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Optical Saturation in the Photothermal Spectroscopy of Fluorescent Materials

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Abstract. The dependence of the fundamental and harmonic photothermal (PT) signal on the intensity I_0 of the illumination source is analyzed. It is shown that both components of the PT signal do not increase indefinitely with I_0, but at sufficiently high power densities begin to decrease as $1/I_0$. Along with photoacoustic saturation, this defines an upper limit for the sensitivity of spectrometers based on PT detection.

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The photothermal, or photoacoustic, effect has recently become the basis for a range of important spectroscopic techniques. The method is based on periodic optical excitation of a sample and subsequent measurement of the nonradiative component of the deexcitation. Classically, this has been carried out by enclosing the sample in a gastight cell and monitoring the induced acoustic wave in the gas by sensitive microphones or piezoelectric transducers [1]; hence the term "photoacoustics". More recently, other techniques have been used to detect the nonradiative deexcitation through the thermoelastic channel; these include laser probes [2] photothermal radiometry [3] and pyroelectric detectors [4, 5]. Because the technique is based on the measurement of the energy actually deposited in the sample, photothermal spectroscopy is complementary to conventional spectroscopic measurements based on the detection of sample fluorescence or transmission [6, 7]. In order to obtain photothermal (PT) data which can be directly related to such spectroscopic parameters as the fluorescence quantum efficiency and the metastable state lifetime, it is important to ensure that signal saturation effects do not occur. One well-studied effect, photoacoustic saturation, occurs when the thermal diffusion length μ in the sample is greater than the optical absorption length $l_\beta = 1/\beta$, where β is the coefficient of absorption. This saturation mode results from the interaction between optical and thermal processes in the sample; it has been investigated extensively for gases, liquids and solids [8, 9]. Although this mode of saturation is important, emphasis on the thermal *(detection)* component of the photothermal signal generation process has led to a possible neglect of saturation occurring in the optical *(excitation)* step.

The primary mode of saturation in the excitation process is that of optical saturation; this occurs when an absorption level in a sample is pumped faster than it can be depopulated, and it can thus become important when lasers are used as excitation sources. This is an ever-present concern in all branches of spectroscopy; with regard to photothermal spectroscopy in particular, the effect of this mode of saturation has been observed in PT studies of gases [10], where it has been found that optical saturation begins to affect the PT signal at intensities on the order of 1 W/cm^2. There has been no attempt to define similar limits for the case of solid-state experiments, where laser powers of up to several watts focussed to millimeter spot sizes have been used to excite weakly-absorbing fluorescent samples [11–14]. It is the purpose of this work to show explicitly the effect of optical saturation on the photothermal signal generation process in solids, and from the results emphasize the importance of considering this effect in photothermal studies.

Theory

The effect of optical saturation on the photothermal signal in gases has been previously examined [1, 10]; our analysis closely follows these studies. We consider an ideal electronic two-level system, as shown in Fig. 1, where the excited state of the absorbing centers is a metastable state. Although this model will be valid only for zero-phonon transitions, and does not account for broadening mechanisms, such a system can easily describe a wide range of fluorescent systems, such as trivalent rare earth-doped crystals or glasses, and for certain laser dyes [12, 16].

In PT spectroscopy the exciting laser beam is modulated such that the beam intensity at the sample surface can be expressed as

$$I=(I_0/2)[1+\cos(\omega t)], \tag{1}$$

where I_0 is the amplitude of the beam intensity and ω the angular frequency of modulation. Absorption of this modulated radiation gives rise to periodic heating of the sample through nonradiative relaxation of the excited state. This heat generation is then measured via a detector/lock-in amplifier combination tuned to either the fundamental or harmonic modulation frequency. As will be shown below, even with the lower average power densities afforded by the *modulated* excitation, optical saturation affects the PT signal in the same way it does an *unmodutaled* experiment.

The radiation-induced transition from the ground state to the excited state in the system described above occurs at a rate W_p, and de-excitation from the metastable state can occur both radiatively, at a rate $W_r=\tau_r^{-1}$, and nonradiatively, at a rate $W_{nr}=\tau_{nr}^{-1}$. The lifetime of the upper level τ is defined by $\tau^{-1}=\tau_r^{-1}+\tau_{nr}^{-1}$. The situation is similar to that in gases [1, 10] except that for gases we must consider the collisional rate W_c in place of the effective rate for nonradiative transition W_{nr}.

