

Hybridized valence electrons of $4f^{0-14}5d^{0-1}6s^2$: the chemical bonding nature of rare earth elements

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Abstract: The chemical bonding nature of rare earth (RE) elements can be studied by a quantitative analysis of electron domain of an atom. The outer electrons of RE elements are within the valence shell $4f^{0-14}5d^{0-1}6s^2$, which are involved in all chemical bonding features. We in this work found that the chemical bonding characteristics of 4f electrons are a kind of hybridizations, and classified them into three types of chemical bonding of $4f^{0-14}5d^{0-1}6s^2$, furthermore, the coordination number ranging from 2 to 16 could thus be determined. We selected $Y(NO_3)_3$, $La(NO_3)_3$, $Ce(NO_3)_3$, YCl_3 , $LaCl_3$, and $CeCl_3$ as examples to *in-situ* observe their IR spectra of chemical bonding behaviors of Y^{3+} , La^{3+} and Ce^{3+} cations, which could show different chemical bonding modes of 4f and 5d electrons. In the present study, we obtained the direct criterion to confirm whether 4f electrons can participate in chemical bonding, that is, only when the coordination number of RE cations is larger than 9.

Keywords: rare earth; orbital hybridization; coordination number; chemical bonding; 4f electrons

Rare earth (RE) elements include 17 elements of Sc, Y and La–Lu, which are active metals between alkaline metals and transition metals^[1,2]. Transition elements often have an electron configuration that allows them to lose different numbers of electrons from their d sub-shell and so form stable ions with different charges^[3]. Similarly, RE elements are allowed to lose different numbers of electrons from their s, d and f sub-shells^[4-7]. For the case of RE elements, the outer electron domain can be expressed as $4f^{0-14}5d^{0-1}6s^2$ (Table 1)^[8,9]. As the valence electrons, these outer electrons positioned outside the nucleus, can be transferred when atoms react together^[10-12]. Generally speaking, the outer electrons are the only electrons that take part in bonding. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The method to get an atomic orbital with the proper character for bonding is called hybridization^[13,14].

The forces of electrostatic attraction between ions in a compound cause the ions to surround themselves with ions of opposite charge^[15-17]. In chemistry, the term co-

ordination number (CN), defined originally in 1893 by Alfred Werner, is the total number of neighbors of a central atom in a molecule or ion^[18]. In the lattice, CN can be used to express the number of ions that surround a given ion. In coordination chemistry, CN serves as an important parameter to describe the interaction between central cation and ligands. In order to reflect the nature of coordination chemistry, Xu^[19] defines the CN of central cation in coordination compounds or metallorganic compounds as the number of coordination atoms in σ ligands or the number of π electronic pairs provided by π ligands. It is well known that the chemical bonding between central cation and ligands directly depends on the number of coordination atoms in σ ligands or the number of π electronic pairs provided by π ligands. Therefore, the coordination number can well reflect the chemical bonding behaviors of valence electrons within RE atomic orbitals^[20,21]. In forming bonds, atoms must allow the combination of their atomic orbitals to generate hybrid orbitals that have an orientation that matched the geometry of the compound. The mixing of atomic orbitals is known as orbital hybridization^[22,23]. Sometimes it is not necessary for all the valence electron orbitals to hybridize, therefore, the coordination number of RE atoms can have a wide range of 2–16^[24-39].

Understanding the chemical bonding nature of RE elements is essential for uncovering the origin of diverse

Table 1 Basic characteristics of RE elements

Atomic number	Symbol	Valence electron
21	Sc	$3d^1 4s^2$
39	Y	$4d^1 5s^2$
57–71	RE (La–Lu)	$4f^{0-14} 5d^{0-1} 6s^2$

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crystalline architectures, and can help to construct novel RE materials. From a traditional synthetic viewpoint, lanthanides are considered as hard Lewis acid with 4f electrons shielded from the external perturbations by the 5d and 6s shells, therefore, 4f electrons are considered not involved in the chemical bonding. However, some systems (e.g., lanthanide trihalides) have shown pronounced 4f hybridization indicative of covalent bonding interactions^[28,40,41]. Orbital hybridization can determine how many bonds an atom can form and the geometry of molecules. The number of hybrid orbitals formed depends on the number of electrons occupying the outermost orbitals, or the so-called valence shell. Using first principles theory, Strange et al. found that there are two types of f electrons: localized core-like f electrons that determine the valency, and delocalized band-like f electrons that are formed through hybridization with the s-d bands and which participate in bonding^[28]. Later, a pronounced 4f hybridization was found for LuF₃ using three different relativistic methods of calculation, demonstrating the participation of 4f electrons in chemical bonding^[40]. Despite the observation of orbital mixings of Ln(4f) in LuF₃, Wang et al. pointed out that they are not evidences of bonding^[42,43]. In this work, we start from the orbital hybridization to study the chemical bonding characteristics of 4f electrons in RE compounds.

