High-energy optical absorption in f-compounds

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Abstract

Over a large energy domain, the electronic spectra of f-compounds arise mainly from three types of electronic transitions: $f-f$ transitions, $f-d$ transitions and ligand to metal charge transfer. The first transitions can be predicted quite successfully via an empirical Hamiltonian exploiting the symmetry of the system under consideration and evaluating the radial dependence of the various interactions felt by the f-electron through adjustable phenomenological parameters. The two other electronic transitions can be modelled via the refined spin pairing theory. Both similarities and differences in chemical and spectroscopic behavior of lanthanides and actinides will be briefly discussed.
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1. Introduction

From optical spectroscopy point of view, lanthanides and actinides behave differently from the other elements. Indeed, the f-orbitals ($l = 3$) which are under completion across the series and contain the unpaired optically active electrons are protected by the most outer s and p shells and therefore, can be considered as belonging to the core shells.

Although iso-electronic 4f and 5f elements appear very similar with respect to various properties, especially when they are in the same oxidation state, they show remarkable spectroscopic differences attributed to different spatial extensions of the 4f and 5f orbitals. As a matter of fact and in contrast to the localized 4f-shell of the lanthanides, in early actinides partially delocalized 5f-orbitals can hybridize strongly. The itinerant character of the 5f electrons in the first-half of actinide series provides a significant f-contribution to the bonding with the neighboring atoms. This behavior leads to a large display of ion oxidation states in the light actinides similar to the d-transition elements, and their electronic properties are strongly influenced by the degree of hybridization. Today, it is well established that atoms and ions of the first-half of the actinide series are in this respect, significantly different from those of lanthanides. A measure of the covalence in the bonding is provided by the so-called "nephelauxetic effect" understood as an expansion of the partly filled f-shell due to hybridization. This effect induces a decrease of the coulomb repulsion between f-electrons in a pair and gives rise to lower effective atomic charges localized on the metallic ions.

In the second-half of the actinide series, the shell contraction due to the increase of the nuclear charge diminishes the spatial extension of the 5f orbitals to form a kind of second rare-earth series with highly localized f-electrons. As a consequence, the heavier actinides all favor a tripositive oxidation state and have similar magnetic behavior to the lanthanides except Ce^{3+}.

Similarities and differences between elements 4f and 5f have brought a steady interest in the studies of their respective electronic structure across both series. Only similarities and differences derived from optical

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spectroscopy in condensed phases will be presented, mainly through $f-d$ and charge transfer (CT) transitions.

2. Optical energy absorption in the f^q-compounds

Within the vacuum UV (VUV) to near-IR energy range, the energy absorption in f-compounds arises from three types of electronic transitions.

2.1. Intra-configuration transitions

Intra-configuration transitions are called $f-f$ transitions and are predominantly electric dipole in nature. They are forbidden to first order by the parity conservation rule but this selection rule is partly relaxed by the admixture of opposite parity configuration states into f^q state wave functions. The mixing is due to the perturbing crystal field (CF) potential. Then, these transitions are called forced electric dipole transitions and they appear on the spectra rather weak and narrow. Allowed magnetic dipole transitions are in general one order of magnitude weaker in intensity.

The energy-level calculations within the f^q configuration in condensed media may be understood in terms of the free ion levels with an additional interaction due to the electrical field generated by the ion environment which removes the J-level degeneracy to give rise to the CF levels. For the free ion-level energy calculation, in order to overcome the difficulty arising from the unknown potential due to the nucleus and the other electrons, a parametric approach is often used. This general theoretical approach separates completely the geometrical and potential aspects of the different interactions experienced by the f-electron considered as individual. The first aspect fully exploits all the symmetry properties in evaluating matrix elements of various operators taking advantages of group theory considerations. The second one treats all the radial dependences as adjustable phenomenological parameters. Following this procedure, electrostatic and magnetic interactions acting on f-electrons in the free ion are described through different Hamiltonians: inter-electronic repulsion, spin–orbit coupling, inter-configuration coupling and higher-order magnetic and electric interactions. For the ion in solid, the CF interaction completes the full Hamiltonian (see, e.g., Ref. [1]). The simultaneous diagonalization of the matrix built on this full Hamiltonian provides the CF level energies. Through a least square procedure, it is possible to adjust all the phenomenological parameters in order to get the best fit between the measured energies and the calculated ones. These parameters and the corresponding Hamiltonians are regrouped in Table 1 borrowed from the famous Carnall report [2]. One can valuably

Table 1
Elements of the parametric Hamiltonian for f^q ions (from Ref. [2])

