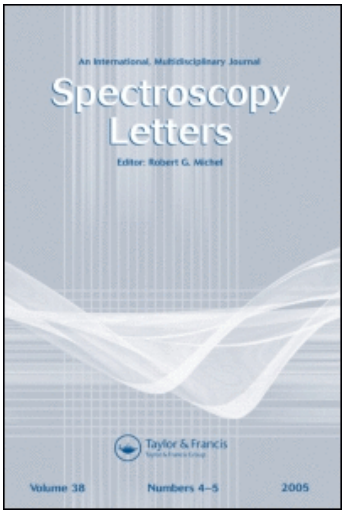

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A. D. Deleva[a]; Z. Y. Peshev[a]
[a] Institute of Electronics, Bulgarian Academy of Sciences, Sofia, Bulgaria

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TEMPORAL INTRACAVITY ABSORBANCE DETERMINATION USING PULSED Ti:SAPPHIRE LASER

Key Words: Laser Intracavity Spectroscopy, Temporal Resolution, Absorbance Determination, Pulsed Ti:Sapphire Laser

A. D. Deleva and Z. Y. Peshev

Institute of Electronics, Bulgarian Academy of Sciences
72, Boul. Tzarigradsko shosse, Sofia 1784, Bulgaria

Abstract

A tunable pulsed Ti:Sapphire laser was used to determine low concentrations using intracavity absorption spectroscopy with temporal resolution. The dependence of the laser-pulse evolution time on the absorbance of a sample introduced in the cavity (solution of 3,3- diethylthiatricarbocyanine iodide in dimethylsulphoxide) was studied theoretically and experimentally. The minimal experimentally measured absorbance was 8×10^{-4}. The possibility was shown of using a Ti:S laser to detect absorbance of 10^{-5} via a temporal technique.

1. Introduction

The Ti:Sapphire lasers possess an exceptionally wide emission spectrum (680 - 1200 nm) covering the absorption lines of many elements and compounds (e.g., K, I, Rb, Cs, Pb, O_3, H_2O, etc). This makes them suitable for such applications as determination of low concentrations by means of intracavity absorption laser spectroscopy[1-3]. This technique exhibits the highest sensitivity when c.w. lasers are employed[4], but some simple-to-use variants of the method are also known[4], having good sensitivity while making use of pulsed lasers.

In Ref [5], a temporal approach was proposed for determination of intracavity absorption: the absorbance of a sample (down to 10^{-3}) was recorded using a pulsed Nd:YAG laser; the ordinary spectral intensities measurements were replaced there by measurements of time intervals.

Since the Ti:S lasers can be tuned within a spectral range of hundreds of nanometers, while the parameters of the pulses emitted (build-up time and pulse width) can vary from a few nanosecondes to a few hundreds of nanoseconds[6-8], they present an attractive opportunity of applying the temporal approach in the determination of low concentrations.

In this work we present the results of absorbance determination carried out by means of an improved by us version of the technique quoted above, where a pulsed laser-pumped Ti:S laser was used. We studied both experimentally and theoretically the dependence of the time-delay of the pulse emitted by the Ti:S laser (with respect to the pumping pulse) as a function of the absorbance of a 3,3-diethylthiatricarbocyanine iodide (DTTCI, Koch-Light Laboratories Ltd) solution in dimethylsulphoxide (DMSO) placed in the cavity. The aim

of the investigation was to analyze the possibilities of using tunable pulsed Ti:S lasers for intracavity determination of low concentrations via measurements of the laser's temporal parameters, as well as to estimate the sensitivity of the method applied in the case of Ti:S lasers.

2. Method of Calculation

When pumped by nanosecond laser pulses, the Ti:S laser operates in the gain-switched mode[6]. The temporal evolution of the laser emission is then analogous to that of "giant pulses" (Q-switching). This allows one to describe well[9] the dynamics of the pulse formation in a Nd:YAG-pumped Ti:S laser by means of the well-known mathematical theory of Q-switched solid-state lasers. We borrowed from there the expression given below in order to estimate the Ti:S pulse build-up time dependence on the absorbance of the sample introduced in the cavity. It yields the delay of the peak of the pulse emitted with respect to the moment of instantaneous Q-switching[10]:

$$t_d = \frac{\tau_c}{x - 1} \ln(q_p) \qquad (1)$$

where τ_c is a photon's life-time in the cavity; $x = E_p/E_{th}$ is the ratio of the pumping energy E_p to the threshold pumping energy E_{th}; and q_p is the number of photons in the cavity at the peak of the laser pulse.