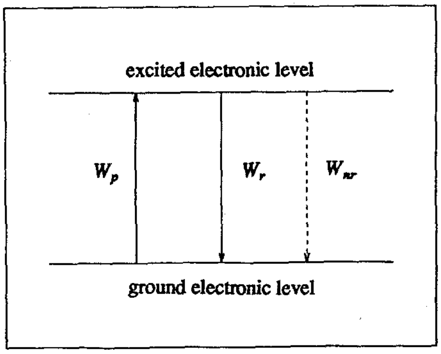

Fig. 1. Absorption and de-excitation processes for an electronic transition. Solid lines refer to radiative transitions and dashed lines to nonradiative transitions

Let N_i be the density of the ith state, and $B \equiv B_{12}h\nu/c = B_{21}h\nu/c$, where $B_{12}=B_{21}$ are the Einstein coefficients for stimulated emission and absorption. Furthermore, let I be the number of incident photons $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ with energy $h\nu=E_2-E_1=E_{21}$. A rate equation analysis of the system gives

$$\frac{d}{dt}(N_2-N_1)=-2B(N_2-N_1)I-2\tau^{-1}N_2. \tag{2}$$

At steady state, the number of ions in the excited state is given by

$$N_2=\frac{BNI}{2BI+\tau^{-1}}, \tag{3}$$

where $N=N_1+N_2$ is the total ion density.

To ensure that the sample has a homogeneous thermal distribution throughout its volume, we must require the further condition that the sample be thermally thin, that is, $\mu \gg d$, where μ is the thermal diffusion length $\mu=(2K/\varrho c w)^{1/2}$, with K, ϱ, and c the thermal conductivity, density and specific heat per gram of the sample, and d is the sample thickness. With this requirement the attenuation and phase shift of the exciting light pulses in traversing the sample will be negligible.

Assuming that no de-excitation occurs through photochemical reactions, the PT signal will be directly proportional to the rate of heat generation in the sample $R=N_2\tau_{nr}^{-1}E_{21}$. Using the above expression for N_2,

$$R=\frac{BNI\tau_{nr}^{-1}E_{21}}{2BI+\tau^{-1}} \tag{4}$$

or

$$R=\frac{E_{21}}{2}\,\frac{BNI_0[1+\cos(\omega t)]\tau_{nr}^{-1}}{BI_0[1+\cos(\omega t)]+\tau^{-1}}. \tag{5}$$

As mentioned above, a photothermal experiment is a *modulated* experiment, and spectroscopic parameters have been measured using either the fundamental or harmonic component of the photothermal signal [11–18], given by (5); narrowband amplification of the signal renders higher-order terms negligible in practice. These two signal components of interest may be expressed explicitly by expanding (5) in powers of $\cos(\omega t)$, retaining terms up to the harmonic component $\cos(2\omega t)$,

$$\begin{aligned}R=\frac{E_{21}}{2}\Bigg[&\frac{BNI_0\tau_{nr}^{-1}}{BI_0+\tau^{-1}}-\frac{BNI_0\tau_{nr}^{-1}\tau^{-1}}{(BI_0+\tau^{-1})^2}\cos(\omega t)\\&+\frac{1}{2}\,\frac{B^2NI_0^2\tau_{nr}^{-1}\tau^{-1}}{(BI_0+\tau^{-1})^3}\\&-\frac{1}{2}\,\frac{B^2NI_0^2\tau_{nr}^{-1}\tau^{-1}}{(BI_0+\tau^{-1})^3}\cos(2\omega t)+\dots\Bigg].\end{aligned} \tag{6}$$

The expression contains a dc term, which corresponds to a constant temperature rise in the sample, and ac contributions at the fundamental ω and the harmonic 2ω of the modulation frequency of the incident light. The thermal variation which is detected in PT spectroscopy is due to the ac terms in R. The fundamental PT signal A_ω is given by

$$A_\omega = k\frac{E_{21}}{2}\frac{BNI_0\tau_{\mathrm{nr}}^{-1}\tau^{-1}}{(BI_0+\tau^{-1})^2}\cos(\omega t) \tag{7}$$

and the harmonic PT signal $A_{2\omega}$ is given by

$$A_{2\omega} = k\frac{E_{21}}{4}\frac{B^2NI_0^2\tau_{\mathrm{nr}}^{-1}\tau^{-1}}{(BI_0+\tau^{-1})^3}\cos(2\omega t), \tag{8}$$

where k is the system sensitivity, which depends on the type of detection – microphone, piezoelectric, laser-probe, pryoelectric – used.