	Interactions	Hamiltonians	Parameters	Labels	Quantum numbers
Free ion					
Dominant interactions	Core potential	$H_0 = p^2/2m$		Configuration	n, l
	Electronic repulsion, n elec. ≥ 2	$H_{ER} = \sum_{k=0}^{6} f_k F^k$	F^0, F^2, F^4, F^6	Terms	L, S
	Spin–orbit	$H_{SO} = A_{SO}\zeta$	ζ	J-levels	L, S, J
Higher-order interactions	Two-body configuration interaction	$H_{CI} = \alpha L(L+1) + \beta G(G+1) + \gamma G(R7)$	α, β, γ		
	Three-body configuration interaction, n elec. ≥ 3	$H = \sum_k t_k T^k$	T^k $K = 2, 3, 4, 6, 7, 8$		
	Magnetic effect due to configuration interaction	$H = \sum_k p_k P^k$	p_k $K = 2, 4, 6$		
	Spin–spin and other-orbit interactions	$H = \sum_k m_k M^k$	M^k $K = 0, 2, 4$		
Ion in solid	Crystal field interaction	$H_{CF} = \sum_{k,q,i} B_q^k (C_q^k)i$	B_q^k K, q depend on site symmetry	Crystal field levels	μ

notice that these parameters are not totally independent and may absorb a part of different interactions of the same nature, electric or magnetic.

2.2. Inter-configuration transitions

For ions with f^q ground configuration, the inter-configuration transitions promote one f-electron into unoccupied orbitals of higher-lying configurations. In the energy range considered in optical spectroscopy, the transitions generally occur between the nf^q and $nf^{q-1}d$ configurations of opposite parity (examples in Fig. 1). They are called $f-d$ transitions and are orbitally allowed. Consequently, they are much more intense than $f-f$ transitions and because of a strong coupling to the lattice vibrations due to the extended nature of the $5d$ wave function, these electronic transitions give rise to broad bands mainly vibronic in character.

2.3. Ligand to metal charge transfer transitions

CT transitions occur when a valence p-electron of the ligand is transferred toward the unoccupied f- or d-states of the central ion. They are parity allowed and cause, generally in the UV and VUV energy domain, very broad vibronic absorption bands. Following Jørgensen [3], the intensity of electron transfer bands recorded in

4f-complexes is 10–100 times lower than in corresponding d-element complexes because of a smaller overlap integral between 4f-ion and ligand p-orbitals. Accordingly, CT intensity should be higher in early actinides than in 4f-compounds due to the 5f-orbital radial extension.

Generally speaking, electron transfer from the metal to the ligand should also be considered especially in coordination compounds with organic ligands as well as metal-to-metal electron transfer.

3. Charge transfer and $f-d$ transition energy modelling in f-compounds

In the high-energy part of the optical spectra of f-compounds, CT and $f-d$ transitions give rise to strong and large absorption bands. As was shown by Carnall [4] for aquo-actinide ions in perchlorate solution, both kinds of bands may largely overlap (Fig. 2) and their assignment is quite difficult and even impossible without the help of calculation.

3.1. Charge transfer

Many works dealing with solutions and extended to solids have followed the Jørgensen's assignment [5] of the very broad and strong absorption band in the spectra of the trivalent lanthanides to CT transition. CT from the ligand to the central f-ion means electronic transitions from states having mainly a ligand character to f-states localized essentially on the central ion. The energy involved in CT which is associated with a chemical reduction process, depends on several factors:

(i) *The electronegativity of the ligand.* This is illustrated by the changes in CT energy from chloride to iodide in a variety of halide complex systems. Jørgensen [6] showed that this variation correlates well with the Pauling electronegativities and he defined a new concept of optical electronegativity χ_{opt} that connects the CT band energy to the change in χ_{opt} between the different halogens. This concept is very useful to predict the energy of the CT band in systems composed by a given f-ion in different environments [7,8]. The electronegativity of the ligand can be directly related to the ionization potential of the ligand or indirectly to the ability of the valence electrons to be delocalized on the metal.

