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Variable photon energy photoelectron spectroscopy of tris-cyclopentadienyl lanthanides.

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The gas phase photoelectron (PE) spectra of LnCp_3 ($\text{Cp} = \eta\text{-C}_5\text{H}_5$; $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$), measured with a wide range of photon energy, are reported. Resonances observed in the photon energy regions of 4d to 4f excitation enable identification of ion states resulting from 4f ionization. For all three compounds molecular ion states characteristic of both $4f^n$ and $4f^{n-1}$ configurations are observed ($\text{Pr}, n=2$; $\text{Nd}, n=3$; $\text{Sm}, n=6$). The molecular ion ground states have a hole in the uppermost ligand orbital of a' symmetry and are reached by either ligand or f electron ionization. The results are discussed in the context of the previously reported spectra of the Ce, Yb and Lu analogues. For SmCp_3 and Yb_3 f orbital/ligand interaction is proposed in the molecular ground state and for CeCp_3^+ in the molecular ion ground state. For PrCp_3 and NdCp_3 final state effects are proposed as the origin of the dual configuration structure in their PE spectra. When the contributing orbitals are close in energy the $4f/a'$ interaction can give rise to significant covalent bonding even in the absence of effective overlap.

For d block transition metal complexes, gas phase photoelectron (PE) spectroscopy has had considerable success in revealing their electronic structure. For closed shell molecules in the valence region, there is normally a close correspondence between the photoelectron bands and the orbital structure predicted by density functional theory (DFT).^{1, 2} Lanthanide complexes are not so straightforward. The f-electrons are energetically part of the valence region, and for some elements are active in redox chemistry, but spatially are part of the core, the f-orbitals lacking significant overlap with ligand orbitals. Core ionization may result in significant perturbation of a molecule's electronic structure, which manifests itself in satellite structure accompanying the primary core PE bands, often referred to as shake-up or shake-down bands. These bands are assigned to many electron processes in which a valence excitation or transition accompanies the core ionization.

Ionization of the 4f electrons of lanthanides gives very characteristic final state structure that depends on the electronic ground state adopted by the $4f^n$ configuration. The relative intensities of the ion states arising from ionization of the 4f electrons have been predicted using a fractional parentage description of the ground state molecule,³ and these predictions are on the whole consistent with data obtained from solid state photoemission studies.⁴ Although consideration of spin orbit coupling leads to modification of the relative intensity predictions,⁵ the pattern of the bands associated with a particular $4f^{n-1}$ configuration are characteristic and may be assigned by consideration of the electronic spectrum of the Ln^{3+} ion of the preceding element, *i.e.* the lanthanide with an atomic number of one less and a $4f^{n-1}$ configuration.⁶

The cross sections of 4f electrons differ substantially from those of the higher lying ligand-based electrons, which are predominantly of p character.⁷ The 4f cross sections have a delayed maximum in the photon energy region between 75 and 150 eV depending on the particular lanthanide. By contrast, the cross sections of s and p bands have maxima close to threshold, hence employing incident photon energies away from p based maxima yet near to 4f maxima will enable unambiguous characterization of the final state structure. The 4f bands also exhibit cross section maxima in the region of the 4d to 4f resonant excitation.^{2, 8, 9} Such excitation opens another channel for photoionization, since

the excitation can be followed by super Coster-Kronig (SCK) decay in which the core hole is refilled and an f electron is ejected. Thus, in a PE experiment, with careful selection of photon energies, as is enabled by synchrotron radiation, ion states accessible by f ionization may be distinguished from those accessible by ligand ionization.

PE studies of lanthanides and their compounds in the solid state normally show f ionization bands superimposed on the valence bands. In some cases, particularly intermetallic compounds and those with counterions of low electronegativity, f ionization bands corresponding to two different f configurations are found. Thus, if the compound has a formal oxidation state implying a $4f^n$ configuration, both $4f^{n-1}$ and $4f^n$ band patterns are observed. Such observations have been interpreted in a number of ways. In some cases the initial state is implicated and a mixture of oxidation states is proposed for the compound.¹⁰ In other cases the $4f^n$ states are presumed to result from ionization of an f electron being accompanied by valence band to 4f electron transfer ie a final state effect.^{11, 12}

Gas phase PE studies on lanthanide complexes are less common than those of solid compounds. This is in part due to their low volatility but also because discharge sources, common in house, are of insufficient energy to be able to identify unambiguously 4f ionization bands. The availability of an angle resolved photoelectron spectrometer (ARPES) on the gas phase photoemission beam line of the Elettra synchrotron¹³ has enabled a programme of study of the tris-cyclopentadienyl lanthanides, LnCp_3 ($\text{Cp} = \eta\text{-C}_5\text{H}_5$). We have reported so far on the PE spectra of CeCp_3 ,^{14, 15} YbCp_3 ⁶ and LuCp_3 .⁶ The PE spectrum of LuCp_3 shows two ion states, $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ associated with a $4f^{13}$ configuration for the molecular ion as might be anticipated on ionizing the closed $4f^{14}$ shell of Lu^{3+} . The PE spectrum of YbCp_3 shows structure corresponding to both $4f^{12}$ and $4f^{13}$ ion configurations. Consequently it was proposed that YbCp_3 has a mixed configuration ground state that can be represented by the superposition of an ionic configuration $\text{Yb(III):}4f^{13}(\text{Cp}_3)$ and a charge-transfer configuration $\text{Yb(II):}4f^{14}(\text{Cp}_3)^{-1}$. Subsequent confirmation was obtained by the study of the magnetism, epr spectrum and analysis of the electronic spectrum of YbCp_3 , which were all in agreement in weighting the charge transfer configuration in the range 12-17%.¹⁶ In addition, the hole in the ligand set in the charge transfer

configuration was found to be in an orbital of a' symmetry (C_{3h} molecular symmetry) which interacts with one of the real parts of the $4f_{\pm 3}$ orbitals. In the case of $CeCp_3$ the PE spectrum also indicated two ion state configurations, but in this case it is the molecular ion that has a mixed configuration ground state, $Ce(IV):4f^0(Cp_3)$ mixed with $Ce(III):4f^1(Cp_3)^{-1}$. The molecular ion ground state is accessible by direct photoionization from the $Ce(III):4f^1(Cp_3)$ molecular configuration by virtue of the former term.¹⁴ Calculations using a CASSCF/CASPT2 approach confirmed the presence of configuration interaction in the ground state of the $CeCp_3^+$ cation.¹⁵

