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PHOTOMULTIPLIER NONLINEAR RESPONSE IN TIME-DOMAIN LASER-INDUCED LUMINESCENCE SPECTROSCOPY

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A new procedure to find the limiting range of the photomultiplier linear response of a low-cost, digital oscilloscope-based time-resolved laser-induced luminescence spectrometer (TRLS), is presented. A systematic investigation on the instrument response function with different signal input terminations, and the relationship between the luminescence intensity reaching the photomultiplier and the measured decay time are described. These investigations establish that setting the maximum intensity of the luminescence signal below 0.3V guarantees, for signal input terminations equal or higher than 99.7 ohm, a linear photomultiplier response.

Keywords: photomultiplier; time-resolved; laser-induced luminescence.

INTRODUCTION

Time-Resolved Luminescence Spectroscopy (TRLS) can be implemented by using time- and frequency-domain instrumentations, the simplest ones are built with oscilloscopes, boxcar integrators/averagers and single-photon detection schemes. Accuracy in excited-state lifetime and time-resolved emission spectra measurements is achieved when the experimental decay curves are obtained under conditions of high signal-to-noise (S/N) ratio, with high time resolution of the instrumentation, by setting a small termination at the oscilloscope or boxcar signal input. For low intensity fluorescent samples it is a common procedure to set the photomultiplier voltage supply close to its typical high voltage value to increase the photomultiplier sensitivity, while keeping the signal input termination at the oscilloscope or boxcar to 50 Ω, to get the highest time-resolution on the instrument. However, by doing so, a distortion of the luminescence signal was obtained in our instrumentation. Photomultiplier tubes provide good linearity in anode output current over a wide range of incident light levels; in other words, they offer a wide dynamic range. However, if the incident light is too intense, the output begins to deviate from the ideal linearity. This is primarily caused by anode linearity characteristics, that are dependent only on the current value if the supply voltage is constant, being independent of the incident light wavelength. This kind of detector nonlinearity has been previously reported in a number of instruments[1-8], but here, we present a new procedure to achieve the photomultiplier linearity range, consisting of extraction of time-resolved laser intensity profile and instrument response function, to be further used in reconvolution methods[9-12] for excited-state lifetime measurements. We report in this paper a systematic investigation on the supply voltage applied to the photomultiplier; the instrument response function with different signal input terminations; the relationship between the luminescence intensity reaching the photomultiplier and the measured decay time; and the extraction of the laser intensity profile in time-resolved luminescence measurements.

EXPERIMENTAL

The instrumentation

The instrumentation (Figure 1) is set up with a Thermo Laser Science mod. VSL-337ND-S (Oriel mod. 79070) pulsed nitrogen laser[13] (λ_{em} = 337,1 nm; < 4 ns Full-Width at Half-Maximum, FWHM) for the photo-excitation of the sample; a 1/4 m Oriel Cornerstone 260 emission monochromator[14] for the spectral resolution of the luminescence emission, coupled to an Oriel diffraction grating mod. 74063 (0.15 nm resolution at 546.1 nm, 1200 lines/mm, blaze at 350 nm), an Oriel mod. 59470 (Schott GG385) color glass filter to block the excitation light at the micrometer-driven entrance slit, and an Oriel mod. 77348 fast (2,2 ns rise-time) side-on photomultiplier tube at the micrometer-driven exit slit; a Tektronix mod. TDS3032B (300 MHz, 2 channels, 2,5 GSamples/s) Digital Oscilloscope[15] to detect the signal. To be appropriated to TRLS, the oscilloscope must meet requirements on
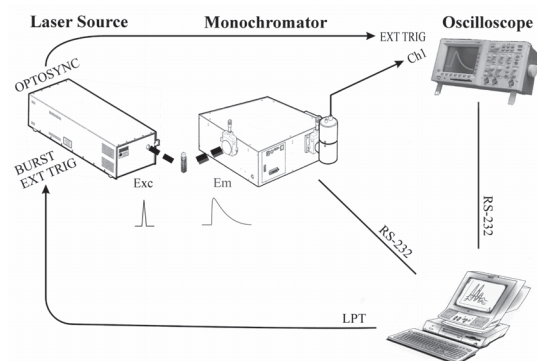