(ii) *The electron affinity of the f-ion.* The CT process corresponds to a chemical reduction mechanism. It means that the f-ion gains one electron. Then, the spectral position of the CT band is connected with the degree of filling of the f-shell or the electron affinity of the f-ion. For instance, the CT from a given ligand to different f-ions requires less energy
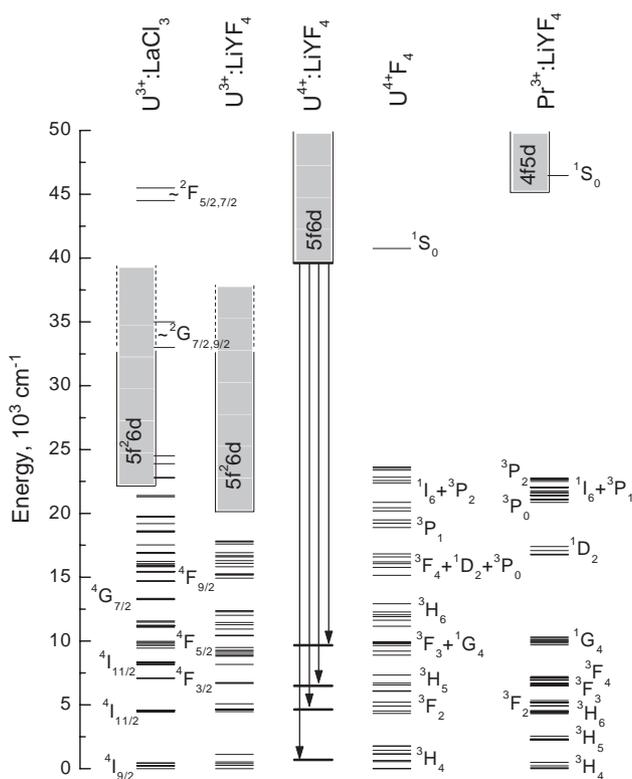

Fig. 1. Energetic localization of the $4f^{n-1}5d$ bands in uranium and praseodymium ions in different solids (from Ref. [17]).
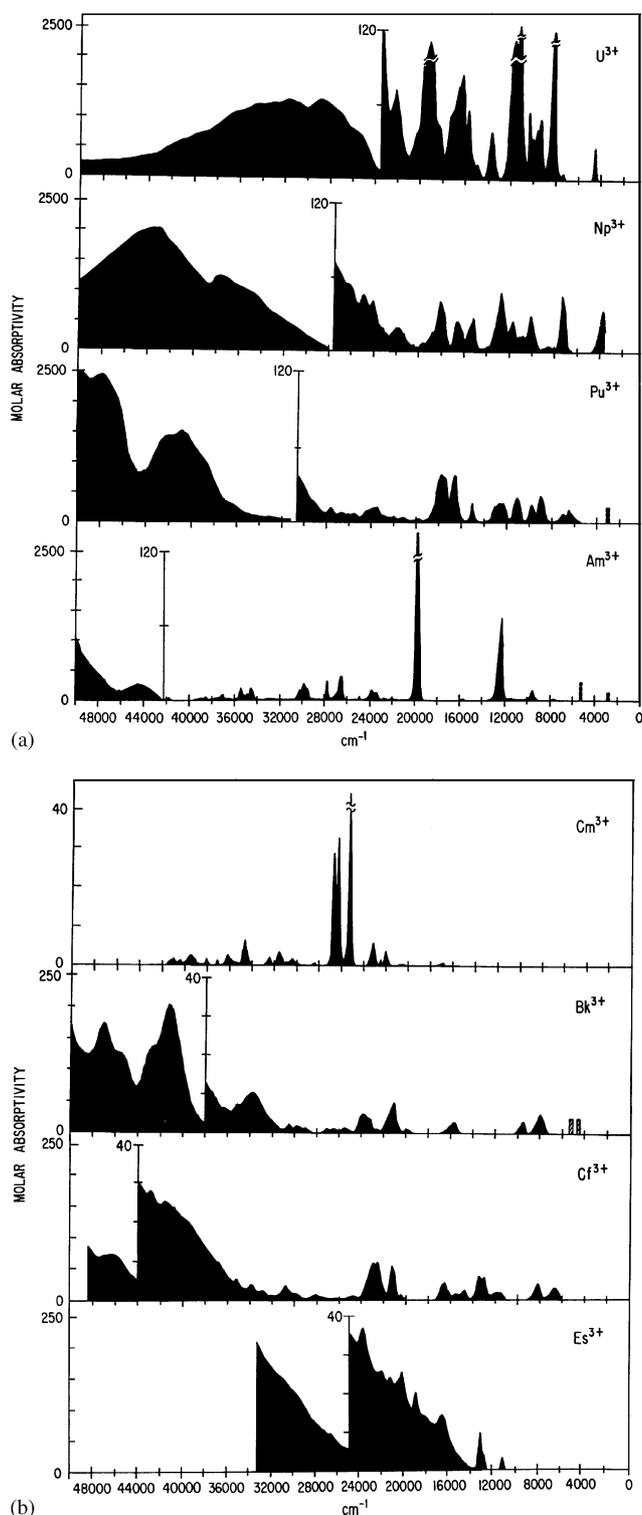
Fig. 2. Absorption spectra of An^{3+} aquo-ions in $HClO_4$ solution (from Ref. [4]). The weak and sharp absorption bands are attributed to 5f–5f transitions and the intense broadbands to CT and $f–d$ transitions (notice the intensity scale change).