Here we present the variable photon energy PE spectra of $PrCp_3$, $NdCp_3$ and $SmCp_3$ and compare the results with those reported previously for Ce , Yb and Lu .
Experimental

The tris-cyclopentadienyl lanthanides of praseodymium, neodymium and samarium were prepared by the method of Birmingham and Wilkinson and sublimed at $200\text{ }^\circ\text{C}/10^{-2}\text{ mm Hg}$ to remove coordinated THF.¹⁷ The resulting product was sealed in a glass ampoule and subsequently transferred to a copper container under nitrogen, which was inserted into an oven attached to the angle resolved photoelectron spectrometer.

Measurements were carried out at the GAs PHase photoemission (GAPH) beam line of the ELETTRA storage ring in Trieste, Italy.¹³ An undulator source provides high-intensity synchrotron radiation in the photon energy range 20–900 eV. The highly polarized light is dispersed by a Variable Angle Spherical Grating Monochromator that is equipped with five interchangeable gratings, to cover the energy range 13 to 900 eV, and fixed entrance and exit slits, with a photon energy resolution $\Delta E/E \leq 10^{-4}$.

The samples were held in an oven close to the ionization region and evaporated through a small hole by holding the temperature of the oven at around $161\text{ }^\circ\text{C}$.

The PE measurements on $NdCp_3$ were carried out using the ARPES chamber. The ARPES chamber was equipped with a 50 mm mean radius electron energy analyser (VSW Ltd.), mounted at the magic angle. Pass energies of 10 eV were used for valence PE spectra at low photon energies and 15 eV at higher photon energies. The PE spectra of $PrCp_3$ and $SmCp_3$ were analyzed by a VG220i hemispherical electron energy analyzer with a mean radius of 150 mm equipped

with six channel electron multipliers. This electron analyser was mounted in the plane defined by the (linearly polarized) electric vector of the light and the photon propagation direction at an angle of 54.7° with respect to the electric vector of the light. In this geometry the axis of the analyzer is set at the pseudo magic angle, and so measurements should be insensitive to the PE asymmetry β parameter. Electron energy resolution is linear along all the kinetic energy scale and equal to 2% of pass band for both analyzers. PE spectra were acquired at the magic angle or pseudo magic angle depending on the analyzed used and normalised using the signal from a calibrated photodiode (IRD, Inc.).¹⁸ Pass energies of 5 eV were used for valence PE spectra. PE spectra of the valence region from 6–20 eV of binding energy were measured at the pseudo magic angle for a series of photon energies ranging from 24–180 eV. The binding energy scale was calibrated according to the Ar photoelectron lines.

Results

A selection of the PE spectra of LnCp_3 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) measured with both low and higher photon energies are shown in Figs 1-3.

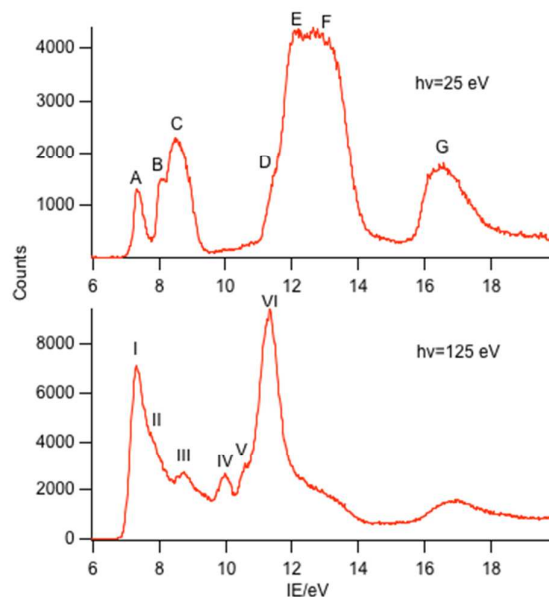


Figure 1. PE spectra of PrCp_3 with photon energies of 25 and 125 eV.

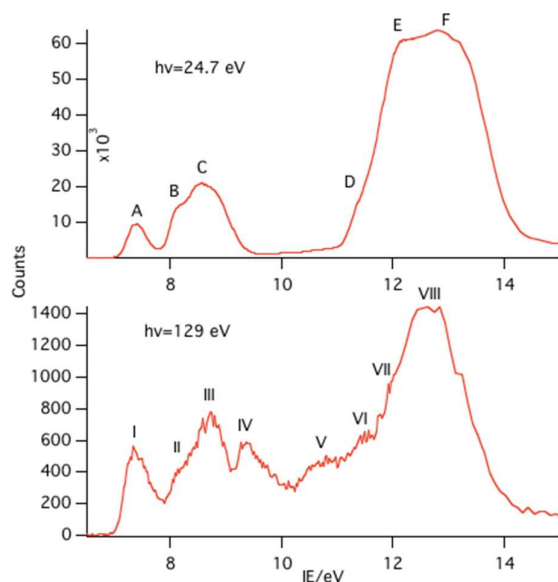


Figure 2. PE spectra of NdCp₃ with photon energies of 24.7 and 129 eV.