Figure 1. Scheme of the Time-Resolved Laser-Induced Luminescence Spectrometer (from left to right: nitrogen laser, sample, monochromator, digital oscilloscope and computer). The monochromator and the oscilloscope are interfaced with the computer by serial RS-232 interfaces. The charging and firing of the laser plasma tube are controlled by the parallel port (LPT1) of the computer. The oscilloscope data acquisition is synchronized with the photo-excitation of the sample by the OPTOSYNC trigger pulse

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time resolution (1.2 ns rise-time and 0.4 ns sampling time for the mentioned oscilloscope), pre-trigger signal acquisition ability (signal waveform capture before the trigger is detected by the oscilloscope), the averaging mode acquisition (for improvement of the signal-to-noise ratio) and digital precision for the waveform acquisition (9-bits for the "sample" acquisition mode and 14-bits for the "average" mode). To acquire low intensity luminescence emission at the nanosecond time scale, an additional pre-amplifier could be used for signal amplification, but that was not used in this work. The PC-compatible computer must have at least two serial communication ports (named RS-232 in the figure) and one parallel port[16] (named LPT) to control the oscilloscope, the monochromator and the laser, respectively. Both the oscilloscope and the monochromator have a built-in GPIB (IEEE-488) interface, but the lower cost serial ports (RS-232 standard interface) were preferred in this work. The source code was developed in BASIC.

The laser used in this work is a new model that has several input and output connections that enable it to be computer controlled. Two input ports, BURST and EXT_TRIG, are used to control the electrical charging and the firing of the laser plasma tube, respectively. These controls save the plasma tube lifetime because the laser is fired only when the oscilloscope is ready for the signal acquisition. A third port, OPTOSYNC, is used to synchronize the laser firing with the signal acquisition by the oscilloscope, with low (less than 1ns standard deviation) time jitter.

The software automatically adjusts some oscilloscope parameters for TRLS data acquisition, such as: vertical menu, for channel 1 (input signal from photomultiplier): Coupling = DC; internal termination = 1 MΩ (Observation: the external termination is chosen by the user and must be appropriated for the time resolution of the experiment); Invert = On; Bandwidth= Full; trigger menu (input trigger from OPTOSYNC laser pulse): Type = Edge; Source = EXT/ 10; Coupling = DC; Slope = Rising edge; Level = 1.3 V; Mode = Normal.

Finally, a home-made metallic sample holder was built to accept either a standard 10 mm-optical path length fluorescence quartz cuvette for liquids or 0.01 mm-optical path length quartz windows for powdered samples.

Decay analysis

The decay curves in this work were analyzed with the recommended method[17] of Levenberg-Marquardt least-squares[18], using 500 points per each curve. Deconvolutions[18] were performed with a spreadsheet.

THEORETICAL BACKGROUND

Response time of the instrument and signal input termination

The knowledge of the instrument response time (or RC time constant of the electric circuitry), is very important because it may distort and limit the time resolution of the experimental data. As an example, the time-dependent photon flux signal reaching the photomultiplier is converted to electrical current, and its temporal profile can be seriously distorted by sources of resistance and capacitance of the instrument[12] like termination (resistance R_{term}) at the oscilloscope signal input, internal resistance and capacitance from the oscilloscope (R_{osc}, C_{osc}), photomultiplier (R_{PMT}, C_{PMT}) and the cable connecting the photomultiplier to the oscilloscope (C_{cable}). All these resistances and capacitances are connected in parallel and thus the reciprocal of the RC response time of the instrument**,** Equation 1**,** can be easily derived through the following steps:

$$R^{-1} = R_{PMT}^{-1} + R_{osc}^{-1} + R_{term}^{-1}$$
$$C = C_{PMT} + C_{cable} + C_{osc}$$
$$(RC)^{-1} = (R_{PMT}^{-1} + R_{osc}^{-1} + R_{term}^{-1}) \times C^{-1}$$
$$(RC)^{-1} = (R_{PMT}^{-1} + R_{osc}^{-1}) \times C^{-1} + C^{-1} \times R_{term}^{-1}$$
$$(RC)^{-1} = Constant + C^{-1} \times R_{term}^{-1} \qquad (1)$$

Equation 1 shows that a linear relationship between $(RC)^{-1}$ and R_{term}^{-1} should be expected when the external termination at the oscilloscope signal input is changed.