Having transformed Eq.(1) in order to express explicitly the dependence of the laser emission temporal parameters on the cavity losses, we derived the following formula for the delay of the Ti:S pulse peak with respect to the the pumping pulse peak:

$$t_d = \frac{L'}{c_0(k - \gamma)} \ln\left[N_e\left(1 - \frac{1 + \ln(k/\gamma)}{k/\gamma}\right)\right] \qquad (2)$$

where L' is the optical length of the cavity; c_0 is the speed of light; N_e is the number of pumping photons absorbed by the active media; $\gamma = [A - 0.5\ln(1 - T)]$ are the cavity losses; T is the overall transmission of the optical elements in the cavity; $A = cab$ is the sample absorbance; c is the concentration of the absorbing substance; a is its absorptivity; b is the cell pathlength; $k = 4\sigma N_e/\pi\omega_0^2$; σ is the crossection for stimulated emission of the Ti:S crystal; ω_0 is the beam-waist diameter.

Equation (2) enabled us to follow theoretically the relation between the delay of the pulse emitted by the Ti:S laser and the absorbance (respectively, the concentration) of the sample. The following values were used (corresponding to the experimental conditions) for the quantities in Eq.(2): $\sigma = 2\text{x}10^{-19}$ cm^2, $N_e = 9.8\text{x}10^{14}$, $T = 33\%$, $\omega_0 = 0.03$ cm, $L' = 15$ cm.

3. Experimental

3.1 Apparatus

The experimental set-up is shown schematically in Fig.1. It comprised an optical part and a detection system. The optical part included a Ti:S laser and a Q-switched frequency-doubled Nd:YAG laser ($\lambda = 532$ nm, pulse duration $\Delta t = 10$ ns, π-polarization) used for pumping. The Nd:YAG laser output energy could be varied from 0 to 5 mJ, and the energy fluctuations were estimated at 15%. The Czochralski-grown Ti:S crystal had dimensions of 14x6x6 mm and was Brewster-angle cut for π-polarization. The crystal absorbed about 80% of the pumping radiation. The Ti:S laser cavity was of the spherical type and included a dichroic mirror M_1 (reflection $R = 10\%$ at 532 nm, and $R = 100\%$ in the 730 - 820 nm range; radius of curvature $r = 8$ cm), an

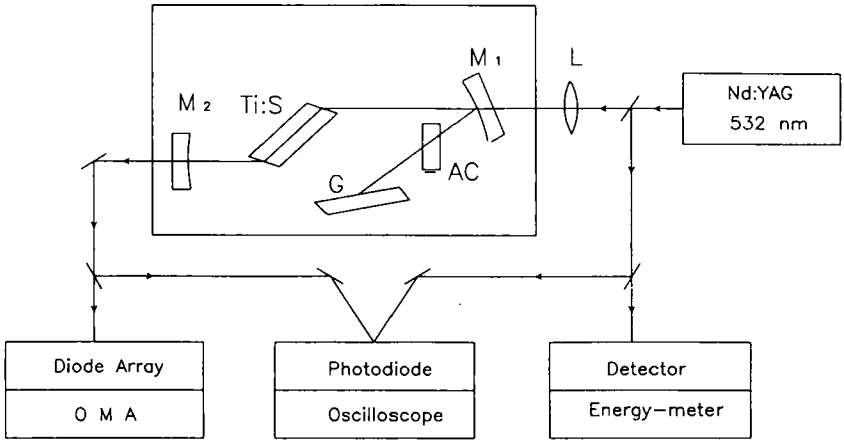

Fig.1. Schematic of the experimental set-up.

output mirror M_2 (R = 92%, r = 7 cm), and a holographic diffraction grating G (Jobin Yvon, 2400 lines/mm). The latter was used to select and tune a line with a width of 0.2 nm from the laser emission. The active element of the Ti:S laser was pumped longitudinally, with the Nd:YAG beam focused into it by means of the lens L (f = 11 cm) and the mirror M_1. A 10-mm pathlength quartz cell containing the solution, was placed in the parallel beam between the mirror M_1 and the grating at an angle of 60^0 with respect to the cavity axis. The concentration of the stock solution was 0.01 mmol/l. In the measurements we used a set of further diluted solutions, down to 1/163 of the stock solution.

The temporal measurements were carried out using a Tektronix oscilloscope and a fast photodiode ensuring time-resolution of 2 ns. The laser energy was monitored by means of a Laser Precision RJ 7200 Ratiometer with a RJP-735 measuring head. The spectral parameters were followed by a computerized system based on a otpical multichannel analyzer (OMA).

3.2 Measurements

A basic feature of the measuring technique used was that we registered the time interval between the peak of the pumping pulse and the peak of the pulse emitted by the Ti:S laser. In this manner, we followed the variation of two temporal parameters (build-up time and pulse width), both of which were affected by the cavity losses. This fact favored an increase of the sensitivity and the dynamic range of the measurements.