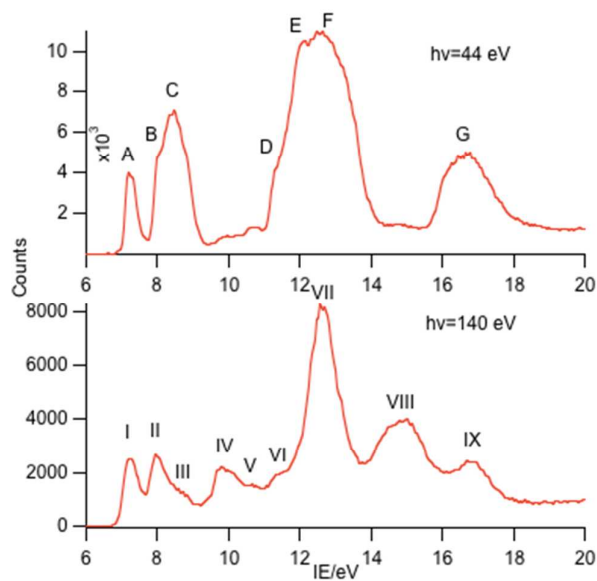


Figure 3. PE spectra of SmCp₃ with photon energies of 44 and 140 eV.

Key features are tabulated (Table 1). The ionization bands fall into two distinct types. Those labelled A-G, identifiable for all three compounds, show a decay in intensity relative to the other bands with increasing photon energy. (Although only two photon energy spectra are presented in the figures, many more were recorded which show a gradual evolution.) Those bands labelled with Roman numerals increase in relative intensity with photon energy and show resonances in the photon energy region of the respective lanthanide 4d to 4f excitation

energies. The emergence of the f-bands over the resonance region is shown for PrCp_3 in Figure 4. Although the f bands dominate in the resonance region they are also visible in the pre-resonance region for example with a photon energy of 100 eV.

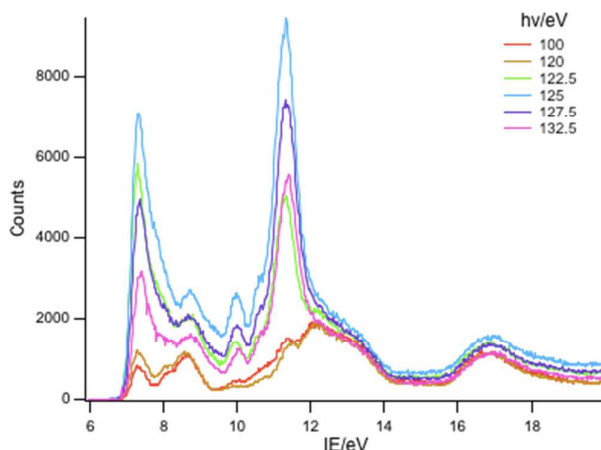


Figure 4. PE spectra of PrCp_3 with photon energies 100 – 132.5 eV.

In the spectra of all three compounds Bands A and I are coincident indicating that the ground ion states are accessible by two different ionization processes.

Discussion

Band assignment

The origin of the bands A-G and their assignment has been discussed previously.^{6, 14-16} The associated ion states have holes in the ligand shells and are accessed from the parent molecules by ionization of ligand based orbitals. PE ionization cross sections of carbon and hydrogen based electrons have a maximum near threshold and decay with increasing photon energy,^{2, 7} thus the ready identification of their ionization bands. Individual assignments are based on comparison with the PE spectra of other cyclopentadienyl compounds and theoretical calculations.

Most crucially bands A, B and C arise from ionization of the highest occupied π orbitals of the cyclopentadienyl rings. In the C_{3h} symmetry of the gas-phase LnCp_3 molecules these transform as $a'+a''+e'+e''$. The Ln 5d transform as $a', e',$

and e'' , and the 6p as a'' and e' . However, the net overlap of the cylindrically symmetrical $5d_{z^2}$ (a') with the $Cp-\pi$ (a') MO, which has six nodes in the horizontal plane (Figure 5), is negligible; in the effective D_{3h} symmetry they would belong to different irreducible representations. The $Cp-\pi$ a' combination does find a nodal match in the $\cos 3\phi$ component of the Ln $4f_{\pm 3}$ orbitals but lack of substantive radial overlap with the core-like 4f orbitals leads to it being less stabilized by interaction with the lanthanide than the other combinations, which can overlap with Ln 5d and 6p orbitals.

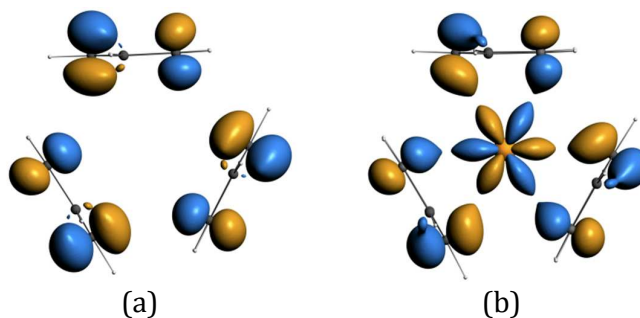


Figure 5. (a) the $cp\pi$ a' symmetry adapted linear combination (b) possible overlap with $\cos 3\phi$ component of the Ln $4f_{\pm 3}$ orbitals.. (These isosurfaces at value 4.8 were generated for $CeCp_3^+$ using the ADF program suite BP/TZP.)¹⁹

Band A is assigned to ionization from this $Cp-\pi$ a' orbital and lies at a lower IE, well separated from bands B and C. Band B is assigned to ionization from the $Cp-\pi$ a'' orbital which can mix with Ln 5p and band C to the e' and e'' orbitals which form more effective bonding combinations with Ln 5d orbitals. Bands D-F are associated with orbitals based on C 2p and H 1s orbitals whereas band G is principally C 2s in character.

