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Analytic Solution to a Three-Level Optical Pumping System with Constant Coefficients

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Abstract

In the process of developing a new senior-level laboratory experience in atomic phosphorescence, a lack of consistency has been noted in the literature[1,2,3] for the room-temperature radiative lifetime associated with the emission of the R-lines of Cr^{3+} in ruby. Much of the existing work on the metastable ^2E term that gives rise to the R-lines focuses on the fluorescence decay of these lines. Here the excitation of the metastable population as a function of time is investigated to supplement an understanding of these radiative transitions. In an attempt to identify an appropriate parent population for the metastable terms during the excitation phase, the dynamical system is approximated as three-energy levels in Cr^{3+} in ruby: a ground state, a "pump" excited state, and a metastable state. Assuming a constant optical pumping rate and natural decay rates for the pump and metastable energy levels, three coupled first-order, linear, differential equations have been deduced for the observed population dynamics for the three states in response to optical excitation. The analytical and numerical solutions of these equations are presented here with preliminary comparisons to experimental data for the radiative excitation and de-excitation of the metastable levels in Cr^{3+} in Ruby.

Keywords: Ruby phosphorescence, Cr^{3+} **rate equations, Solution to three-coupled first-order, linear, rate differential equations.**

1. Introduction

Ruby consists of sapphire (Al_2O_3) which has been doped with chromium ions, Cr^{3+}. For consistency with the more recent published work[3] for the room-temperature fluorescence lifetime of the ^2E levels in ruby, industrial ruby samples were obtained with a manufacturer-indicated Cr^{3+} concentration of ~ 2%. Atomic phosphorescence of Cr^{3+} in ruby has been widely studied in the past[1,2,3,4], and references therein. Moreover, unpublished senior-level laboratory experiences to measure the fluorescence lifetime of the ^2E metastable term of Cr^{3+} are in place at a few universities, e.g.[5,6]; some of which list an accepted lifetime of 3.6 ms. As we developed our version of this laboratory experience, we found a significant discrepancy relative to one of the more recent pedagogical reports in the literature. In that work[3] a single lifetime (4.268 ± 0.006 ms) was reported for the two ^2E metastable levels. Our present result for the ^2E lifetime is most consistent with that of Nelson and Sturge[2].

Our phosphorescence data (Figure 1) for the radiative decay of the ^2E terms indicates that a single exponentially decaying population is not an appropriate parent population for the observed data.

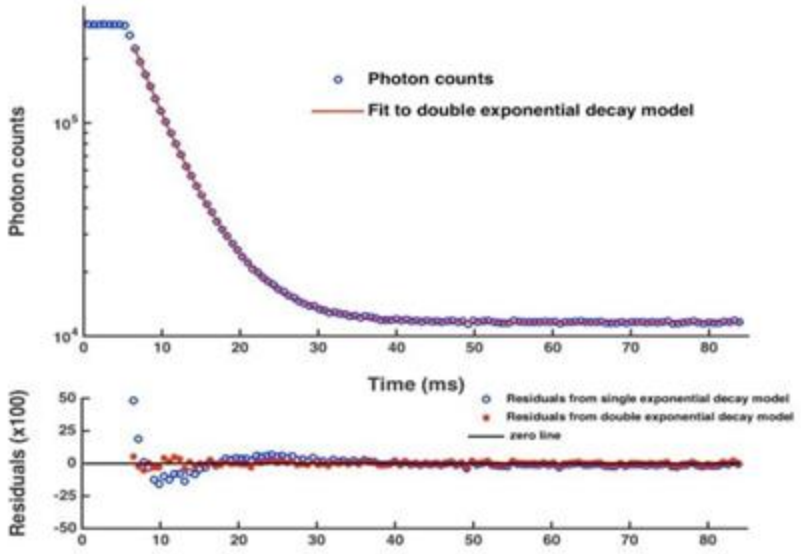

Figure 1. Photon counts and residuals of single-and double-exponential decay model fits to the data versus time.

