Unraveling the ground state and excited state structures and dynamics of hydrated Ce^{3+} ions by experiment and theory.

Autorzy

Patric Lindqvist-Reis

Florent Réal

Rafał Janicki

Valérie Vallet

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Streszczenie

The 4f-5d transition of Ce^{3+} provides favorable optical spectroscopic properties such as high sensitivity and quantum yield, making it a most important dopant for lanthanide-activated phosphors. A key for the design of these materials with fine-tuned color emission is a fundamental understanding of the Ce^{3+} ground state and excited state structures and the dynamics of energy transfer. Such data is also crucial for deriving coordination chemistry information on Ce^{3+} ions in different chemical environments directly from their optical spectra. Here, by combining 4f-5d absorption and luminescence spectroscopy and highly accurate quantum chemical electronic structure calculations, we study the interplay between the local structure of Ce^{3+} in aqueous solutions and in crystalline hydrates, the strengths of Ce–O/Cl interactions with aqua and chloride ligands, and the resulting absorption and luminescence spectra. Experimental and theoretical absorption spectra of $[Ce(H_2O)_9]^{3+}$ and $[Ce(H_2O)_8]^{3+}$ with defined geometries provide a means for analyzing the equilibrium between these species in aqueous solution as a function of temperature (K(298) = 0.20 ± 0.03), while analyses of spectra of different aqua-chloro complexes reveal that eight-coordinate aqua-chloro complexes are present in solution at high chloride concentration. An intriguing feature in these systems concerns the large observed Stokes shifts, 5500–10100 cm^{-1}. By exploring the excited state potential energy surfaces with relativistic multireference calculations, we show that these shifts result from significant geometrical relaxation processes in the lowest $5d^1$ excited state. For $[*Ce(H_2O)_8]^{3+}$ the relaxation gives shorter Ce–O bonds and a Stokes shift of ∼5500 cm^{-1}, while for $[*Ce(H_2O)_9]^{3+}$ the lowest $5d^1$ state results in a spontaneous dissociation of a water molecule and a Stokes shift of ∼10100 cm^{-1}. These findings are important for the understanding and optimization of luminescence properties of cerium complexes.

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