As discussed in the introduction, the cross sections of 4f ionizations are very low near threshold with the consequence that the associated ionization bands are not readily detectable with low photon energies.^{2, 7} They rise in intensity with photon energy passing through a maximum. In addition 4f ionizations commonly show resonances when the photon energy promotes 4d to 4f excitation. Intensity borrowing from this transition may lead to considerable enhancement of a 4f band intensity.² The ionizations labelled with Roman numerals show such cross section features and are associated with ionizations from the 4f orbitals. The number and intensity of the 4f bands is characteristic of the number of f

electrons in the molecule.

PrCp₃

Figure 6 shows a difference spectrum of PrCp₃ consisting of the pre-resonance spectrum at 117.5 eV subtracted from that at the height of the resonance at 125 eV. This process removes the ligand bands from the spectrum leaving only the f band spectrum. Pr³⁺ has a 4f² configuration and a ³H₄ ground state. Fractional parentage methods predict that on direct photoionization the spin orbit states ²F_{5/2} and ²F_{7/2} are accessed with relative intensity 1.714 to 0.286. The spin orbit splitting of Pr⁴⁺ is 865 cm⁻¹ (0.1 eV)²⁰ so resolution of these states is not expected under the experimental conditions. Thus the presence of six 4f bands in the PE spectrum indicates that simple direct photoionization from a Pr³⁺ ion is not the only process to be considered.

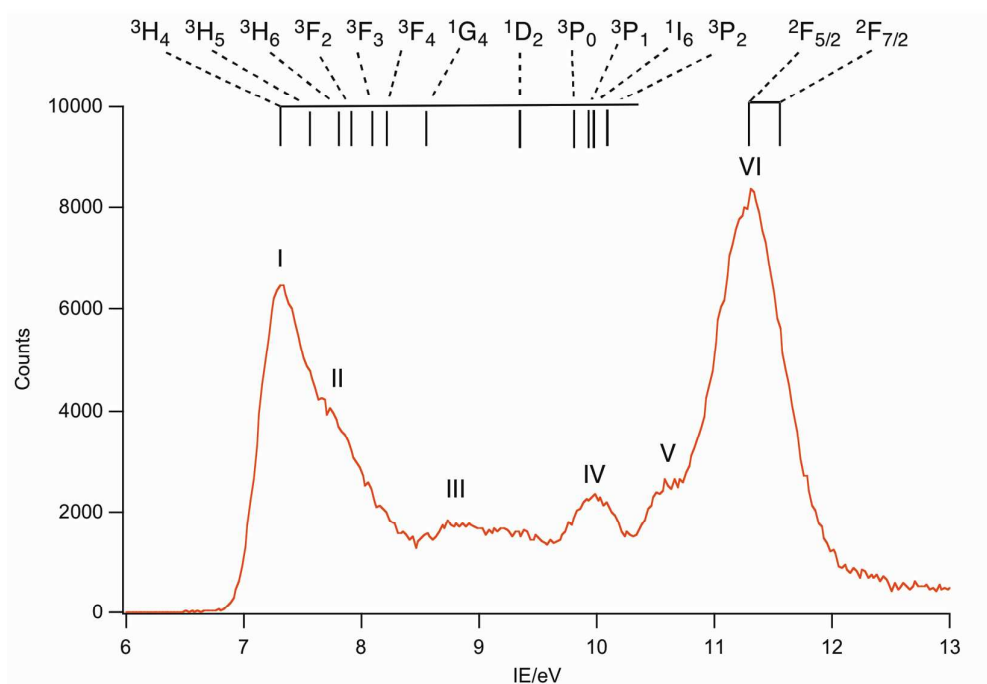


Figure 6. Difference of PE spectrum at 125 eV minus PE spectrum at 110 eV for PrCp₃. The highest energy 4f band, VI, is assigned to the ²F states.

Band I, being coincident with Band A, corresponds to an ion state with a hole in the Cp- π a' orbital and Pr(III) in its ³H₄ ground state. We denote this ion state |4f²(³H₄)a'⁻¹>. Bands II-V are assigned to excited states of the 4f² configuration and are assigned by comparison with electronic spectra of Pr(III) compounds

and associated calculations.^{21, 22} Such calculations include consideration of the crystal field, and that splitting of the spin-orbit states can cover an energy range of up to 0.2 eV. In Fig. 6 we indicate the relative energies of the lowest crystal field term of a particular spin orbit state of Pr^{3+} . It is evident that the spin-orbit states span the energy range of bands I- V.

NdCp₃

Figure 7 shows a difference spectrum of NdCp₃ consisting of the pre-resonance spectrum at 110 eV subtracted from that at the height of the resonance at 129 eV. Nd(III) with an f^3 configuration and a $4I_{9/2}$ ground state is predicted to give $3H_4$, $3H_5$ and $3F_2$ states upon direct photoionization with relative intensities 1.890:0.424:0.563. In PrCp^*_3 ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$) these states span an energy range of 0.7 eV.²¹ For Nd^{4+} an expansion of the range is anticipated but all three states are likely to occur within the 1.5 eV range covered by band VIII, which is consequently assigned to these $3H_4$, $3H_5$ and $3F_2$ states.

