

intensities over a 3-fold range without suffering severe optical problems. Chemical actinometers and a thermopile system were used to monitor beam intensity.

With a columnated laser beam we found the formation of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ to be the predominant photochemical process with ϕ_{aq} ca. 5×10^{-3} and $\phi_{\text{aq}}/\phi_{\text{redox}} > 10^2$, consistent with 365 nm photolyses at lower intensities.⁴ When the laser beam was focused so that the beam waist was approximately 0.5 mm \times 2 mm, inside, and toward the front face of the photolysis cell, the ratio of aquation to redox yields was reversed with the redox yield approaching 10^{-2} and the aquation yield being nearly unchanged. In twenty four experiments using the focused beam, the redox yield was found to decrease dramatically with beam intensity; $\log \phi_{\text{redox}} = (2.0 \pm 0.2) \log I_{\text{a}} + \text{const.}$ (I_{a} = intensity of absorbed radiation).

Since 337 nm is near the absorption maximum of the ${}^1T_{2g}$ band of $\text{Co}(\text{NH}_3)_6^{3+}$, the laser photolyses may be described as in the Scheme. LF represents the implicated ligand-field excited state (or states). Clearly the ligand-field excited states must have lifetimes comparable to or greater than the laser pulse (*i.e.*, $\geq 10^{-9}$ s). If (1) has an absorption coefficient comparable to that of ${}^1A_{1g} \rightarrow \text{CT}$ transitions, then a kinetic treatment implies that the *LF lifetime would be of the order of 10^{-8} s. In addition to providing clear evidence that ligand-field excited states of $\text{Co}(\text{NH}_3)_6^{3+}$ have finite, if short, lifetimes, these studies demonstrate at least for $\text{Co}(\text{NH}_3)_6^{3+}$ that the photoaquation and photoredox modes are uncoupled.

We thank the National Science Foundation for support.

(Received, 26th September 1974; Com. 1213.)

¹ V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds,' Academic Press, New York, 1970.

² P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1973, **95**, 2470.

³ N. A. P. Kane-Maguire and C. H. Langford, *J.C.S. Chem. Comm.*, 1974, 351.

⁴ M. F. Manfrin, G. Varani, L. Moggi, and V. Balzani, *Mol. Photochem.*, 1969, **1**, 387.