Spin Multiplicities of Luminescent Energy Levels for Rare Earth Ions

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Abstract

We obtain the multiplet energies for several rare earth (RE) ions by *ab initio* molecular orbital calculations including spin-orbit interaction working on $4f$ electrons of RE. Because of a limitation of the ability of computations, the lower lying multiplet energies for Ce^{3+}, Nd^{3+}, Gd^{3+}, Eu^{3+} and Er^{3+} ions are calculated in this report. For the excitations of $4f$ electrons, spin multiplicity for $4f^n$ electrons is not unchangeable (not always $\Delta S = 0$) both in initial and final states by selection rule under spin-orbit interaction. We estimate the possibility of transitions for the multiplet terms for RE ions with use of the obtained electronic spin states in the present case.

1. Introduction

As fluorescent materials, a series of RE ions has been investigated about the luminescence spectra and applied to a light source of instruments by researchers. The sharp luminescence spectra are observed due to the intra-transitions of $4f$ electrons in the $4f$ orbitals because the $4f$ orbitals are shielded by outer $5d$ and $6s$ orbitals and maintain the narrow shape even in an applied electric potential field. RE doped fluorescent materials are utilized in lamps for the suitable feature of presenting naturally coloured spectra and of that the luminescence spectra of RE does not much depend on the host materials and temperature. Multiplet energy structures for REs are constructed by the electronic configurations of $4f^n$ electrons of REs ($n=1 \sim n=13$) and show the complex energy levels in the region of energy in far-infrared and up to near-ultraviolet. Because Coulomb and spin-orbit interactions are working on the $4f$ electrons and the complex multiplet energy structures for a RE ion are generated by these interactions. Thus, it is important to take into account these interactions for obtaining the multiplet energy levels of REs.

The naturally coloured spectra in fluorescent lamps can be realized by the luminescence of REs because the luminescence of activated REs can be colourcoded by the three colours with the sharp spectra of blue, green and red at ~ 22700., 18500. and 16400. (cm^{-1}), respectively, which have been considered to be need for producing naturally coloured luminescence. Eu^{3+} is utilized as red fluorescent activator and Tb^{3+} is done for green fluorescence. For these ions fluorescence spectra can be observed in visible region [1]. The densed multiplet energy levels are lying in farinfrared up to ultra-violet energy region. For the two ions a large gap exists between infrared and visible multiplet energy region by the interactions, relatively. Since the $4f$ orbitals are stable for external effect, the multiplet terms do not much change for the constructions when RE is activated in host compounds. Because of being of use of the sharp spectra, optical device applications of REs to light sources have also been studied. The luminescence wavelength of 1.54μm for the first excited state of Er^{3+} corresponds to that of the least energy loss for optical propagation in optical fiber cable. Nd^{3+} is also frequently investigated because strong luminescence can be observed for the lower lying multiplet terms. In the case of that the REs are incorporated in semiconductors for the device applications, the interested energy levels of luminescence are focused on the infrared region because of existing the energy band gap of host semiconductors in infrared.

The aims of this calculation are, first, to obtain electronic structures of REs of which relatively strong luminescence spectra can be observed, and second, to verify the precision in the present molecular orbital calculation for applying this calculation to further realistic RE doped fluorescent materials. The program package COLMBS at Insutitute of Molecular Science, Okazaki, Japan is used in this calculation.

In the present paper, we report the multiplet energies for some of trivalent lanthanide ions, Ce^{3+}, Nd^{3+}, Gd^{3+}, Eu^{3+} and Er^{3+} by *ab initio* calculations and consider the relationship between the electronic structure and the luminescence. *Ab initio* method for the multiplets of RE performed in [2-4]. This method does not any parametrization and can be used for analysis of electronic structure. Spin multiplicities are related to the possibility of luminescence because the selection rule is established for an atom, i.e. $\Delta S=0$ in electric-dipole and magnetic-dipole transitions, here ΔS is the difference of the spin multiplicities between the ground and excited states. In the case of strong spin-orbit coupling, spin multiplicities may be not be always effective as a character for selection rule. In the present case, different spin multiplicities are mixed in a multiplet energy levels by spin-orbit interactions which is largely working on the $4f$ electrons. By counting the large components of mixed spin multiplicities, we estimate the possibility of transition.