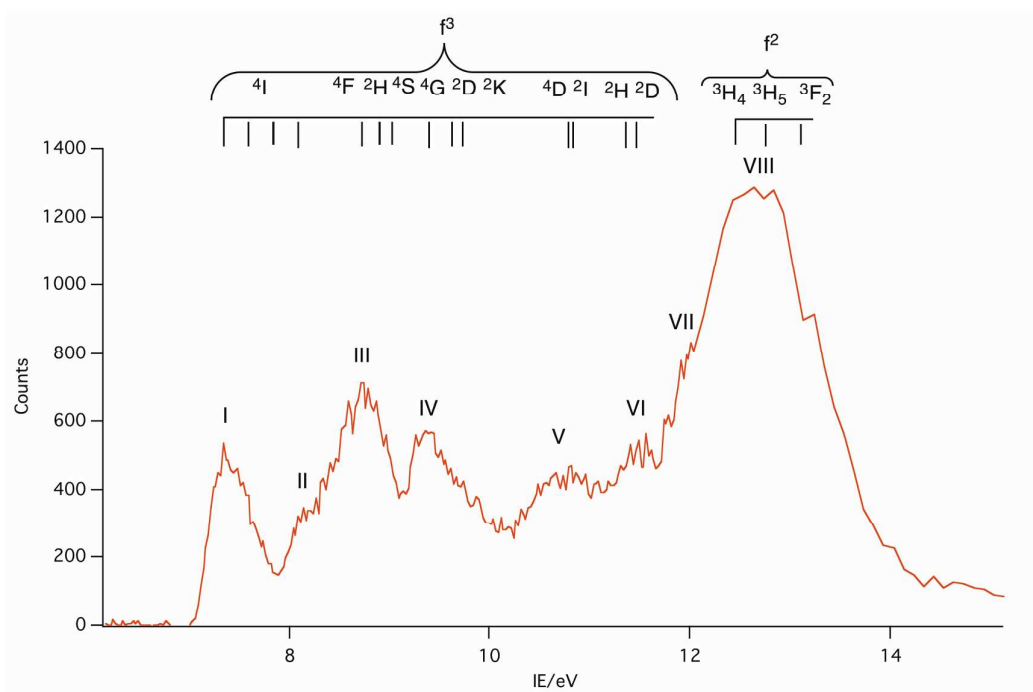


Figure 7. Difference of PE spectrum at 129 eV minus PE spectrum at 110 eV for NdCp₃ showing the energy range of identified $4f^3$ spin-orbit states for Nd^{3+} and shows the likely energy range of $4f^2$ states for NdCp_3^{3+} accessible by direct photoionization.

Like PrCp_3 , NdCp_3 has many more 4f PE bands than can be accounted for by direct photoionization. The lowest energy 4f band, I, is again coincident with the lowest energy ligand band, A, and can be assigned to the molecular ion ground

state $|4f^3(4l_{9/2})a^{-1}\rangle$. Nd(III) has a plethora of spin-orbit states. In Fig. 7 we indicate the energy range of identified states for Nd³⁺^{23, 24}. Bands II-VII all lie within this range.

SmCp₃

Figure 8 shows a difference spectrum for SmCp₃ consisting of a pre-resonance spectrum acquired at 130 eV subtracted from one at the height of the resonance at 140 eV.

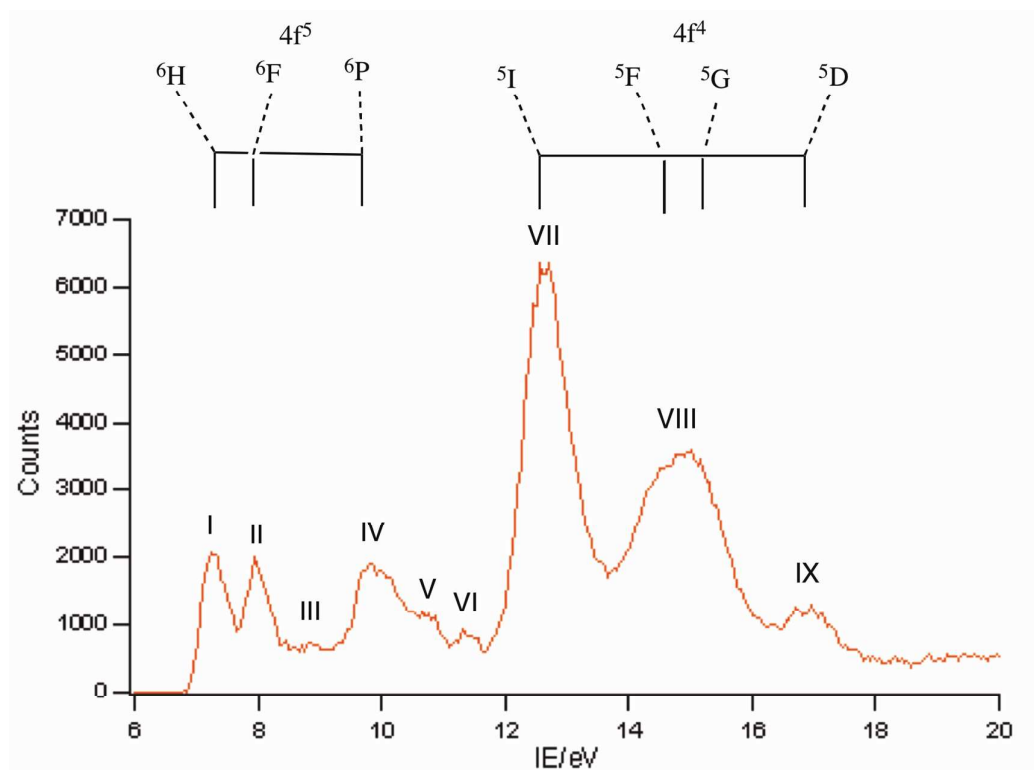


Figure 8. Difference of PE spectrum at 140 eV minus PE spectrum at 130 eV for SmCp₃. The lower energy 4f bands are assigned to states from a 4f⁵ configuration and those attributed to accessible sextet states from a 4f⁴ configuration are labelled with their ^(2S+1)L symbols. Bands III, V and VI are likely to arise from the many quartet states of Sm³⁺.