(Yb^{3+} and No^{3+}). In other words, the holes or empty states in the f-shell develop a more or less important electric field to attract electrons.

(iii) *The distance between the metallic ion and the ligands or indirectly the coordination number* . In a given system (f-ion + ligand), CT shifts toward higher energy when covalency in the bonding increases or the bond length decreases. In case of purely ionic bonding, it is necessary to spend more energy to remove one electron from the ligand when the distances become shorter. This can be explained as ligand stabilization due to the surrounding positive ions. A smaller cation, which carries a higher charge density, should even induce a more pronounced effect. Therefore, the effective charge of both partners in the electron transfer is the main parameter to take into account as far as the energy of the CT band is considered.

3.2. Inter-configurational transitions: $f^q–f^{q-1}5d$

The $f^q –f^{q-1}5d$ electronic transitions can be related to an oxidation process. Then, the energy of the lowest $f–d$ transition shifts toward lower energy for Ce^{3+} ($4f^1$), Tb^{3+} ($4f^8$) and Pa^{4+} ($5f^1$), Bk^{3+} ($5f^8$), which may easily lose one electron to reach the more stable configurations f^0 and f^7, respectively.

As was already mentioned, CT and $f–d$ transitions are parity-allowed transitions and consequently, they are relatively intense and show a large vibronic character. However, $f–d$ transitions are generally weaker and if they are superimposed on a CT absorption band, they are no longer distinguishable. This is one of the reasons for modelling the CT or $f–d$ energy variation across the f-series using the linearization procedure and the "Spin Pairing Energy Theory" initiated by Griffith [9] for d-elements, developed and refined by Jørgensen for the 4f-elements [10] and extended by Nugent et al. [11,12] to the 5f-series. This simple model expresses the stabilization energy of the ground J-level versus the number of f-electrons by decreasing inter-electronic repulsion and spin–orbit coupling when one f-electron is added or removed from the f^q configuration. Unfortunately, the CF stabilization effect is omitted in this approach. This simplification seems acceptable for the 4f-elements where the CF interaction can be simply considered as a perturbation. But for the 5f-ions, the CF interaction is no longer negligible since its magnitude is as large as the spin–orbit coupling and may change drastically from one environment to another. On the other hand, the CF interaction is very important for the splitting and stabilization of d-levels. Moreover, the modification of the effective oxidation number of the central ion through covalency in the bonding is also ignored in this model. However,

to make complete a half-filled or a more stable fully filled f-shell. This is respectively the case for the configurations nf^6 (Eu^{3+} and Am^{3+}) and nf^{13} ions

such electronic interactions are certainly taken into account through the phenomenological values of the inter-electronic repulsion parameters used in the calculations.

3.3. Spin pairing energy theory

In spite of above-mentioned approximations, Jørgensen's refined spin pairing energy theory has been successfully applied for useful prediction of CT and $f-d$ transition energy in a variety of lanthanide complexes. Extension to 5f-ions developed by Nugent et al. [13,14] has been found efficient for correlations across the actinide series.

Following Nugent et al., the total energy change, ΔE, when an electron is added to a f^q configuration via an electron transfer process to produce the f^{q+1} configuration can be formulated as follows:

$$E_{CT} = \Delta E = W + q(E - A) - \frac{9}{104} N(S)E^1 - M(L)E^3$$
$$- P(S, L, J)\zeta_{nf}, \qquad (1)$$

where W takes into account the f-electrons and core interaction. It would correspond to the energy transfer of an electron from the ligand molecular orbitals to the f-shell, if all electron shielding interactions were perfect, if there was no repulsion among the f-electrons, and if there were no relativistic interactions. $E-A$ reflects the difference between a stronger nuclear attraction E and an increased inter-electronic repulsion A across the f-shell when the nuclear charge Z increases to $Z+1$ ($q(E-A)$ monotonically decreases when q increases). One can notice that more covalent complexes tend toward higher ($E-A$) because of a reduced coulomb repulsion in f-electron pairs. $N(S)\,E^1$ is the ground-state energy stabilization induced by the total spin momentum change between f^q and f^{q+1} configurations. It takes into account the coupling of f-electron spins in the total spin angular momentum S. The first-order Racah parameter E^1 of inter-electronic repulsion is assumed to be the same for both (III) and (IV) oxidation states of the same ion. $M(L)\,E^3$ reflects the ground-state energy stabilization related to the total orbital angular momentum L. It accounts for the difference in inter-electronic repulsion responsible for the configuration degeneracy removal and the term energy and represents energy differences between ground terms, which have the maximum S value. The function $M(L)$ provides the difference between the coefficients of the Racah parameter E^3, describing the ground term in ions of (III) and (IV) oxidation state, respectively. $P(S, L, J)\,\zeta_{nf}$, accounts for the stabilization related to the coupling of spin and orbital angular momentum. J is the total angular momentum and ζ_{nf}, the spin–orbit interaction parameter which varies with the number of f-electrons.