There are two possible causes for the deviation of the data from single-exponential behavior: 1) the absorption and reemission of ~ 692.8 and 694.2 nm photons within the ruby, or 2) there are slightly different lifetimes for the two ^2E terms in Cr^{3+}; which give rise to the R-lines at 692.8 and 694.2 nm. Figure 2 shows an R-line emission spectrum with the remaining 543-nm optical-pump source during excitation. In order to help identify the correct parent population, the optically-pumped excitation dynamics of Cr^{3+} in ruby have been theoretically and numerically explored in this work. Preliminary comparisons with experimental results are also presented.

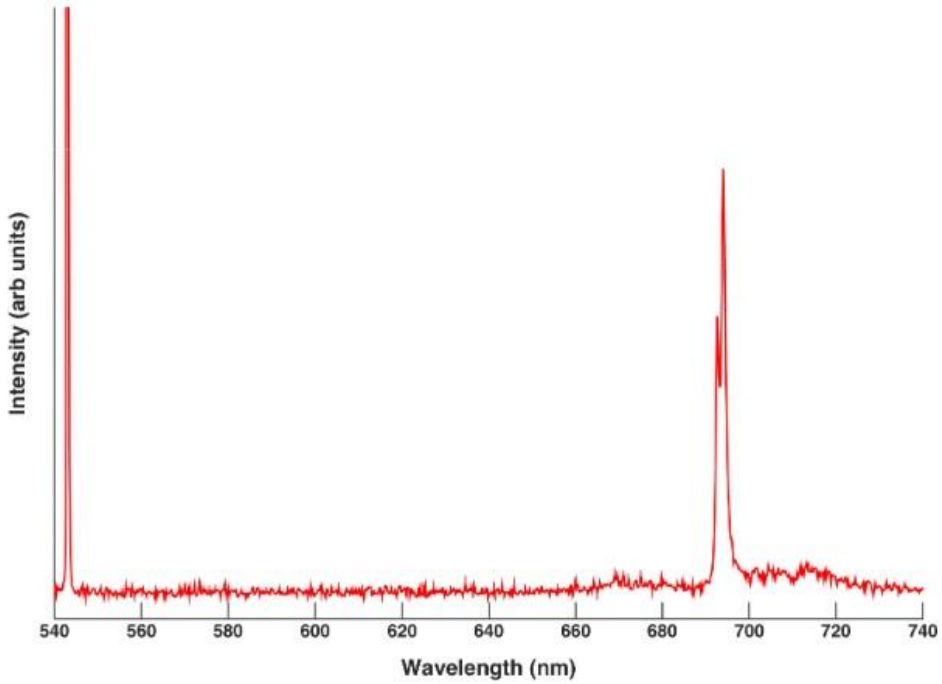

Figure 2. Emission spectra showing the closely-spaced R-lines of ruby at 692.8 and 694.2 nm. The 543-nm excitation pulse from a HeNe laser is also shown in this spectrum.

2. Optical Excitation Theory & Approximations

Figure 3 illustrates an energy-level diagram (not to scale) for the crystal-field split energy levels of Cr^{3+} in ruby. The ^2E metastable levels are populated by optically pumping the $^4T_1$ or $^4T_2$ levels with ~ 410- or 543-nm photons, respectively. The ^4T levels rapidly decay to the ^2E levels via radiationless transitions and subsequently emit photons at 692.8 and 694.2 nm as the ^2E levels transition to the $^4A_2$ ground term of Cr^{3+}. In the following mathematical model, the subscripts *g*, *e*, and *m* denote the Ground, Excited, and Metastable populations, respectively.