Instrument response function and time-resolved laser intensity profile:

The true time-dependent decay of a luminescent sample (also known as Impulse Response Function, IRF) can be recorded when the sample is illuminated by a δ-function excitation pulse, and its emission is detected by an ideal equipment, possessing a δ-function instrument response, SR. However, real excitation sources and detection equipments show finite temporal-profile, $I_0(t)$, and finite instrument time-response, SR(t), respectively. Therefore, the recorded fluorescence decay, F(t), can be described by the convolution of the IRF(t), SR(t), and $I_0(t)$ functions (Equation 2).

$$F(t) = IRF(t) \otimes SR(t) \otimes I_0(t) \qquad (2)$$

The sample's true luminescence decay, IRF, can be therefore extracted by least-squares reconvolution methods, using SR and I_0 functions.

RESULTS AND DISCUSSION

In this work, we acquired time-resolved spectra and decay curves of the nitrogen laser and of the uranyl nitrate hexahydrate emissions, with different terminations. The temporal and spectral profiles of the nitrogen laser emission, and of the uranyl nitrate hexahydrate emission (Figure 2) exemplify the TRLS data that can be obtained with this instrumentation. The systematic investigations that were conducted are discussed in detail below.

Supply voltage applied to the photomultiplier and noise sources

Attempts to set the photomultiplier supply voltage to its typical value (-1000V) produced nonlinear distortion in the measurements and at least three sources of noise are present in this instrumentation: Johnson noise (thermal noise), caused by the random motion of carriers in a conductor and resulting in fluctuations in the internal resistance of the detector. The amplitude of this random noise was observed to be within the range –0.46 mV to +0.46 mV (This noise amplitude is within the 1 mV/div minimum vertical scale of the oscilloscope). Shot noise, composed of photons arriving the photomultiplier randomly in time. The manufacturer recommends[19] to make this noise three times bigger than the Johnson noise, in order to measure signals with a high degree of linearity. The observed shot noise amplitude was within the range 0 to +1.4 mV, with -600V applied to the photomultiplier tube. Electromagnetic interference (EMI) of the laser plasma tube discharge, that appears in all signal and baseline acquisitions as a pattern within the range of –2.25 mV to +2.25 mV when the laser is fired. The acquisition software disables the laser plasma tube charging during the data acquisition, to avoid extra EMI noise.

The lowest limit for the photomultiplier linear response is given by the shot noise amplitude, 1.4mV, achieved by setting the photomultiplier high voltage supply to -600V. The laser EMI follows a pattern that could
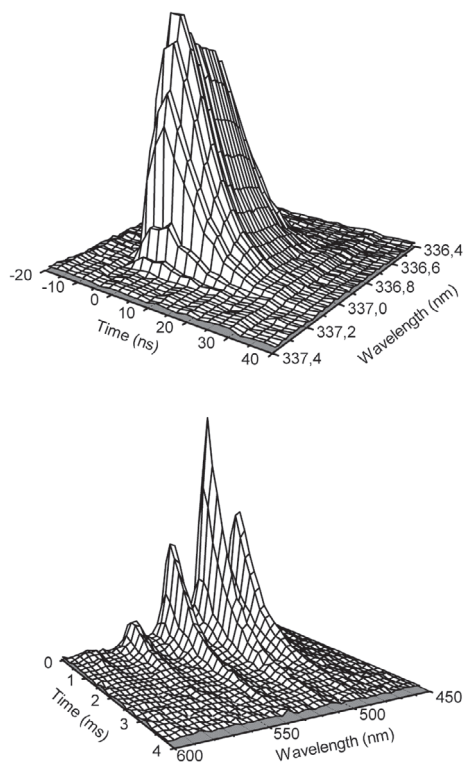
Figure 2. *Examples of two-dimensional data obtained with the instrumentation: Time-Resolved Luminescence Spectra and luminescence decays of the laser emission (top), acquired with 99.7 Ω termination at the oscilloscope signal input, and uranyl nitrate hexahydrate emission (bottom). Each decay curves were obtained with 10000 points, but only 100 points for each decay are displayed in the figure for clarity*

be minimized by subtracting a baseline signal, previously acquired with the monochromator shutter closed. With this procedure, a 4 mV amplitude laser EMI noise in the original signal was reduced to 1 mV, matching the amplitude of the Johnson noise. All decay curves reported in this paper were previously submitted to such baseline subtraction.