For low incident intensities, such that $BI_0 \ll \tau^{-1}$, the amplitude of the signals is given by

$$|A_\omega| \rightarrow k\frac{E_{21}}{2}\left(\frac{\tau}{\tau_{\mathrm{nr}}}\right)BNI_0, \tag{9}$$

$$|A_{2\omega}| \rightarrow k\frac{E_{21}}{4}\left(\frac{\tau^2}{\tau_{\mathrm{nr}}}\right)B^2NI_0^2, \tag{10}$$

and both fundamental and harmonic PT signals increase with increasing I_0. This is the usual operating regime for PT spectrometers. Calibration of PT spectrometers, and the normalization of PT spectroscopic data, are always done using an absorbing reference sample where A_ω is proportional to I_0 [1]. This procedure is valid as long as this condition applies when taking actual sample data. However, when I_0 is sufficiently large, the signal saturates, and indeed when $BI_0 \gg \tau^{-1}$,

$$|A_\omega| \rightarrow k\frac{E_{21}}{2}\left(\frac{1}{\tau_{\mathrm{nr}}\tau}\right)\frac{N}{BI_0}, \tag{11}$$

$$|A_{2\omega}| \rightarrow k\frac{E_{21}}{4}\left(\frac{1}{\tau_{\mathrm{nr}}\tau}\right)\frac{N}{BI_0}. \tag{12}$$

Thus unnecessarily high powers can lead to a great reduction in the PT signal. In addition, in this regime, the calibration and normalization procedures are invalidated, and the corresponding data must be re-analyzed in order to extract the correct values for the spectroscopic quantities of interest.

A plot of $|A_\omega|$ and $|A_{2\omega}|$ is shown in Figs. 2 and 3. The two intensity regimes are clearly identifiable. The amplitude of the fundamental and harmonic PT signals remain linear as long as $BI_0\tau \ll 1$; as $BI_0\tau$ approaches unity, the signals begin to saturate. The fundamental signal is fully saturated when the intensity level is high enough such that $BI_0\tau = 1$; the harmonic signal completely saturates when $BI_0\tau = 2$. Above the intensities defined by these limits, both the fundamental and harmonic PT signals show a steady decrease.

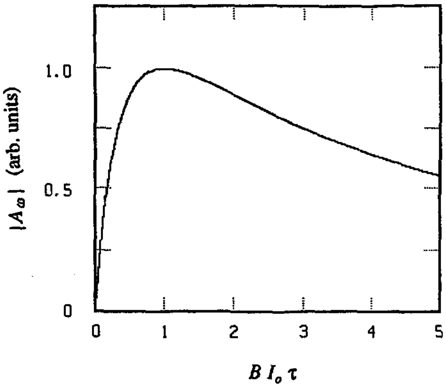

Fig. 2. Theoretical plot of $|A_\omega|$ vs the parameter $BI_0\tau$. The curve has been normalized to 1 at its maximum

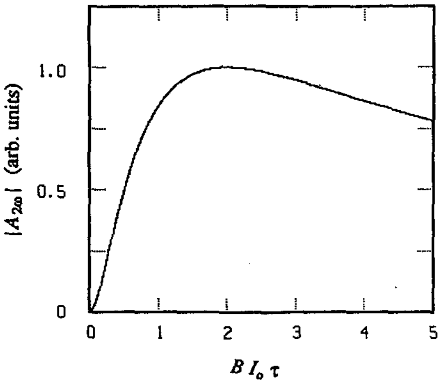

Fig. 3. Theoretical plot of $|A_{2\omega}|$ vs the parameter $BI_0\tau$. The curve has been normalized to 1 at its maximum

Conclusion

Although photoacoustic saturation, which occurs when $\mu \gg l_\beta$ in the sample, remains an important consideration in the photothermal spectroscopy of condensed matter, we have shown explicitly that saturation during the excitation process, through optical saturation, is not negligible. The idea that higher detectability in PT spectroscopy may be achieved by using more powerful excitation sources is only valid below saturation; when this limit is reached the sensitivity of the technique should be increased instead by a reduction in the noise level. An attempt to increase the PT signal by increasing the excitation intensity may, in fact, lead to a drastic decrease in the signal amplitude. Ultimately the sensitivity of a particular PT detection method will be limited by both optical and photoacoustic space saturation.

We should point out that considerations of optical saturation are important when relative PT measurements are used to obtain absolute quantities, or when high excitation powers are used, for example, for work with weakly absorbing samples and in imaging applications. Discrepancies in the values for the radiative quantum efficiency of various solids determined by PT methods may be partly due to this effect, because of the range of excitation intensities in different experiments [13, 17, 18].

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