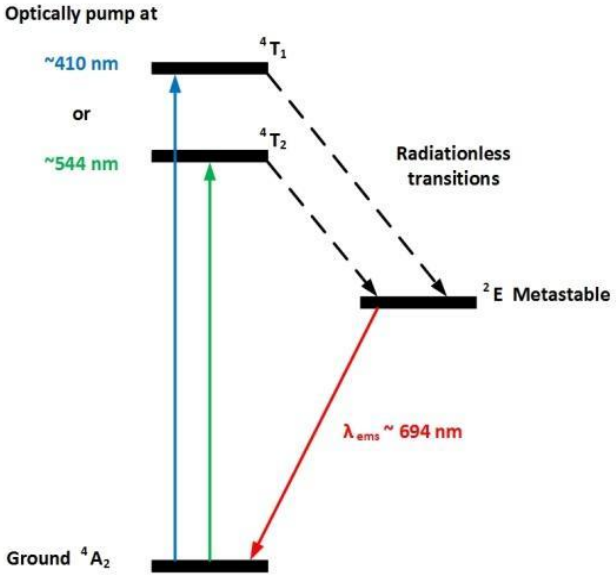

Figure 3. The approximate energy-level structure and the relevant transitions. Near-UV- , Green-output LEDs, or a 543-nm HeNe laser were used for the optical pumping of the $^4T_{1,2}$ excited states.

During the absorption and excitation phase of the experiment, a constant optical pump rate, Γ, is assumed. The radiationless transitions from either of the ^4T levels occur at γ_n and the radiative decay rate from the ^2E levels is γ. Both γ_n and γ are also constants with $\gamma_n >> \gamma$. With these parameters the rate equations for the populations of the ground state, N_g , excited state, N_e , and the metastable levels, N_m , as functions of time are given by three coupled, linear, differential equations with constant coefficients as seen in equations (1), (2), and (3).

$$\frac{dN_g}{dt} = \gamma N_m - \Gamma N_g \tag{1}$$

$$\frac{dN_e}{dt} = \Gamma N_g - \gamma_n N_e \tag{2}$$

$$\frac{dN_m}{dt} = \gamma_n N_e - \gamma N_m \tag{3}$$

3. Analytic Solutions

The Laplace Transform, L_s, method for solving a system of coupled ordinary differential equations permitted the determination of analytic solutions for N_m , N_g , and N_e .

3.1 Metastable Population

The metastable population, N_m, was first deduced; in part, because the metastable population can readily be observed

as a function of time. Applying the Laplace Transform to the set of differential equations and solving for the transformed metastable population, $M(s)$, $N_m(t)$ is obtained from $N_m(t)=L_s^{-1}(M(s))$. $M(s)$ and $N_m(t)$ are shown in equations (4) and (5), respectively.

$$M(s) = \left(\frac{G_0\gamma_n\Gamma}{(s+\gamma)(s+\gamma_n)(s+\Gamma)-\gamma\gamma_n\Gamma}\right) \tag{4}$$

Inverting the transformed solution, $L_s^{-1}(M(s))$, for the metastable population, equation (5) is acquired which yields, (where G_o is the initial ground state population),

$$N_m(t) = L_s^{-1}(M(s)) = \frac{G_0\gamma_n\Gamma}{\alpha}\left(1 - \frac{\mu e^{-\varepsilon t}+\varepsilon e^{\mu t}}{\sqrt{\beta}}\right) \tag{5}$$

The following definitions (6), (7), (8), and (9) were made for readability and computation,

$$\alpha = \gamma\gamma_n + \gamma\Gamma + \Gamma\gamma_n \tag{6}$$
$$\beta = \gamma^2 + \gamma_n^2 + \Gamma^2 - 2\alpha \tag{7}$$
$$\varepsilon = \frac{1}{2}\left(\sqrt{\beta} + (\gamma + \gamma_n + \Gamma)\right) \tag{8}$$
$$\mu = \frac{1}{2}\left(\sqrt{\beta} - (\gamma + \gamma_n + \Gamma)\right) \tag{9}$$

3.2 Ground State

The solution to the ground state population equation is found by the same method as the metastable. Solving for *G(s)* yields equation (10),

$$G(s) = \left(\frac{G_0(s+\gamma)(s+\gamma_n)}{(s+\gamma)(s+\gamma_n)(s+\Gamma)-\gamma\gamma_n\Gamma}\right) \tag{10}$$