Instrument Response Function with different signal input terminations

From Equation 1 a linear relationship between $(RC)^{-1}$ and R_{term}^{-1} should be expected when the external termination at the oscilloscope signal input is changed. To verify this, a series of decay curves were acquired by setting the monochromator to the laser emission ($\lambda = 336.93$ nm), with seven different terminations at the oscilloscope signal input. Five acquired curves are shown as semilogarithmic plots in Figure 3. The four upper curves (9950 Ω, 1996 Ω, 1000 Ω and 498 Ω) in this figure have an acceptable linearity because the laser pulse duration was shorter than the decay time scale and, therefore, they follow the exponential decay defined by the RC time constant of the instrumentation. The curves acquired with terminations 255 Ω and 99.7 Ω (not shown in Figure 3) were acquired with the photomultiplier within its linear response range, but the decay deviate considerably from the linearity because the laser width is comparable to the decay time scale. The least-squares fit, within the linear region of the four upper curves, assuming $V = V_{max} \times \exp(-t/RC)$, gave the parameter RC for each termination. The relationship between RC^{-1} and R_{term}^{-1} has a linear correlation coefficient of 0.99998, which is in agreement with Equation 1, and that was used to extrapolate the RC response time of
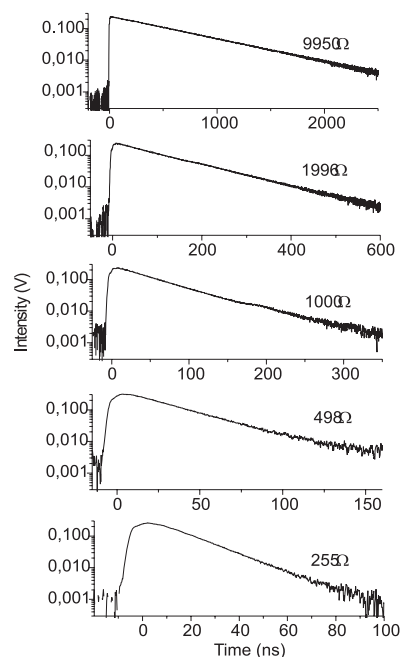

Figure 3. *Semilogarithmic plots of decay curves of the laser emission at 336.93 nm, acquired with different terminations at the oscilloscope signal input. These curves were acquired with the photomultiplier response maintained within its linear response range (maximum signal voltage at the oscilloscope less than 0.3V). For clarity, we omitted the curves acquired with 99.7 and 49.8 Ω terminations*

Table 1. Response time of the instrument, RC, for different terminations (R_{term}) used in this work, calculated with equation $(RC)^{-1} = Constant + C^{-1} \times R_{term}^{-1}$, where Constant = (-5.135 ± 8) 10^4 s^{-1} and $C^{-1} = (1601 \pm 7)$ 10^7 F^{-1}. The last column gives the estimated photomultiplier anode current ($i_{anode, max} = V_{max}/R_{term}$), assuming $V_{max} = 0.3$ V for all decay curves observed at the oscilloscope screen

Termination, R_{term} (Ω)	Response time of the instrument, RC (ns)	Estimated anode current, $i_{anode, max}$ (µA)
49.8	3.111[1]	6024
99.7	6.230[1]	3009
255	15.94[1]	1176
498	31.16	602
1000	62.66	300
1996	125.5	150
9950	642.0	30

[1] Extrapolated values

the instrument for the three lower terminations (Table 1). Note that for these fast signals (laser emission), the maximum anode current with termination 99.7 Ω is 20 times higher than that with termination 1996 Ω (Table 1). In the last section we will see evidences that with terminations 255 and 99.7 Ω the photomultiplier still operates in its linear region.

Relationship between the luminescence intensity reaching the photomultiplier and the measured decay time

The investigation of the photomultiplier behavior was performed in two independent experiments: (1) acquisition of a faster signal (laser emission, < 4ns Full-Width-at-Half-Maximum, FWHM), and (2) acquisition of a slower signal (685 µs luminescence decay of

uranyl nitrate hexahydrate) than the 125.5 ns response time of the instrumentation, with the 1996 Ω termination at the oscilloscope signal input.