1 Experimental

Ce(NO₃)₃·6H₂O and CeCl₃·7H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification. La(NO₃)₃·6H₂O, Y(NO₃)₃·3H₂O, LaCl₃·7H₂O, and YCl₃·6H₂O were self-synthesized. In a typical synthesis process, by dissolving RE₂O₃ (RE=La, Y) in concentrated HNO₃, La(NO₃)₃·6H₂O and Y(NO₃)₃·3H₂O were respectively crystallized from RE(NO₃)₃ aqueous solutions. Moreover, LaCl₃·7H₂O and YCl₃·6H₂O were obtained by dissolving RE₂O₃ (RE=La, Y) in concentrated HCl, and further crystallizing from RECl₃ aqueous solutions.

Attenuated total reflection infrared (ATR-IR) spectroscopy is a promising technique to record the structural variations of IR-active groups in both liquid and crystalline states taking the advantage of the non-water-soluble internal reflection element^[44,45]. The spectral studies of solution specimens were carried out at 20 °C by ATR-IR technique with ATR cell (Thermo Nexus 6700). Internal reflection element is a diamond wafer. Thermo-Nicolet-Nexus FT-IR spectrometer was utilized to record the IR spectra. The absorption measurements of all samples were conducted using a Nicolet 20DXB FT-IR spectrometer in the spectral range of 4000–525 cm⁻¹. In particular IR measurement, we can directly obtain the ATR-IR spectra of crystalline samples. Moreover, 5 μL RE(NO₃)₃·nH₂O (RE=Y, La, Ce; n=3, 6) and RECl₃·nH₂O

(RE=Y, La, Ce; n=6, 7) aqueous solutions are located onto the diamond wafer, forming the detectable liquid film. Measurements were carried out after aqueous solution dropped on diamond wafer. In the phase transition from liquid to crystalline nitrates, successively IR spectra measurements were carried out to probe the intermediate structures during this process, and the time interval was selected as 50 s.

2 Results and discussion

In previous study of the chemical bonding nature of RE compounds, the bonding in f-element compounds has been described as d sub-shell participation. According to the Pauling approximate energy level diagram and Cotton atomic orbital energy level diagram, it can be found that the 5d and 4f sub-shells have very similar energies. Therefore, those 4f electrons can also go to 5d orbitals like Ce, Gd and Lu, as shown in Table 2. Owing to the similar energies between 5d and 4f sub-shells in RE atoms, the hybridization probability between two types of orbitals is larger. Compared with 4f energy level, the position of 5d energy level is more sensitive to the surrounding crystal field. That is, the position of 5d energy level of RE cations will be modified by selecting different ligands. This will create conditions for orbital overlap between 4f and 5d orbitals, and the f orbitals also have the probability to participate in chemical bonding via hybridization with the other sub-shells in RE atoms, such as 4f, 5d, 6s and 6p.

Orbital hybridization can determine how many bonds an atom can form and the shape of molecules. That is, the coordination number of the central atom in molecule depends on the atomic orbital hybridization. As shown in Table 3, the atom orbital set determines the hybrid orbital set and consequently the chemical bonding type. The chemical bonding types of RE elements with the valence

Table 2 Valence electrons of lanthanide elements

Atomic number	Symbol	Valence electron
57	La	5d ¹ 6s ²
58	Ce	4f ¹ 5d ¹ 6s ²
59	Pr	4f ³ 6s ²
60	Nd	4f ⁴ 6s ²
61	Pm	4f ⁶ 6s ²
62	Sm	4f ⁶ 6s ²
63	Eu	4f ⁷ 6s ²
64	Gd	4f ⁷ 5d ¹ 6s ²
65	Tb	4f ⁹ 6s ²
66	Dy	4f ¹⁰ 6s ²
67	Ho	4f ¹¹ 6s ²
68	Er	4f ¹² 6s ²
69	Tm	4f ¹³ 6s ²
70	Yb	4f ¹⁴ 6s ²
71	Lu	4f ¹⁴ 5d ¹ 6s ²

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