The spontaneous emission rates of emitter outside and inside of the core-shell nanoparticle

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**Abstract**—Here we present the theoretical study of the emission rate modification of rare-earth ions inside and outside of the subwavelength core-shell nanoparticles.

**Keywords**—spontaneous emission rate; radiative lifetime; rare-earth ions; core-shell nanoparticles; size confinement.

Over the past decades, the dynamics of localized excited states in doped nanoparticles has fashioned rapid expansion of interest from both fundamental physics and practical applications. Among them, rare-earth (RE) doped nanoparticles (NPs) have attracted many researchers [1-3]. RE-doped luminescent nanoparticles (NPs) possess superior physicochemical features and are regarded as a new generation of biosensors. These functional NPs have stimulated the growing interests in the deep insights of their spectroscopic properties coupled with their biomedical applications in diverse fields such as biodetection, disease diagnosis, and therapeutics [2,3]. The RE ions have so called hypersensitive transitions, which are very sensitive with respect to the field of neighboring ligands. The hypersensitive nature of certain electron transitions of RE ions is known for a long time [4-6]. This peculiarity make these ions especially prospective tool to use as a sensitive reporter of the local properties of the medium – the task which nowadays becomes more and more important, e.g. in biophysical and biochemical researches. In Ref. [5], Judd has analyzed the earlier proposed so called inhomogeneous dielectric and dynamic coupling mechanisms of the hypersensitivity, demonstrated their equivalency and gave clear physical interpretation of the phenomenon. Most importantly, he showed that the ligand field effect on the corresponding radiation transition rate amounts to the following increase of an electric dipole moment of the RE ion:

\[ \Delta D = e \sum_{s,a} \alpha_s \rho_{sa} / \rho_{s0}^2 \]

where \( e \) is an elementary charge; \( \gamma_s \) – the polarizability of \( s \)-th ligand supposing the isotropic polarization, and \( \rho_{sa} \) - the vector connecting \( s \)-th ligand with \( a \)-th electron of the RE ion. In light of the quite known circumstance that in the frame of an electrostatic approximation, a spherical nanoparticle, subject to incoming plane electromagetic wave, creates an additional field equivalent to an electric dipole field, a similarity of this problem to the hypersensitive transition problem considered by Judd becomes quite evident. Taking into account such a similarity and allowing for the specificity of \( 4f \) states, we have determined the following Judd – Ofelt intensity parameter for RE ion resident near spherical coated NP or inside of shell:

\[ \Omega_2 = (28/15) \left| \alpha_s \right|^2 \langle \xi^2 \rangle^2 \gamma_s^2 r^{8-2} \quad (1) \]

Here \( \langle \xi^2 \rangle \) is the mean square 4f-electron radius averaged over the 4f wave function; \( r \) is distance between RE ion and center of NP. \( \alpha_s \) is the polarizability of NP core if RE ion placed inside of NP shell and the polarizability of whole NP if RE ion placed outside of NP. According to Judd-Ofelt theory, the rate of radiative electrical dipole intermultiplet \( J \rightarrow J' \) transition is proportional to the line strength

\[ S(J,J') = \sum_{k=2,4,6} \Omega_k \left| J \right| \left| U^{(k)} \right| \left| J' \right|^2. \]

Hypersensitive transitions are characterized by large values of the square of reduced matrix elements and Eq. (1) readily enables to estimate the enhancement of hypersensitive transitions of RE ions caused by an optical near field of nanoobjects.

**References**