Sm(III) has a 4f⁵ configuration and a ⁶H_{5/2} ground state. Direct ionization is predicted to give four LS states, ⁵I, ⁵G, ⁵F and ⁵D with relative intensities 2.758:1.266:0.500:0.476.³ Bands VI, VII and VIII have relative intensities 2.76:2.1:0.13 suggesting that band VII incorporates both the ⁵F and ⁵G states as has been assigned previously.²⁵ Bands I, II and IV are clearly visible in the spectra of Sm(II) compounds and are assigned to the ⁶H, ⁶F and ⁶P states of the 4f⁶ configuration.^{10, 25-27} Other states from this configuration are also visible as

bands III, V and VI which to the best of our knowledge haven't been reported previously in photoemission studies. Assignment of these states is difficult. There is a plethora of excited states for the Sm^{3+} ion. Various quartet states lie between the ${}^6\text{F}$ and ${}^6\text{P}$ levels and above the ${}^6\text{P}$ levels²⁸ and we hesitate to make a definite assignment.

Electronic structure and state access

It is helpful at this juncture to propose two orbital schemes for the ground states of tris-cyclopentadienyl lanthanide systems (Fig. 9). Both include as the basis set the highest occupied cyclopentadienyl π orbitals, the lanthanide 4f, 5d and 6p orbitals. Mixing with the 5d and 6p orbitals stabilizes the a'' , e' and e'' linear combination of the ring orbitals. Although, formally, in the C_{3h} symmetry of the molecule the ring a' orbital may interact with the d_{z^2} orbital, their nodal properties are incompatible (Fig. 5). In the first case (Fig. 9a) the 4f orbitals are sufficiently separated in energy from the ring a' orbitals, such that the interaction is not applicable.

This is the case in CeCp_3 . In the second case (Fig 9b) the 4f orbitals are sufficiently close in energy to the ring a' orbital for interaction and charge transfer to take place resulting in a stabilized ring orbital and a destabilized f orbital, specifically one of the real components of the $f_{\pm 3}$ pair. It is noteworthy in the latter case that even with minimal overlap as a consequence of the radially contracted 4f orbitals significant interaction may occur when the interacting orbitals are close in energy.²⁹ Case 9b pertains to CeCp_3^+ cation and YbCp_3 . For CeCp_3^+ $1a'$ is filled and is the HOMO while for YbCp_3 $3a'$ is the SOMO occupied by one unpaired electron.

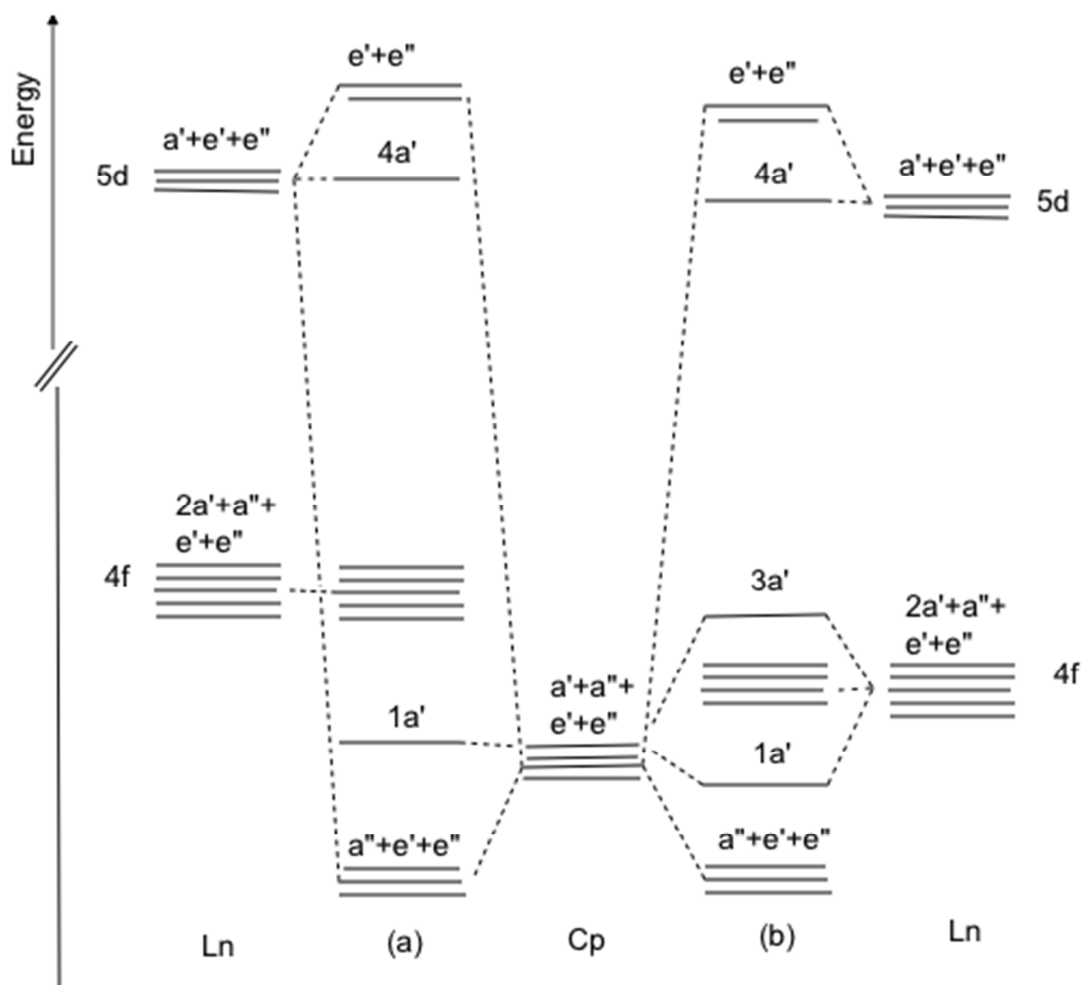


Figure 9. Orbital interaction diagram for LnCp_3 (a) 4f orbitals non-interacting (b) 4f orbitals close in energy to ring $\pi a'$ orbital.