During the experiments, the laser system operated in a single-pulse mode, which enabled us to control accurately the energy parameters and to avoid the measurement errors due to the pump energy fluctuations. Inaccuracy of this type is inevitable if the laser operates at high pulse repetition rate with automatic averaging of a large number of pulses, when controlling the energy of each one is impossible [5].

Another feature to be emphasized was that the Ti:S operated near the lasing threshold (1.4 above threshold for a blank solution). Under such conditions, the temporal parameters mesured are most strongly influenced by the degree of exceeding the pump threshold which, in its turn, depends on the cavity losses.

As established by preliminary experiments, as well as by numerical estimates using Eq.(2), the response of the system to changes of the intracavity losses was inversely proportional to the cavity length. We, therefore, shortened the cavity down to 15 cm, a length limited by the laser's design parameters.

4. Results and Discussion

The absorbance spectrum of the stock solution, versus the DMSO absorbance, was measured within the 580 - 800 nm range by using a two-channel SPECORD UV

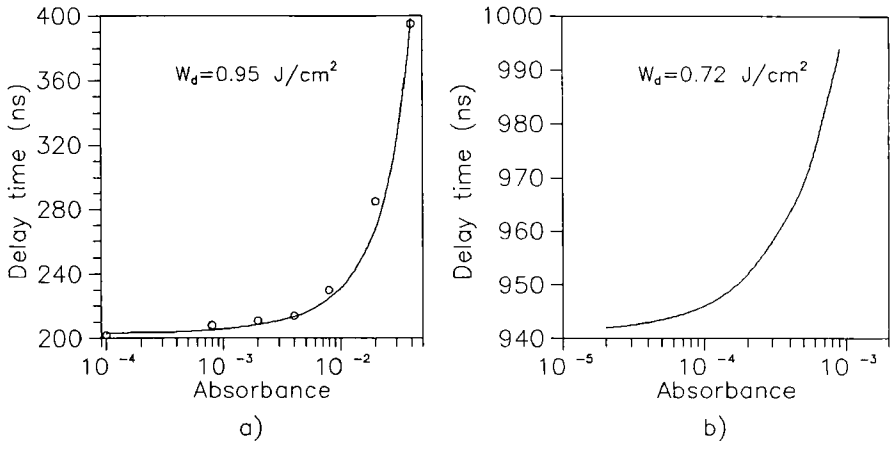

Fig.2. Dependence of the Ti:S-laser pulse delay-time on the sample absorbance.

VIS spectrometer. The spectrum was asymmetric, with a tail extending to the short wavelengths, and a peak at about 765 nm. This peak is very close to the maximum of the Ti:S-crystal IR fluorescence (760 - 780 nm) within which the Ti:S-laser was tuned (at 775 nm). The absorbance for the stock solution at 775 nm was determined to be 0.13.

Fig.2a shows the Ti:S-pulse delay versus the sample absorbance at pump energy density of W_d = 0.95 J/cm^2 (or pulse energy of E_p = 1.2 mJ) at the crystal front face. The points correspond to the experimental data obtained, while the solid line represents the values calculated using Eq.(2). The delay measured for a blank solution was 200 ns, that for the least diluted solution (1/3 of the stock solution concentration), 395 ns, while the delay for the most diluted solution (1/163 of the stock solution concentration) was 207 ns. Each experimental point on

Fig.2a, denoting a specific absorbance value, was obtained as follows: Of all pulses registered, we selected 50 pulses for which the pump energy did not differ from 1.2 mJ by more than ± 5 μJ (i.e., ± 0.4%). The Ti:S-pulse delays, corresponding to these pumping energies, were averaged and the mean value obtained was used to calculate one point on the figure. The maximal deviation of the delay values from the average value computed as described did not exceed ± 3 ns, which was within the error committed when determining the oscilloscope-screen readings. The deviation amounted to ± 0.8% of the average experimental delay value for the stock solution, and ± 1.5% of that of a blank solution. The minimal absorbance detected during the experiments was 8×10^{-4}, corresponding to a concentration of 6.28×10^{-5} mmol/l. Measuring lower concentrations was impeded in our case by the insufficient temporal resolution of the apparatus, and by the difficulties in obtaining laser action when the pump-energy threshold was further approached.

As one can see in Fig.2a, a good agreement exists between the theoretical and experimental results. Based on this, we estimated (using Eq.(2) for W_d = 0.72 J/cm^2, or E_p = 2.55 mJ) the minimal absorbance which could be registered by the system described if the delays were close to those maximally obtained in a gain-switched Ti:S laser (about 1μs) [8]. The results are presented in Fig.2b. It is seen that using a Ti:S laser could make it possible to detect absorbances as low as 10^{-5}.

The results obtained demonstrate that pulsed Ti:S lasers can be successfully applied in measurements of low concentrations in the near IR region.

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