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Spectroscopy of Holmium Glasses

N. SPECTOR

Soreq Center, Yavne 70600, Israel

R. REISFELD*, G. KATZ and E. GREENBERG

Department of Inorganic and Analytic Chemistry, The Hebrew University, Jerusalem 91904, Israel

The electronic energy levels of holmium in fluoride glasses of the composition $57ZrF_4 \cdot 36BaF_2 \cdot 3LaF_3 \cdot 4AlF_3 \cdot 4AlF_3$ were calculated by the diagonalization of the energy matrices of the $4f^{10}$ configuration including electrostatic and spin–orbit interactions as well as the α (Trees) β and γ (Casimir operator) corrections.

The observed spectra of holmium in these glasses were fitted by least-squares calculations to the 7 radial parameters involved to obtain the latter's best values.

The resulting intermediate coupling eigenvectors were used for the calculation of the squares of the reduced matrix elements between any pair of energy levels, thus giving the spectroscopic characteristics of the transitions in the energy range between 5000 and 25000 cm^{-1}.

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*Enrique Berman Professor of Solar Energy.

B16

Photophysical and Photochemical Properties of Europium Cryptates

N. SABBATINI*, M. CIANO, S. DELLONTE, A. BONAZZI and V. BALZANI

Istituto Chimico 'G. Ciamician' dell'Università, Bologna, Italy and Istituto di Fotochimica e Radiazoni d'Alta Energia del CNR, Bologna, Italy

Several diazapolyoxabicyclic ligands ('cryptands') [1, 2] are able to encapsulate metal ions to form coordination compounds ('cryptates') which have been the object of extensive thermodynamic, kinetic, structural, electrochemical, and analytical investigations [2–12]. By contrast, only a few studies [12–14] have been reported on the electronic absorption and emission spectra of these compounds because both the cryptands and, in most cases, the encapsulated metal ions are spectroscopically 'mute' species. The spectroscopic behavior of rare earth complexes is a topic of great interest, both theoretical [15–17] and applicative [18–20]. We have thus begun spectroscopic studies on cryptates containing europium or other rare earth ions.

The spectroscopic and photophysical properties of the complexes between En^{2+} and the 2.2.1 and 2.2.2 cryptands are reported and compared to those of the Eu^{2+} aquo ion. Both complexes show broad, relatively intense absorption bands in the near u.v. region due to $4f^7 \rightarrow 4f^6 5d$ transitions. Some weak narrow bands due to transitions within the $4f^7$ configuration also appear in the 310–320 nm region. Both complexes exhibit a strong blue luminescence from $4f^6$. At 77 K the emission quantum yield is unity, and some vibrational structure can be observed in the broad emission band. Luminescence is also maintained in aqueous solution at room temperature with τ of the order of a few nanoseconds, and ϕ of the order of 10^{-3}, in contrast with the behavior of the Eu^{2+}_{aq} ion which does not exhibit any luminescence emission under such conditions. The results obtained are discussed in the light of the interaction between Eu^{2+} and water molecules and of the size and symmetry of the cryptand cage.

The spectroscopic and photophysical properties of the Eu^{3+} complex of the 2.2.1 cryptand are investigated in aqueous solution. The absorption spectrum of the complex, besides the f → f transition of the Eu^{3+} ion, shows two broad bands at 298 and 248 nm (ϵ, 111 and 93, respectively) which are assigned as charge transfer transitions from N and, respectively, O atoms of the ligands to Eu^{3+}. High resolution emission spectra show that in aqueous solution there is only one Eu-containing species with C_{2v} symmetry. The emission quantum yield is 3×10^{-2} upon excitation at 393 nm in the $^5L_6$ metal centered band and 3×10^{-3} and 1×10^{-3} upon excitation in the charge transfer bands at 350 nm and 260 nm, showing that the conversion of the charge transfer levels to the $^5D_0$ emitting state is relatively inefficient. Luminescence decay measurements in H_2O and D_2O solutions and comparison with the data obtained for Eu^{3+}_{aq} show that encapsulation of Eu^{3+} in the cryptand cage does not shield the metal ion towards interaction with solvent since three water molecules are still coordinated to Eu^{3+} through the cryptand holes.

