublet states are used in the RASSI procedure (i.e. without quartet states), both the SCF and the PT2 spectrum are blue-shifted relative to the spectra including the quartets, and the lowest-energy simulated band peak from the PT2 spectrum lines up better with the experiment (Fig. S11, ESI†). Furthermore, between the second and the third negative band the simulated MCD intensity rises just to zero but not above zero. However, since the quartet states clearly have an influence on the MCD spectral features they must be included in the calculations.

Due to a sizable positive $C$-term at 26 $\times$ 10$^3$ cm$^{-1}$, the first negative band in the simulated PT2 spectrum is relatively small in intensity compared to the experimental peak and followed by a weak positive band not seen in the experimental spectrum. However, relatively small changes in the calculated energy of the transitions in this part of the MCD spectrum can have a strong impact on the spectral envelope, as shown in Fig. S12 (ESI†). The LMCT transition that causes the presence of a weak positive third MCD band is calculated at 26.5 $\times$ 10$^3$ cm$^{-1}$ ($E_{5/2g}$, $C = +0.181$, Table 5). There is another excitation very close in energy, at 26.6 $\times$ 10$^3$ cm$^{-1}$ ($E_{5/2g}$, $C = -0.101$), that would easily cancel the weak positive band if the two transitions were even closer in energy and a little more similar in intensity. Moreover, we point out that the calculated spectra are based on vertical excitations subject to empirical broadening, rather than a detailed simulated vibronic structure which may influence the spectrum in regions where excitations with positive and negative intensities largely cancel each other. Examples of this type are well known from natural circular dichroism.$^{38}$

The sign of the MCD absorption bands in UCl$_6^-$ can be rationalized by taking into account symmetry considerations. As discussed above, the SO GS of UCl$_6^-$ corresponds to a Kramers doublet of symmetry $E_{5/2g}$ in which the two components denoted $\vert M_0^g \rangle$ and $\vert M_1^g \rangle$ are related by time reversal symmetry.$^{21,89}$ Accordingly to Abragam and Bleaney,$^{90}$ the electronic g-factor of the SO GS is defined as

$$g = 2\langle M_0^g \mid \hat{L}_z + 2\hat{S}_z \mid M_0^g \rangle = -2\langle M_1^g \mid \hat{L}_z + 2\hat{S}_z \mid M_1^g \rangle$$ \hspace{1cm} (6)
and therefore, the C-term of eqn (2c) is given by ($g_M = 2$)

$$C = \frac{g}{4} \sum_n \left[ |\langle M| z' |\hat{a}_{+1} | N_n \rangle|^2 - |\langle M| z' |\hat{a}_{-1} | N_n \rangle|^2 \right] - |\langle M| \beta |\hat{a}_{+1} | N_n \rangle|^2 + |\langle M| \beta |\hat{a}_{-1} | N_n \rangle|^2 \right] \right]$$

(7)

Note that time reversal symmetry implies $\langle M| z' |\hat{a}_{+1} | N \rangle = \pm \langle M| z' |\hat{a}_{+1} | N' \rangle$ where $|N_n \rangle$ and $|N' \rangle$ can be evaluated with the help of the $3jm$ symbols tabulated by Piepho and Schatz. In the case of a four-fold excited state of symmetry $F_{3/2g}$ with components $|N\rangle$, $|N\rangle$, $|N\rangle$, and $|N\rangle$, the non vanishing terms in eqn (7) are $\langle M| z' |\hat{a}_{+1} | N \rangle = -\frac{1}{2\sqrt{3}} |\langle M| \hat{d} | N \rangle|$ and $\langle M| z' |\hat{a}_{+1} | N \rangle = -\frac{1}{2} |\langle M| \hat{d} | N \rangle|$, along with the time-reversed counterparts, where $|\langle M| \hat{d} | N \rangle|$ is the reduced matrix element. The C-term associated with an $E_{5/2u} \rightarrow F_{3/2g}$ transition is therefore

$$C(E_{5/2u} \rightarrow F_{3/2g}) = -\frac{g}{3\sqrt{3}} |\langle M| \hat{d} | N \rangle|^2$$

(8)

and it is positive, because the electronic $g$-factor is negative (see Fig. 4). On the other hand, for an excited state of symmetry $F_{3/2g}$, with components $|N\rangle$ and $|N\rangle$, the non vanishing matrix element is $\langle M| z' |\hat{a}_{+1} | N \rangle = \langle M| \beta |\hat{a}_{+1} | N \rangle = -\frac{1}{\sqrt{3}} |\langle M| \hat{d} | N \rangle|$, and therefore

$$C(E_{5/2u} \rightarrow E_{5/2g}) = \frac{2g}{3\sqrt{3}} |\langle M| \hat{d} | N \rangle|^2$$

(9)

leading to a negative C-term for a $E_{5/2u} \rightarrow E_{5/2g}$ transition.

4 Conclusions

We have presented the first combined ab-initio theoretical and experimental study of the UV-Vis MCD spectrum of an actinide complex, $UCl_{6}^{-}$. The ground state of the octahedral $UCl_{6}^{-}$ complex ion is an orbitally non-degenerate doublet $E_{5/2u}$, and the MCD C-term intensity is entirely caused by SO coupling, a relativistic effect. Calculations of the electronic spectrum at various levels of theory indicate that differential dynamic electron correlation has a strong influence on the excitation energies. SO coupling causes the absorption spectrum to display three major peaks below $40 \times 10^{3}$ cm$^{-1}$, instead of two predicted by scalar relativistic wavefunction calculations and hybrid TDDFT. The envelope of the simulated MCD spectrum is strongly affected by the dynamic electron correlation. Many of the excited states with intense absorption also have strong multi-configurational character.

Based on the calculations, the experimentally observed bands are assigned predominantly to dipole-allowed LMCT, but it is likely that the observed second positive MCD band is dominated by dipole-allowed 5f to 6d transitions. LMCT transitions into the U 6d orbitals are calculated to arise at energies beyond those currently accessible experimentally.

Owing to the high symmetry of the $UCl_{6}^{-}$ complex, the MCD-allowed transitions can be clearly separated via their signs of the C-terms: The $E_{5/2u} \rightarrow E_{5/2g}$ transitions have negative C-terms whereas $E_{5/2u} \rightarrow F_{3/2g}$ transitions have positive C-terms. These calculated signs are in agreement with the signs of the transition dipole matrix elements expected from tabulated data for the $O_n$ double group and tied to the negative ground-state EPR $g$-factor of the complex. If the $g$-factor were positive, the MCD spectrum would have the opposite sign.

The agreement of our most accurate simulated spectrum, obtained from SO-CASPT2 wavefunction calculations, with the experiment is quite acceptable. The spectral region where the calculated spectrum displays a weak positive band not seen experimentally is sensitive to the balance of canceling C-terms of opposite signs. It is likely that an improved agreement with the experiment will be obtained in simulations that include vibronic effects. An improved treatment of the dynamic electron correlation is also expected to lead to improved simulations, as the PT2 correlation appears to over-correct the blue shift of the electronic spectrum obtained at the CASSCF level.

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