2. Method for calculation

In *ab initio* calculation, the total energy and molecular orbital energy for RE ions are obtained in self-consistent field (SCF) Hartree-Fock calculation and following to SCF the multiplet energies for excitation of $4f$ electrons are obtained. In excited states, all of the intra-excitations in $4f$ orbitals are take into account (Configuration Interaction (CI) method) and spin-orbit interaction is considered. The total angular momentum $J=L+S$ is effective for selection rule under spin-orbit interactions, here L is total orbital angular momentum and S is total spin angular momentum and the multiplet terms are denoted by ${}^{2S+1}L_J$. In the CI method, different spin multiplicities from $2S+1$ in ${}^{2S+1}L_J$ can exist in the multiplet by spin-orbit interactions and the ratio of the mixture in the multiplet is determined due to the strength of spin-orbit coupling with another multiplet terms. For example, the ground state for Er^{3+}, ${}^4I_{\frac{15}{2}}$, are expressed as,

$$\Phi(gr)=C_1\phi({}^4I_{\frac{15}{2}})+C_2\phi({}^2K_{\frac{15}{2}})+C_3\phi({}^2L_{\frac{15}{2}}) \tag{1}$$

where the ground state with $J=\frac{15}{2}$ in the left side consists of a linear combination of the ground (first term) and the excited (following ones) terms with the same J. It is supposed that the component of first term largely exists and furthermore the components for excited states with the spin multiplicities of 2 can also exist in the ground state. We calculated the percentages of the component with spin multiplicities of 4 as C_1^2. The dimensions of matrix to be solved for excited states always exceed ~ 5000 in the present case and it is difficult to obtain the multiplet energies lying in visible or ultraviolet region. Even in the present case, with use of the obtained spin multiplicities for multiplet terms, we discuss about the relationship between the spin multiplicities and the oscillator strength reported in [5,6].

3. Calculated results

The calculated multiplet energies are listed in Table 1 and referenced date are also listed. The results are in good agreement with the reference of calculations [7] and experiments and these agreements can be derived from the expanded $4f$ wavefunctions toward outwards. This effect of expansions for $4f$ wavefunctions can be thought to be a relativistic effect which is pointed out in some papers [4,8]. Experimentally observed data for the trivalent ions are also listed in the table, respectively. The discrepancy may arise from the surrounding crystal field effect of aquo ions.

Spin multiplicities $2S+1$ obtained in the CI calculation for Nd^{3+}, Gd^{3+} and Er^{3+} are specified in Table 2 as well as oscillator strength printed in [5,6]. In Table 2, the percentages of specified "$2S+1$" components which mainly exists in the multiplet term are specified. It can be seen that different spin multiplicities from the specified "$2S+1$" also exist in the $^{2S+1}L_J$ multiplet. For Gd^{3+}, the spin multiplicity for the ground state is largely $2S+1=8$ and another components are much small (96 and 4%), and that for the first excited state is largely $2S+1=6$. Here, the same

Table 1. Multiplet Terms of RE^{3+} (in cm^{-1}).