The emission of [Eu^{3+} C 2.2.1] is quenched by $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, $Mo(CN)_8^{4-}$ with $K_q = 6.4 \times 10^8$, 1.9×10^8, 1.2×10^9 l mol^{-1} sec^{-1}, respectively. The quenching takes place via charge-transfer interaction, as shown by the appearance of a new absorption band in the visible region for solutions containing the cryptate and the quencher. Spectrophotometric and electrochemical analysis show that 1:1 complexes are formed with stability constants of the order of 10^2 l mol^{-1}.

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Dependence of the $^5D_0$ → $^5D_1$ Fluorescence Dynamics *Versus* the Optical Pumping Frequency in Sm^{2+}:BaClF

J. C. GÂCON*, M. F. JOUBERT and B. JACQUIER

E.R.A. 1003 C.N.R.S. et Université Lyon I, 43, Bd. du 11 Novembre 1918, 69622 Villeurbanne, France

Very recently, the role of the $^5D_0 \rightarrow {^5D_1}$ upwards radiationless transition in the de-excitation mechanisms of the Sm^{2+} ion in BaClF at temperatures ranging from 295 to 650 K was clearly established [1]. Using selective pulsed laser excitation into the first metastable excited state $^5D_0$ (14533 cm^{-1}), the fluorescence of the $^5D_1$ multiplet located at 1339 cm^{-1} above $^5D_0$ was detected. Both $^5D_1$ and $^5D_0$ fluorescence at long times after the laser pulse were observed to decay exponentially with the same time constant (~1.5 ms at room temperature) characteristic of the $^5D_0$ lifetime in this material, as shown in Figs. 1a) and b). This experiment confirms that a thermalization process between levels $^5D_0$ and $^5D_1$ takes place in this system, as observed 16 years ago using an ultraviolet excitation promoting the Sm^{2+} ion up to $4f^5$-5d states [2, 3]. Surprisingly enough, the $^5D_0$ and $^5D_1$ fluorescence decays under excitation into the $^5D_1$ level do not bear evidence of such a thermalization process, as shown in Figs. 1c) and d), the $^5D_1$ fluorescence being observed to decay exponentially with a time constant equal to the intrinsic $^5D_1$ lifetime (~150 μs at room temperature). Moreover, all the measurements we performed in previous works pumping the system either in the $^5D_1$ or $^5D_2$ level were found to be consistent with the assumption that the $^5D_0 \rightarrow {^5D_1}$ radiationless transition did not contribute signi-

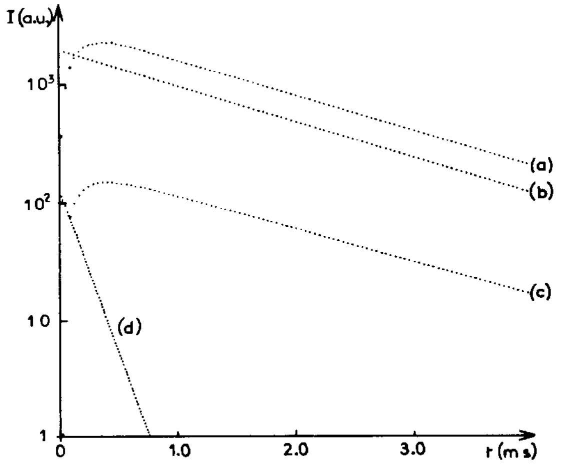

Fig 1. Fitted decay-curves of the $^5D_0$ (b, c) and $^5D_1$ (a, d) fluorescences under selective excitation into the $^5D_0$ (a, b) and $^5D_1$ (c, d) levels.