

XEOL SPECTROSCOPY OF Tb^{3+} IN AQUEOUS SOLUTION

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X-ray spectroscopy probes the local structure of the absorbing atom. Thus, it can provide information about the chemical bonding in highly disordered systems, including liquids. As part of a study of the electronic interactions between solute ions and water molecules a method for XEOL (x-ray excitation optical luminescence) analysis of aqueous solutions was developed at the DCM beamline of CSRF, and tested with a series of solutions containing Tb^{3+} . The samples were contained in a sample holder for liquids with a 3 μm Mylar window separating them from the vacuum ($\leq 2.5 \times 10^{-6}$ torr) in the solid-state absorption chamber of the DCM beamline.

Terbium, a rare-earth element, has four intense and narrow luminescence peaks between 450 and 650 nm. These peaks result from radiative $^5D_4 \rightarrow ^7F_{0,1,2,3}$ de-excitation transitions involving electrons in the 4f orbitals. They are well separated from the luminescence peak of the Mylar window between 300 and 425 nm (Figure 1). Thus, it is possible to extract the luminescence of the Tb^{3+} ion from the measured XEOL spectrum of the solution and the window.

The intensity of the Tb^{3+} luminescence peaks was lower for the solutions than for solid $TbCl_3 \cdot 6H_2O$. In part, this was caused by the lower Tb^{3+} concentration in the solutions (6×10^{20} Tb atoms/cm³ for the most concentrated solution studied, ~ 1.0 M $TbCl_3$) than in the solid (7×10^{21} Tb atoms/cm³). In addition, the solvent (water) acts as a quencher. The disorder and the molecular motion in the solution increase the availability of non-radiative de-excitation pathways. Finally, some of the luminescence photons are absorbed by the solvent and by the window, further reducing the intensity of the detected peaks. Thus, the luminescence was only detected for solutions with $[Tb^{3+}] \geq 0.125$ M. The ability of other ions to act as enhancers or quenchers of the luminescence was also investigated. High concentrations of Cl^- , SO_4^{2-} , $S_2O_3^{2-}$ and NH_4^+ in the solution all enhanced the Tb^{3+} luminescence, probably by inhibiting some non-radiative de-excitation pathways.

Figure 1: The XEOL spectrum of 1.0 M $TbCl_3$

