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Quantum efficiency and metastable lifetime measurements in ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) via lock-in rate-window photothermal radiometry

A. Mandelis, Z.H. Chen and R. Bleiss

Photothermal and Optoelectronic Diagnostics Laboratory, Department of Mechanical Engineering, University of Toronto, Toronto, Canada, M5S 1A4

The newly developed photothermal detection technique of rate-window infrared radiometry has been applied to the measurement of the metastable state de-excitation parameters of a ruby laser rod. By applying the photothermal lock-in rate-window concept, the radiative lifetime and quantum efficiency of $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ have been measured with optimal signal-to-noise ratio (SNR) and simple, unambiguous interpretation from the extremum in the lock-in analyzer in-phase rate-window signal.

I. INTRODUCTION

In this work we introduced the recently developed technique of lock-in rate-window photothermal radiometry (PTR) [1] to perform accurate measurements of the non-radiative quantum efficiency, η_{NR} , in ruby. We used luminescence lock-in rate-window signals from a ruby sample to measure the metastable lifetime τ_{21} optically, with the photodiode signal being proportional to the metastable level population $N_2(t; \tau_{21})$. PTR rate-window signal analysis was based on a simple time-resolved PTR model for ruby.

2. TIME-RESOLVED PTR OF LASER MATERIALS

For a solid state laser medium exhibiting three-level dynamic behavior, such as $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$, under the time-gated square-pulse excitation of a rate-window type of experiment [1], the rate equation for level $|2\rangle$ is given by

$$\frac{d}{dt} N_2(t) = N_1 W_p(t) - \frac{N_2(t)}{\tau_{21}}, \quad (1)$$

where

$$\tau_{21} = \frac{1}{W_R + W_{\text{NR}}}, \quad (2)$$

with W_R and W_{NR} being the probabilities for radiative and nonradiative decay, respectively. In Eq. (1) it is assumed that N_1 is constant, a condition valid for sufficiently weak pumping of the ground state $|1\rangle$, which is also always heavily populated in a three-level laser medium. The pumping rate $W_p(t)$ to level $|3\rangle$ is given by

$$W_p(t) = \begin{cases} W_{p0}, & t < \tau_p \\ 0, & t > \tau_p \end{cases} \quad (3)$$

where τ_p is the square laser pulse duration. The solution to rate Eq. (1) under the initial condition $N_2(t=0) = 0$ is $N_2(t; \tau_{21}) =$

$$N_1 W_{p0} \tau_{21} \begin{cases} 1 - \exp(-t/\tau_{21}), & t \leq \tau_p \\ [\exp(\tau_p/\tau_{21}) - 1] \exp(-t/\tau_{21}), & t \geq \tau_p \end{cases} \quad (4)$$

As the result of the nonradiative decays in the optical medium, which include the relatively slow $|2\rangle \rightarrow |1\rangle$ decay preceded by the fast nonradiative $|3\rangle \rightarrow |2\rangle$ transition, the thermal power density in $\text{J/cm}^3\text{s}$ released in the laser material is

$$A(t) = N_1 E_{32} W_p(t) + \left(\frac{\eta_{NR}}{\tau_{21}} \right) E_{21} N_2(t; \tau_{21}), \quad (5)$$

where

$$\eta_{NR} = 1 - \eta_R = \frac{\tau_{21}}{\tau_{NR}} = \frac{W_{NR}}{W_R + W_{NR}}. \quad (6)$$

The increase in the surface temperature of the laser medium can be monitored using infrared photothermal radiometric detection. For this purpose, the coupled heat diffusion equations in the sample (s), surrounded by two gaseous regions (air; (g)) can be written

$$\frac{1}{\alpha_g} \frac{\partial T_g(x,t)}{\partial t} - \frac{\partial^2 T_g(x,t)}{\partial x^2} = 0, \quad x \leq 0 \text{ and } x \geq L, \quad (7a)$$

$$\frac{1}{\alpha_s} \frac{\partial T_s(x,t)}{\partial t} - \frac{\partial^2 T_s(x,t)}{\partial x^2} = \frac{A(t)}{k_s} \exp(-\beta_{31}x), \quad 0 \leq x \leq L, \quad (7b)$$

where α_j is the thermal diffusivity of the j -th layer, k_s is the solid thermal conductivity, and $\beta_{31}(\lambda)$ is the absorption coefficient of the optical medium (s) at the excitation wavelength and is proportional to the population of level $|1\rangle$:

$$\beta_{31}(\lambda) = N_1 (W_{p0} E_{31} / I_0), \quad (8)$$

where I_0 in W/cm^2 is the incident laser intensity.