Experiment 1: The photomultiplier linearity range was investigated by acquiring decay curves of the laser emission ($\lambda = 336.97$ nm), at different slit widths in the monochromator. In this experiment, the laser can be considered as a delta function and the observed curves follow the exponential RC decay of the electrical circuitry of the instrumentation. The least-squares fit of these curves, between 50 and 500 ns, assuming $V = V_{max} \times \exp(-t/RC)$, gave the parameters V_{max} (maximum intensity at zero time, in volts), RC, and the reduced least-squares sum (Reduced χ^2) that are plotted in Figure 4. This Figure shows that RC is nearly constant at 126 ns and the Reduced χ^2 is greater than 0.998 when V_{max} is below 0.3 V. Therefore, this 0.3 V value corresponds to the maximum signal voltage that assures the acceptable linear response for the photomultiplier. Thus, the maximum anode current at the photomultiplier, under these conditions, is 150 µA, higher than that reported by manufacturer's specifications (100 µA, for a DC signal).
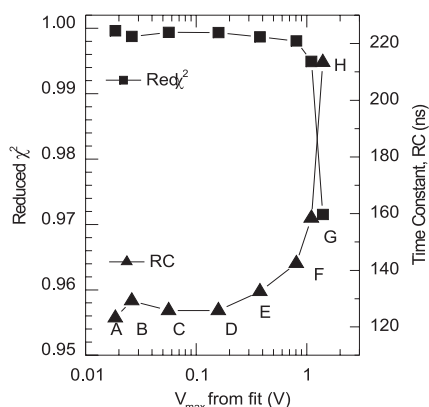

Figure 4. *Instrument decay time constant (RC) and reduced least-squares sum (Reduced χ^2) versus maximum intensity (V_{max}) obtained by the least-squares fit of the laser emission decay curves*

Experiment 2: The linearity range was investigated by acquiring decay curves of the luminescence emission of solid uranyl nitrate hexahydrate ($\lambda_{max} = 510$ nm), using different slit widths at the monochromator. In this experiment, the observed decay curve follows the characteristic excited-state decay of the uranyl nitrate. The least-
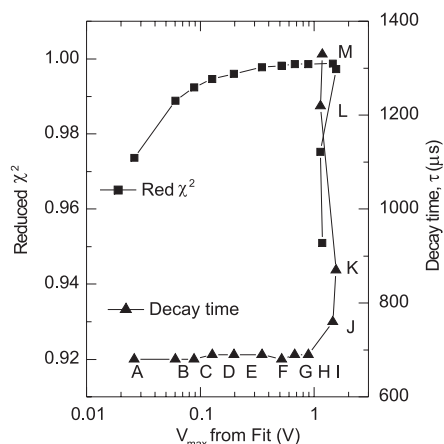

Figure 5. *Decay time and reduced least-squares sum (Reduced χ^2) versus maximum intensity (V_{max}) obtained by the least-squares fit of the uranyl nitrate hexahydrate emission decay curves*

squares fit of these curves, between 0.7 and 2.5 ms, assuming $V = V_{max} \times \exp(-t/\tau)$, gave the fitted parameters V_{max}, τ, and Reduced χ^2, that are plotted in Figure 5. This Figure shows that τ is nearly constant at 685 µs and the reduced χ^2 is greater than 0.97 when V_{max} reaching the photomultiplier is below 1.0V for 1996 Ω termination. Therefore, this 1.0V value corresponds to the maximum signal voltage that assures the acceptable linear response for the photomultiplier for slow signals. Thus, the maximum anode current at the photomultiplier, under these conditions, is 501 µA, higher than that reported by manufacturer's specifications. The 685 µs value obtained for the lifetime of solid uranyl nitrate hexahydrate is in very good agreement with the values 695 µs[20] and 719 µs[21] found in the literature, showing the accuracy of the instrumentation.

In these two experiments, the lowest limit for the photomultiplier response range is given by both, the 5mV/div vertical scale limit (for full 300MHz bandwidth) at the oscilloscope and by the noise magnitude. These two experiments show that the maximum intensity limit to achieve linearity in the photomultiplier response can be extended over its reported maximum DC anode current.