The resulting ground state wave function is most conveniently described by configuration interaction between two terms (L represents the remaining electrons) where one configuration has n f electrons as expected for a Ln^{x+} ion and the other has a hole in the ring a' orbital and one more f electron.

$$\Psi_{GS} = c_0 \psi_0 + c_1 \psi_1 = c_0 |f^n a'^2 L\rangle + c_1 |f^{n+1} a' L\rangle \quad [1]$$

The two terms must have the same symmetry so the crucial 4f orbital is of a' symmetry as shown in Fig. 5b.

For the LnCp_3^+ cations the PE spectra inform as to the relative energies of the ground and excited states. In the cases of $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Yb}$ and Lu the states associated with an $f^{n-1} a'^2 L$ configuration, where one f electron has been ionized, are unambiguously identified. Removal of a 4f electron results in

significant stabilization of the other f electrons and states from this configuration lie at higher energies than the molecular ion ground state. For Ln = Pr, Nd, Sm, Yb and Lu the cationic ground states correspond simply to the removal of one electron from the Cp π a' orbital and belong to the configuration $f^n a'^1 L$. For Ln=Ce there is a lower energy cationic ground state with a mixed configuration as described by equation 1. The ionization energies of the lowest states associated with a configuration are plotted in Figure 10.

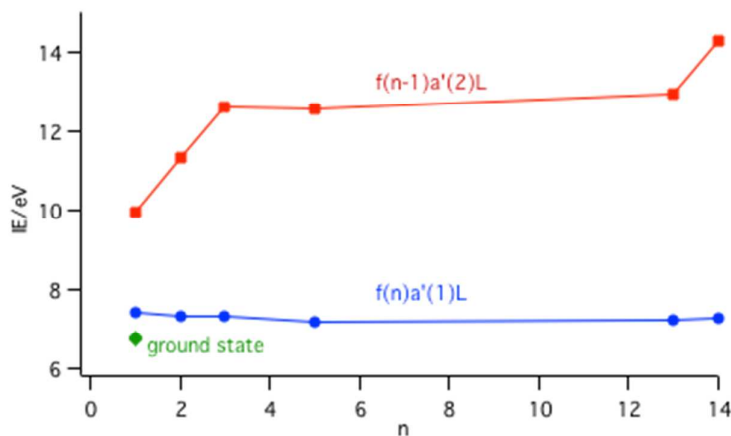


Figure 10. Plot of the IE to the lowest energy state of a configuration across the lanthanide series; red points are associated with an $f^{n-1}a'^2L$ configuration and blue points with an $f^n a'^1L$ configuration. The green point represents the ground state of $CeCp_3^+$

The ionization energy to the $f^n a'^1L$ configuration remains fairly constant across the series; removal of an electron from the Cp π a' orbital is insensitive to the Ln nuclear charge. In contrast the ionization energy to the $f^{n-1}a'^2L$ configuration rises across the series because the 4f electrons are not effectively shielded from the increase in Ln nuclear charge. Calculations on the $CeCp_3^+$ cation have shown that in the $f^0 a'^2L$ state there is a considerable increase in the population of the metal 5d orbitals compared with the ground state as the ligand metal covalency increases with f ionization.¹⁵ This is described as screening in solid state studies. The ground state of $CeCp_3^+$ is 0.68 eV (65 kJmol⁻¹) more stable than the excited state with an $f^1 a'^1L$ configuration. This separation provides a convenient measure of the binding energy afforded by the configuration interaction (CI) described by [1]. Delocalizing the f electron into the hole in the ligand a' orbital rather than maintaining pure f character provides a significant covalent interaction. Modeling of the electronic spectrum of $YbCp_3$ gave a CI matrix

element of a similar order of magnitude, namely -3900 cm^{-1} (47 kJmol^{-1}).¹⁶ Thus in these situations of close energy proximity significant covalent binding can occur with minimal overlap.

The matrix element governing the band intensity for direct f ionization is given by

$$\langle Lf^n | O | Lf^{n-1} \varepsilon \rangle$$

where O is the dipole moment operator and ε is the free electron wave. Thus the $f^{n-1}a^2L$ configuration may be accessed by direct removal of an f electron as can the ground state of the CeCp_3^+ cation as a result of its mixed configuration. For $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$ and Yb the $f^{n-1}L$ configuration can also be accessed by $4f$ ionization. The question arises as to whether this is an initial or final state effect. For YbCp_3 it has been shown conclusively that the neutral molecule has a mixed configuration ground state with a value for c_1^2 of 0.12 ± 0.03 . An alternative mechanism by which the states associated with an $f^{n-1}L$ configuration can be accessed is ionization coupled with electronic relaxation in the ion; an electron moves from the $\text{Cp } \pi a'$ orbital into the stabilized $4f$ shell. Such processes are commonly found for core ionizations. Chemical intuition suggests that such a shake down is more likely for $\text{Ln} = \text{Pr}$ and Nd whereas SmCp_3 may have a mixed configuration ground state (Sm can form compounds in the II oxidation state). Consideration of charge transfer energies results in the prediction that SmCp_3 may have between 3 and 4% Sm(II) character.¹⁶ However, the intensities of the bands belonging to the $4f^6$ configuration constitute 28% of the total $4f$ band intensity, thus it is unlikely that all access to this configuration is a consequence of a mixed configuration ground state. Other techniques for probing the f orbital covalency that explicitly avoid major perturbation to the ground state are epr and variable temperature magnetism. However these are normally made on solid samples. In the solid state SmCp_3 has an infinite chain structure,³⁰ unlike YbCp_3 , which has a molecular crystal structure with the molecule possessing C_{3h} symmetry.³¹ With lower symmetry the a' ligand orbital may interact with the metal d orbitals and be lowered in energy. Thus its energy proximity to the metal f orbitals will change. Given the covalency is energy driven this is likely to change between the gas phase and the solid state. In addition the electronic configuration of SmCp_3 is not a Kramer's doublet, unlike YbCp_3 . Thus magnetic