After inverting the transformed solution, $L_s^{-1}(G(s))$, for the ground state population as a function of time, equation (11) is acquired. Where again for readability and computation, ρ and σ are defined as equations (12) and (13) respectively,

$$N_g(t) = L_s^{-1}\big(G(s)\big) = \frac{G_0}{\alpha}\left(\gamma\gamma_n + \frac{\sigma e^{\mu t}-\rho e^{-\varepsilon t}}{2\sqrt{\beta}}\right) \tag{11}$$
$$\rho = \Gamma\left(\gamma^2 + \gamma_n^2 - \gamma\Gamma - \gamma_n\Gamma - \sqrt{\beta}\,(\gamma + \gamma_n)\right) \tag{12}$$
$$\sigma = \Gamma\left(\gamma^2 + \gamma_n^2 - \gamma\Gamma - \gamma_n\Gamma + \sqrt{\beta}\,(\gamma + \gamma_n)\right) \tag{13}$$

3.3 Excited State

Again, by the same method the equation for the excited state as a function of time is found and solving for *E(s)* yields equation (14). Inverting *E(s)*, for the excited state population as a function of time, equation (15) is obtained. Where ω and v are defined respectively as equations (16) and (17),

$$E(s) = \left(\frac{G_0\Gamma(s+\gamma)}{(s+\gamma)(s+\gamma_n)(s+\Gamma)-\gamma\gamma_n\Gamma}\right) \quad (14)$$

$$N_e(t) = L_s^{-1}\big(E(s)\big) = \frac{G_0\Gamma}{\alpha}\left(\gamma - \frac{\omega e^{\mu t}+\nu e^{-\varepsilon t}}{2\sqrt{\beta}}\right) \quad (15)$$

$$\omega = \gamma\sqrt{\beta} - (2\alpha - \gamma(\gamma + \gamma_n + \Gamma)) \quad (16)$$

$$\nu = \gamma\sqrt{\beta} + (2\alpha - \gamma(\gamma + \gamma_n + \Gamma)) \quad (17)$$

4. Solution Verification & Data

Prior to attempting to identify an analytical solution to the three-level system a numerical solution to the system of differential equations is obtained. This was done using a 4th-order Runge-Kutta numerical integration of the differential equations. The apparent structure of the numerical solution provided a sense that an analytical solution could be identified. Figure 3(a) shows the numerical solutions for each of the relevant populations as a function of time and Fig. 3(b) compares our analytical solution to the numerical result for the metastable population.

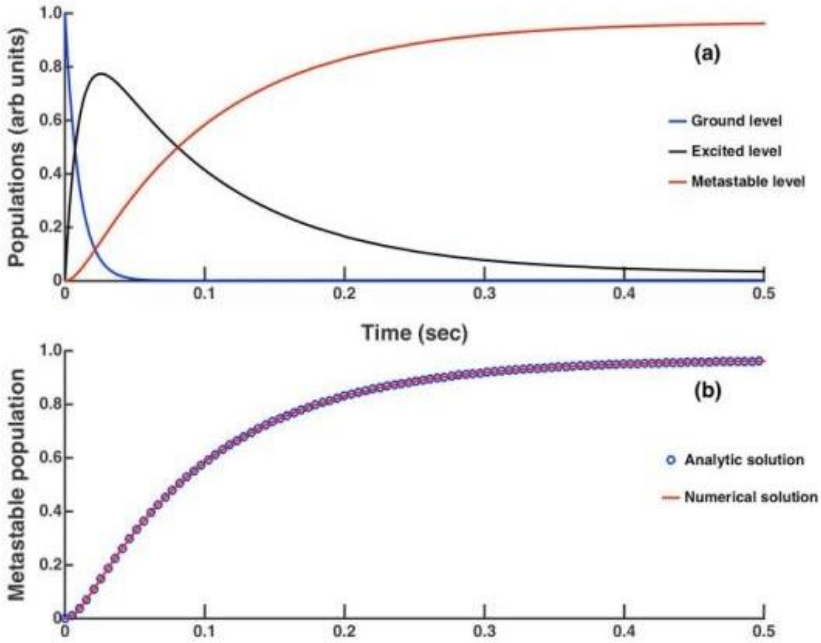

Figure 4. (a) Numerical solutions for the relevant Cr^{3+} populations as a function of time. G_o was set to 1.0 and $\gamma_n >> \gamma$. (b) The analytical solution for the metastable population compared to the numerical solution shown in 3(a). Within the round-off error associated with the numerical result the two solutions are identical for $N_m(t)$.