Equations (7a) and (7b) are subject to the usual temperature and heat flux continuity. Under thermally thick and optically thick conditions, realistic for PTR detection at early times:

$$t \ll \tau_L \equiv L^2/\alpha_s ; \quad t \ll \tau_\beta \equiv (\beta_{31}^2 \alpha_s)^{-1} \quad (9)$$

the Laplace transforms of these equations can be explicitly inverted to yield the backscattered signal

$$S_B(t) = C\tau_{21} \begin{cases} (1 + Q)(t/\tau_{21}) - Q[1 - \exp(-t/\tau_{21})], & t \leq \tau_p \\ (1 + Q)(\tau_p/\tau_{21}) - Q[\exp(\tau_p/\tau_{21}) - 1] \exp(-t/\tau_{21}), & t \geq \tau_p, \end{cases} \quad (10)$$

where

$$C = \text{const.} \times (I_0 R \beta_{31} \alpha_s / k_s) ; \quad Q \equiv \eta_{\text{NR}}(E_{21}/E_{32}) \quad (11)$$

3. EXPERIMENTAL AND DISCUSSION

Experiments were performed with a cylindrical ruby sample, 6 cm in length and 1 cm in diameter [2]. The two flat surfaces were polished smooth, whereas the curved surface was rough and light scattering. Luminescence emitted through the curved side surface of the optically pumped ruby rod was filtered from excitation line photons and measured.

The in-phase (IP) luminescence rate-window signals were measured for three pulse durations τ_p : 1 ms, 4 ms, and 10 ms. The lock-in signal extremum was analyzed using explicit rate-window expressions, yielding the simple linear relationship:

$$(T_0)_{\text{max}} = 2.5681 \tau_{21} + 1.9973 \tau_p \quad (12)$$

The range of τ_{21} values obtained from all three τ_p curves was

$$\tau_{21} = 3.789 \pm 0.14 \text{ ms} \quad (13)$$

in excellent agreement with our earlier calculations using frequency-domain PTR [2].

The results of the rate-window PTR measurements on ruby are shown in Fig. 1a. The data points on this figure belong to two separate experimental runs and their low scatter is a measure of the excellent reproducibility of this technique. The lock-in IP signal maximum was analyzed using the τ_{21} value obtained from the luminescence experiment. Figure 1b shows that for the range of τ_{21} values obtained experimentally, the condition for the rate-window extremum, yields a simple, nearly linear dependence on Q . In the range of experimentally expected Q -values (< 50%) with $\tau_p = 6$ ms, the relationship shown in Fig. 1b can be expressed numerically as

$$(T_0)_{\text{max}}/\tau_p = 0.361 Q + 1.397 \quad (14)$$

The linearity of the $(T_0)_{\text{max}}/\tau_p$ vs. Q relation improves with increased τ_p . From Figure 1b one thus obtains $Q = 0.121$. Using [3] $E_{21} = 1.79$ eV and $E_{32} = 0.62$ eV in the Q -defining expression, one obtains the value of non-radiative quantum efficiency:

$$\eta_{NR} = 0.042 \pm 0.006 \quad (15)$$

This new value is in excellent agreement with $\eta_{NR} = 0.04$, the value calculated using the harmonically-modulated PTR phase in Ref. [2]. Note the greater standard deviation in the value $\eta_{NR} = 0.10 \pm 0.05$ reported by Quimby and Yen, [3]. The SNR of the rate-window IP signal, Fig. 1a, is superior to that of the PTR phase [2], as expected from theory [1], which makes the present value of η_{NR} more reliable. This advantage in SNR of rate-window PTR becomes more pronounced with shorter τ_{21} , for which the required probe modulation frequency range has very low thermal energy content.

Fig 1 a) In-phase lock-in rate-window luminescence signals from a ruby crystal. Pulse duration τ_p : ($\square$) 1 ms, ($\cdot$) 4 ms, and ($*$) 10 ms; b) Simple dependence of the lock-in rate-window maximum on the optical-to-thermal energy conversion efficiency Q of ruby: ($***$) $\tau_{21} = 3.94$, ($\cdots$) $\tau_{21} = 3.78$ ms, ($\square\square\square$) $\tau_{21} = 3.64$ ms and pulse duration $\tau_p = 6$ ms. The straight line is there to aid the eye.

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