and epr measurements that were able to establish the mixed configuration ground state for YbCp₃ are not accessible for SmCp₃.^{6, 16} Sm LIII/II-XANES involves major perturbations to the Sm core hence, like PES, is likely to perturb the valence electronic structure. From the PE results we cannot rule out f orbital covalency but the magnitude of the intensity of the fⁿ bands indicates that such covalency is not the cause of their presence.

Conclusions

The gas phase PE spectra of LnCp₃ (Cp = η-C₅H₅; Ln = Pr, Nd, Sm) have been measured using synchrotron radiation. Variation of band intensity with photon energy, including in the region of 4d to 4f excitation, has enabled unambiguous assignment of the ion states. In all three cases, ion states associated with both 4fⁿ and 4fⁿ⁻¹ configurations are identified, where *n* is the number of f electrons in the molecular ground state. The data are discussed in the context of the previous results for Ln= Ce, Yb and Lu. The cationic ground state of LnCp₃ for all members of the series except Ce have a fⁿ configuration with a hole in the ligand shell, specifically in an orbital of a' symmetry. Ce is exceptional in having an intermediate valence ground state comprised of a mixture of f⁰a'² and f¹a'¹ configurations, where a' is the highest occupied orbital of the Cp₃ ligand set. The f electron in the latter occupies the cos 3φ component of the Ln 4f_{±3} orbitals giving a singlet state overall. The 4f band intensities are similar to those observed previously in solid state studies but in general are better resolved. The 4fⁿ⁻¹ states are accessed by direct ionization or by a 4d-4f resonance process coupled with super Koster-Kronig decay. The more intense of the 4fⁿ states are observable outside the resonance region but become most clearly visible within the resonance region. The mechanisms of their access are discussed. SmCp₃ is the most likely candidate to have an intermediate valence ground state as has been established for YbCp₃. However, the intensity of the 4fⁿ bands suggest that an alternative mechanism for their access on 4f ionization must be present.

Figure Titles.

Figure 1. PE spectra of PrCp₃ with photon energies of 25 and 125 eV.

Figure 2. PE spectra of NdCp₃ with photon energies of 24.7 and 129 eV.

Figure 3. PE spectra of SmCp₃ with photon energies of 44 and 140 eV.

Figure 4. PE spectra of PrCp₃ with photon energies 100 – 132.5 eV.

Figure 5. (a) the $c_{\pi} a'$ symmetry adapted linear combination (b) possible overlap with $\cos 3\phi$ component of the Ln $4f_{\pm 3}$ orbitals.. (These isosurfaces at value 4.8 were generated for CeCp₃⁺ using the ADF program suite BP/TZP.)¹⁹

Figure 6. Difference of PE spectrum at 125 eV minus PE spectrum at 110 eV for PrCp₃.

Figure 7. Difference of PE spectrum at 129 eV minus PE spectrum at 110 eV for NdCp₃ showing the energy range of identified $4f^3$ spin-orbit states for Nd³⁺ and shows the likely energy range of $4f^2$ states for NdCp₃⁺ accessible by direct photoionization.

Figure 8. Difference of PE spectrum at 140 eV minus PE spectrum at 130 eV for SmCp₃. The lower energy 4f bands are assigned to states from a $4f^5$ configuration and those attributed to accessible states from a $4f^4$ configuration are labelled with their $(2S+1)L$ symbols.

Figure 9. Orbital interaction diagram for LnCp₃ (a) 4f orbitals non-interacting (b) 4f orbitals close in energy to ring $\pi a'$ orbital.

Figure 10. Plot of the IE to the lowest energy state of a configuration across the lanthanide series; red points are associated with an $f^{n-1}a'L$ configuration and blue points with an $f^n a'L$ configuration. The green point represents the ground state of CeCp₃⁺

Table 1. Ionization energies (eV) of key features in the PE spectra of LnCp₃ (Ln = Ce,¹⁴ Pr, Nd, Sm, Yb,⁶ Lu⁶)

Band\Ln	Ce	Pr	Nd	Sm	Yb	Lu	Associated MO
A	7.45	7.34	7.39	7.21	7.16	7.28	a'
B	8.13	8.04	8.17	8.08			a''
C	8.58	8.46	8.57	8.50	8.46	8.81	e'+e''
D	11.53	11.46	11.57	11.50			
E	12.25	12.19	12.22	12.07	12.4	12.4	
F	12.80	12.94	12.79	13.00			
G	16.53	16.49	16.53	16.60	16.7	17.2	
I	6.77	7.33	7.34	7.21	7.26	14.30	
II	9.97	7.76	8.14	7.96	8.58	15.74	
III		8.77	8.74	8.61	12.93		
IV		9.97	9.39	9.86	13.73		
V		10.61	10.79	10.66	14.91		
VI		11.34	11.49	11.46	15.98		
VII			11.99	12.56	16.71		
VIII			12.64	14.96	17.66		
IX				16.81			

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Gas-phase photoelectron spectra are presented for LnCp_3 ($\text{Cp} = \eta\text{-C}_5\text{H}_5$; $\text{Ln} = \text{Pr, Nd, Sm}$) in which f ionization gives rise to bands associated with $4f^n$ configurations in addition to the expected $4f^{n-1}$ bands.

