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Experimental and *Ab Initio* study on the intensities of f-f transitions for the molecular Eu(III)-DOTP system.

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Streszczenie

The experimental f-f transition intensities, derived from UV-vis absorption and emission spectra of Eu(III)-DOTP systems (where DOTP is 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayl)tetrakis-(methylene))-tetraphosphonate anion) in $[C(NH_2)_3]_5[Eu(DOTP)]\cdot 12.5H_2O$ and $K_5[Eu(DOTP)]\cdot 11H_2O$ crystals and in solution, were analyzed in terms of Judd-Ofelt theory. A non standard approach was used to calculate Ω_λ parameters by including both the absorption $^7F_0 \rightarrow {}^{2S+1}L_J$ and emission $^5D_0 \rightarrow {}^7F_J$ bands in the calculation procedure. The f-f transition intensities of two $\{K_4[Eu(DOTP)]\}^-$ clusters representing the two different forms of Eu(III)-DOTP complex in $K_5[Eu(DOTP)]\cdot 11H_2O$ crystal, calculated within *ab initio* approach were compared with the experimental counterparts. The theoretical results provided a deeper insight into the nature of the hypersensitive and highly-forbidden f-f transitions for system under study. The possible improvements of the theoretical approach are discussed in the light of the known mechanisms contributing to the intensities of f-f transitions. Finally the solution structure of the $[Eu(DOTP)]^{5-}$ complex was examined by complementary techniques including temperature dependent UV-vis absorption and time-resolved emission spectroscopy. This enabled us to show that the structure of the $[Eu(DOTP)]^{5-}$ complex in solution is practically the same as those in crystals. In particular it means that there are no water molecules coordinated to the central Eu(III) cation. The observed decrease of luminescence integral intensities of the $^5D_0 \rightarrow {}^7F_J$ bands at elevated temperatures of solution, usually assigned to a chemical reaction, is brought about actually by the changes of solution viscosity.

Słowa kluczowe

ab initio calculations, DOTP, Eu(III), f-f transitions, UV-vis

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