RE^{3+} Ions.	$^{2S+1}L_J$	Multiplet Energy(cm^{-1})		
		Present Results	Calculation [7]	Experiment [1]
Ce^{3+}	$^2F_{\frac{7}{2}}$	2679.2	–	2300 [a]
	$^2F_{\frac{5}{2}}$	0.0	–	0 [a]
Nd^{3+}	$^4I_{\frac{13}{2}}$	4576.1	4659.	4050 [b]
	$^4I_{\frac{11}{2}}$	2208.0	2243.	2028 [b]
	$^4I_{\frac{9}{2}}$	0.0	0.	146 [b]
Eu^{3+}	$^7F_5$	4652.9	4692.	3909.0 [c]
	$^7F_4$	3401.9	3421.	2877.2 [c]
	$^7F_3$	2238.7	2246.	1882.0 [c]
	$^7F_2$	1229.1	1225.	1044.8 [c]
	$^7F_1$	448.4	441.	380.16 [c]
	$^7F_0$	0.0	0.	0.0 [c]
Gd^{3+}	$^6P_{\frac{5}{2}}$	42996.0	42352.	32780. [d]
	$^6P_{\frac{7}{2}}$	42315.6	41694.	32200. [d]
	$^8S_{\frac{7}{2}}$	0.0	0.	0.0 [d]
Er^{3+}	$^4I_{\frac{13}{2}}$	7126.5	7383.	6485.9 [e]
	$^4I_{\frac{15}{2}}$	0.0	0.	0. [e]

Experimental observations are summarized in a figure of ref. [1]. Listed numerical data of experiments are referred to the following papers, respectively. [a] Reference [1], [b][e] Reference [9], [c] Reference [10] and [d] Reference [11].

Table 2. Spin Multiplicity and Oscillator Strengths.

RE^{3+} Ions.	$^{2S+1}L_J$	$2S+1$	ratio (%)	ΔS	Osc. Str. ($\times 10^6$)
Nd^{3+}	$^4I_{\frac{13}{2}}$	4	99	0	0.71 a)
	$^4I_{\frac{11}{2}}$	4	87	0	–
	$^4I_{\frac{9}{2}}$	4	84	–	–
Gd^{3+}	$^6P_{\frac{5}{2}}$	6	83*)	1	0.041 b)
	$^6P_{\frac{7}{2}}$	6	83*)	1	0.073 b)
	$^8S_{\frac{7}{2}}$	8	96	–	–
Er^{3+}	$^4I_{\frac{13}{2}}$	4	88	0	1.76 a)
	$^4I_{\frac{15}{2}}$	4	84	–	–

*) The component with $2S+1=8$ is 2% at most. a) Reference [5]. b) Reference [6].

ΔS shows the difference of spin multiplicities between the ground and excited states and ratio is that of the component with $2S+1$ in the multiplet. It is noted that different spin multiplicities from "$2S+1$" can be mixed by spin-orbit interaction.

spin multiplicity as that in the ground state of $2S+1=8$ is included only 2% in the first excited state. On the other hand, for Er^{3+}, the spin multiplicity ($2S+1=4$) largely exists both in the ground and first excited state and also can be said for Nd^{3+}. From the Table 2, it can be seen that the oscillator strengths are related to the obtained spin multiplicities. The oscillator strengths for Nd^{3+} and Er^{3+} in which $\Delta S=0$ are much larger than that for Gd^{3+} in which $\Delta S=1$. This agrees with the selection rule of $\Delta S=0$ and shows that selection rule for spin multiplicity is still effective for REs.

The large gap of energy between the ground and the first excited states for Gd^{3+} comes from the electronic configuration of half filling in $4f$ orbitals. For the configuration with the maximum spin multiplicity to be considered for $4f^7$ configurations, Coulomb repulsive energy of $4f$ electrons is weakest. The second excited state I for Nd consists of the spin multiplicity of $2S+1=4$ nearly perfectly though the first excited state $^4I_{\frac{13}{2}}$ for Er^{3+} involves the different spin multiplicity from 4 about 12%. This is because of spin-orbit interaction with the multiplet term with the same total angular momentum $J=\frac{13}{2}$ as that of $^2K_{\frac{13}{2}}$ which exists in near ultraviolet region. This J-J coupling is not effective to the $^4I_{\frac{13}{2}}$ of Nd^{3+} since the effective state with the same J does not exist in the near upper states.

4. Conclusion

The multiplet energy levels for RE ions of which luminescence spectra are observed are calculated with use of *ab initio* molecular orbital calculations. For the lower lying multiplet terms in infrared and ultraviolet range, it is discussed that the multiplet terms with spin multiplicities which satisfy selection rule show strong oscillator strength for the multiplet terms.

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