Application of the three-level model: Rise and decay kinetics of the temperature-dependent emission of metal ions with s^2 -valence electron configuration

M DIEHL*, J DEGEN and H H SCHMIDTKE

Institut für Theoretische Chemie, Heinrich-Heine Universität Düsseldorf, Universitäts
Strasse 1, D-40225 Düsseldorf, Germany

Abstract. Temperature-dependent rise time and lifetime results, by measuring the photon emission in the temperature range 10–200 K, were obtained on *cis*-(NEt₄)₂[TeCl₄Br₂]²⁻ (*C*_{2v}) and [SeCl₆]²⁻ (*O_h*). The kinetics of excitation and relaxation are described by a three-level model containing transition rate constants which are related to different symmetry selection rules between corresponding electronic levels. The transient emission can be modified by varying the excitation pulse length. Besides a slow component in the luminescence decay-curve (0.5 ms at *T* = 12 K) a second, faster component can be detected. The amplitude ratio of these components can be increased by decreasing the excitation pulse length, which can be explained by assuming non-thermally equilibrated excited states. The results allow the assignment of the lowest levels which arise from the excited *sp* electron configuration of the central ion.

Keywords. Three-level model; temperature-dependent emission of metal ions; s^2 -valence electrons.

1. Introduction

The three-level system is well established to explain kinetic experiments (Stepanov 1968). For the general case, the nomenclature and a schematic diagram are given in figure 1, Γ_i denote terms of the s^2 and sp configuration. The solution for the corresponding rate equations is

$$n_i(t) = \sum_{j=1}^2 A_{ij} \exp(-t/\tau_j) + A_{i,3}, \quad i = 0, 1, 2. \quad (1)$$

A thorough treatment of the three-level system can be found in the book of Stepanov (1968), hence, no further details are given here. In this work, the model is applied to the interaction between electronically excited states and the ground state of metal complexes with s^2 -electron configuration of the central ion. The limitation of the model lies in the number of parameters (k_{ij}) which are necessary to describe the system completely. In the description of transient luminescence a total number of six rate constants are involved. There is even an unsteadiness in the two rates k_{01} and k_{02} if the whole process of excitation and relaxation is to be described. Every rate

*For correspondence

Figure 1. Three level system.

constant consists of two contributions, a radiative and a nonradiative part. Despite the fact that the magnitude of some of the rate constants can be estimated sufficiently well, e.g. there is no nonradiative excitation from the ground state and no radiative interaction between the excited states, there is still a discussion going on, on how to assign some rate constants found from kinetic experiments to the transitions in the examined systems (Hughes and Pells 1975; Meidenbauer and Gliemann 1988; Donker *et al* 1989a). There are many papers dealing with the application of the three-level model to systems with s^2 electron configuration and the energy difference ΔE between the lowest excited states (Degen and Schmidtke 1989; Donker *et al* 1989a; Schmidtke *et al* 1992). In order to be able to apply the three-level model, one has to make assumptions on these rate constants. It is common to assume that the rates which connect the two excited states are related by the Boltzmann factor as

$$k_{12} = k_{21} \exp(-\Delta E/kT). \quad (2)$$

This is reasonable because of the small energy difference (in the magnitude of some 100 cm^{-1}) and since there are only nonradiative contributions to these rates. On the other rate constants, there exist different opinions, especially whether the largest rate which can be determined from time-dependent lifetime measurements must be assigned to a radiationless deactivation (k_{20}) or is the Boltzmann rate (k_{21}). The value of ΔE , estimated from the experiment, seems to be relatively independent from the assumption for the rate constants (Meidenbauer and Gliemann 1988; Donker *et al* 1989a; Degen *et al* 1993).

2. Experimental

Excitation is achieved by an argon-ion laser (Spectra Physics 2016, 457.5 nm line), the plasma light is removed with a LASERSpek III monochromator. The cw-beam is modulated by an optoacoustic modulator (Matsushita EFC-C200-P11). The pulse/pause ratio can be adjusted in a wide range, the maximum frequency with this setup is 10 MHz. Cooling of the sample is performed with a Leybold Heraeus R 219 closed-cycle cryostat (minimum temperature 12 K). The transient detection of the luminescence is done via standard single photon counting equipment which is described elsewhere (Schmidtke *et al* 1992). Sample preparation for the Te(IV)-compound is precipitation

with SnCl_4 under inert gas conditions resulting in doped crystals with 1% Te (Schmidtke *et al* 1992). The Cs_2SeCl_6 samples are used undoped (Degen and Schmidtke 1989).

3. Results

We examine the transient luminescence of $\text{cis-}[\text{TeCl}_4\text{Br}_2]^{2-}$ (C_{2v}) and $[\text{SeCl}_6]^{2-}$ (O_h). The shortest excitation pulse length applied is 100 ns. The longest pulse width is several milliseconds. Upon excitation with pulse widths in the order of 100 μs , both systems respond with a single exponential [$\propto 1 - \exp(-t/\tau)$ for the rise and $\propto \exp(-t/\tau)$ for the decay]. The interpretation of the time dependencies is described elsewhere (Degen and Schmidtke 1989; Donker *et al* 1989b; Schmidtke *et al* 1992; Degen *et al* 1993). If the excitation pulse length is decreased, the response changes to a transient luminescence which can no longer be fitted to a single exponential. Figure 2 shows the response of $\text{cis-}[\text{TeCl}_4\text{Br}_2]^{2-}$ to a 1- μs excitation pulse. It can be seen that two exponentials are necessary to fit the observed transient. The fast component is governed by the rise time of the excitation pulse which is of the order of 20 ns. By decreasing the width of the excitation pulse, the amplitude of the fast component is increased. This can be shown in a quantitative manner for the Se-compound (Degen *et al* 1993).

4. Discussion

With excitation pulse-width dependent lifetime measurements additional information about the rate constants in Ti^+ -like systems can be obtained. Since the observed pulse width dependencies exist, the Boltzmann-related rates (k_{12} and k_{21}) cannot be

Figure 2. Transient luminescence of $\text{cis-}(\text{NEt}_4)_2\text{TeCl}_4\text{Br}_2$ at $15,500\text{ cm}^{-1}$ under excitation with a 1- μs laser pulse ($\lambda_{\text{ex}} = 457.5\text{ nm}$).

the rates with the greatest magnitude because thermal equilibrium would be expected even shortly (some 10 ns) after application of the excitation pulse. It can be concluded that the depopulating rate k_{20} corresponds to the observed fast decay constant. This is consistent with the dominant transition rate for $\Gamma_4 \rightarrow \Gamma_1$ (Se-compound, O_h symmetry), as deduced from selection rules (Degen and Schmidtke 1989; Donker *et al* 1989b) for molecular transitions.

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