Extraction of the time-resolved laser intensity profile

The extraction of the time-resolved laser intensity profile was done with the TRLS surfaces of the laser pulse with 99.7 Ω (Figure 2), 255 Ω and 498 Ω terminations. Figure 6 shows that the FWHM of the baseline-corrected signals, acquired at 336.93 nm, are 14.4, 21.8 and 34.4 ns for the three terminations, respectively. The curves observed at the oscilloscope are distorted by the RC response time of the instrument and they are the result of the convolution of the real laser pulse temporal profile with the RC response of the instrument. Therefore, in order to extract the "true" laser pulse profile from these observed curves, a deconvolution between the observed (distorted) signal and the RC decay function of the instrument must be performed. The RC decay functions were assumed to be a single exponential decay with RC equal to 6.230, 15.94 and 31.16 ns, for that three terminations, respectively (Table 1 – Observation: the 6.230 and 15.94 ns RC time constants were obtained by extrapolation of Equation 1). The deconvoluted curves showed a FWHM laser profile with 3.4, 3.0 and 3.2 ns, for the 99.7, 255 and 498 Ω terminations, respectively, which are in excellent agreement with the manufacturer's specification (< 4 ns FWHM). These consistent results show that the
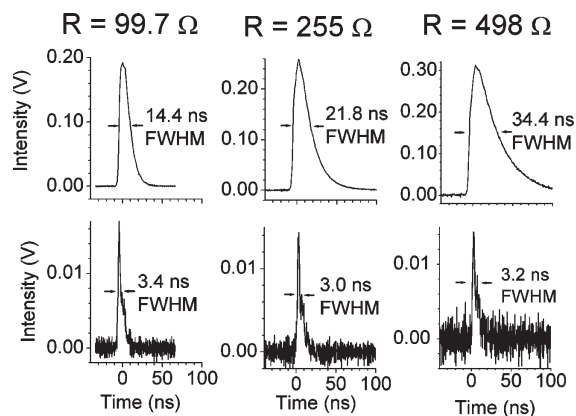

Figure 6. *Time-resolved laser intensity profiles: the top plots show the baseline-corrected, "RC-distorted" temporal profiles of the laser emission at 336.93 nm, with 99.7, 255 and 498 Ω terminations. The bottom plots show the "true" time-resolved laser profile, as obtained by deconvolutions of the observed laser profiles with the single exponential RC response of the instrument, by assuming time constants of Table 1*

photomultiplier still operates within its linear response range, for the terminations 99.7, 255 and 498 Ω. The laser widths obtained fluctuate within 0.4 ns, as we are working at the time limit of the instrumentation, this fluctuation can be assign to the maximum sampling rate of the oscilloscope and to the temporal jitter of the OPTOSYNC trigger pulse. The deconvolution of the signal acquired with the 49.8 Ω termination and with 0.13V maximum intensity, gave a 4.8 ns FWHM laser profile showing that for these settings the photomultiplier response is no longer linear.

CONCLUSION

The goal of the present work was the investigation of the photomultiplier nonlinear response when it is illuminated with pulsed light, in time-domain luminescence experiments. To achieve the photomultiplier linear response range, several investigations had to be performed, such as: (i) Effect of the supply voltage applied to the photomultiplier; (ii) Instrument Response Function with different signal input terminations; (iii) Relationship between the luminescence intensity reaching the photomultiplier and the measured decay time; and (iv) Extraction of the time-resolved laser intensity profile. These investigations showed that the photo-multiplier linear response can be achieved by a simple visual inspection at the oscilloscope screen: Setting the maximum intensity of the luminescence signal below 0.3V guarantees that, for signal input terminations equal or higher than 99.7 ohm, the photomultiplier response is linear. For signals with intensities higher than 0.3V, the photomultiplier response is nonlinear and a distorted decay curve is observed at the oscilloscope. The lowest limit for the photomultiplier linear response is given by the shot noise amplitude, 1.4mV, achieved by setting the photomultiplier high voltage supply to –600V, with the laser EMI noise amplitude minimized by baseline subtraction.

The instrumentation presented in this paper is being used for the characterization of photophysical and photochemical processes in intercalation compounds, macrocyclic complexes, conducting polymers, and photochromic materials by least-squares Levenberg-Marquardt global analysis, whose source code was recently developed in our laboratories. Further improvement in this source code will be made, by the use of the time-resolved laser intensity profile and the instrument response function with reconvolution methods, for the extraction of the excited-state lifetime of luminescence samples at the nanosecond time scale.

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