Figure 5 shows the metastable-level excitation data using a 543-nm output HeNe laser as an optical pumping source. The laser beam was incident on the ruby samples and temporally chopped on/off to provide alternating excitation (Figure 5) and de-excitation (Figure 1) intervals for data acquisition. The fit to the proposed parent population, $N_m(t) + B$, where B is a constant, has not converged to an acceptable degree. This may be related to the complicated form of the parent distribution and currently other non-linear least-squares algorithms are being considered to accomplish this task.

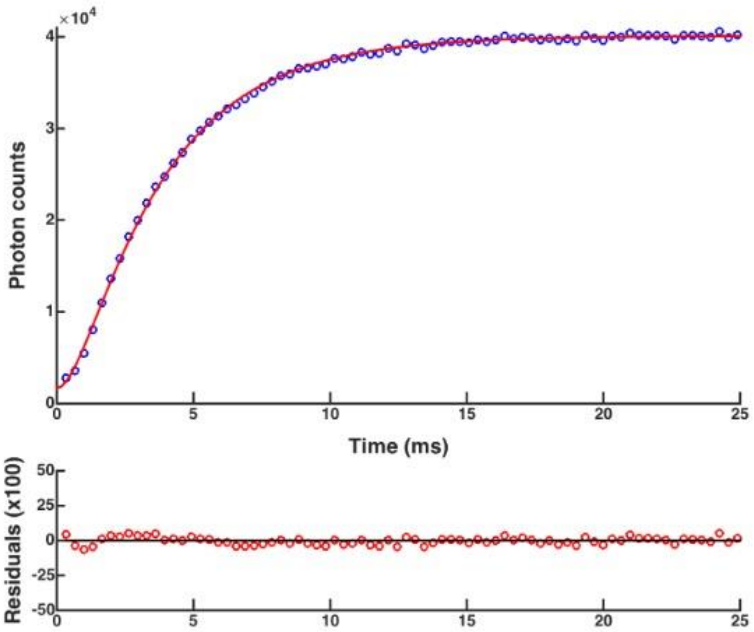

Figure 5. Photons (blue circles) and the results of an unconverged (red-line) fit to the photons detected as a function of time. Residuals (red circles) plotted over time.

5. Conclusion

Work to develop a new senior-level laboratory project to measure the fluorescence lifetimes of the metastable ^2E levels of Cr^{3+} in ruby was initiated. In doing so, a significant variation of results for the room-temperature lifetime in the literature[3] was discovered. Further experimentation regarding the fluorescence decay of the R-lines as a function of wavelength indicates that a deviation from single-population decay structure existed and subsequently appears related to the reabsorption of 694.2 and 692.8-nm photons within the ruby sample. In order to more fully understand the radiative dynamics of this system, the optical excitation phase of the ruby was examined and a basic three-level model for the populations of the ground, excited, and metastable states of Cr^{3+} in ruby is proposed. We were able to solve these coupled differential equations using the method of Laplace Transform and show fair agreement with measurements. Further experimentation has indicated that our room-temperature lifetime for the levels that give rise to the R-lines are equivalent with a two-sigma preliminary value of 3.3 ± 0.1 ms. Our results are consistent with the report of Nelson & Sturge[2] and more than 30% shorter than the high-precision result reported by Espositi & Bizzocchi[3]. At this time, we plan to incorporate the excitation dynamics and reabsorption corrections, developed in this work, into a senior-level laboratory experience in the future at Appalachian State University

6. Acknowledgements

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7. References

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