Values for the functions $N(S)$, $M(L)$ and $P(S, L, J)$ versus q are tabulated in Ref. [10]. W and $(E-A)$ are determined for both series by fitting experimental data [15].

Eq. (1) can be used for $f-d$ transitions where one f-electron is removed from the f^q ground configuration to reach the $f^{q-1}d$ excited configuration.

After simplifying well-documented approximations in Ref. [16], one can write the following expressions:

$$E_{CT} = W_{CT} + q(E - A')CT - F_q, \qquad (2)$$

$$E_{fd} = W_{fd} + (q - 1)(E - A')_{fd} - F_{q-1}, \qquad (3)$$

where F_q and F_{q-1} are linearization functions tabulated in Ref. [16].

The results of the energy modelling for the first CT and the lowest $f-d$ transition are plotted in Fig. 3 for LnCl$_6^{3-}$ and AnCl$_3$. Although many approximations are introduced in the refined spin pairing theory, regular trends in the variation of E_{CT} and E_{fd} are obtained for
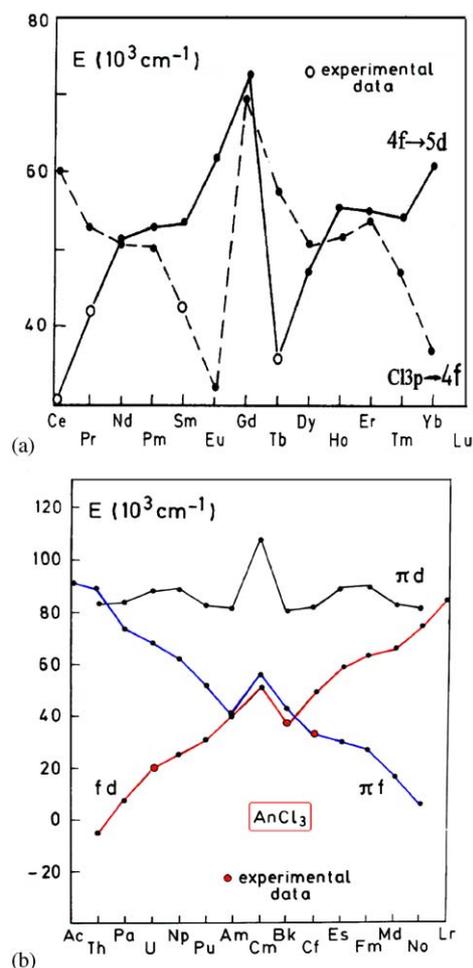

Fig. 3. Variation of Cl3p–4f CT and 4f–5d lowest electronic transition in LnCl$_6^{3-}$ across the tripositive lanthanide ion series. In AnCl$_3$, the energy of Cl3p–6d, Cl3p–5f and 5f–6d transitions is plotted across the tripositive actinide ion series (from Ref. [16]).

both lanthanide and actinide series. This is apparently due to the fitting of W and $(E-A')$ from $\pi-f$ CT and $f-d$ transitions recorded experimentally for some f-ions in the same environment. From these plots, it appears clearly that for the light actinide trichlorides up to $BkCl_3$, the first strong broadband in the absorption spectra is a $f-d$ transition while for $CfCl_3$ and beyond, the first strong absorption feature is a CT band. In addition, E_{CT} and E_{fd} energies have opposite trends at the ends of the series with an important overlapping in the middle, which depends on the nature of the ligands, especially their respective electronegativity. Finally, the half-shell stabilization effect is reduced for the actinides on account of the more extended character of $5f$-orbitals.

4. Conclusion

This article is trying to pay humble homage to two great scientists who recently passed away, C.K. Jørgensen and W.T. Carnall. They played a key role in the development of our understanding of the f-element behavior. It is beyond doubt that without their different personal approaches, this field would have never become so enthusiastic. We are all grateful to them.

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