

MODERN ASPECTS OF MEASUREMENT TECHNIQUE FOR EXCITED STATE SPECTROSCOPY

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The paper deals with some special kinds of measurement technique useful for the determination of molecular parameters in higher excited energy states. This technique was developed for special purposes of spectroscopy but is very convenient to solve many other problems connected with ultrafast phenomena in physics and technology.

The selective population of higher excited electron states is of common interest in photochemistry, photophysics as well as photobiology. This definite population makes applicable the great variety of new reaction courses of molecules to new material properties and chemical process courses. A very impressive work in this connection was published by V. S. Letokhov and coworkers [1]: In different excited states (T_1 , T_K , S_n) the same molecule of maleic acid undergoes different reaction courses to different products (isomerization, dimerization, reaction with water, forming a saturated oxyacid).

To use excited levels some problems must be solved: To define the level the molecule was excited to; to define the condition for the effective population of a given energy level; to determine the parameters for the energy transfer within the molecule. To analyse this situation one needs: i) an extensive knowledge of the energy level diagram for the given molecule including all excitation and desactivation channels. ii) the mathematical treatment of the light-matter-interaction under the given condition.

To solve this problem we improved existing ideas creating a new method to overcome the difficulty connected with the manifold of involved levels at the light absorption in the case of organic molecules. Furthermore, we installed a numeric program to combine the theoretical results with measured data. Finally, we developed new experimental apparatus to get the needed information about systems under investigation with high accuracy and high time resolution [2].

A physicomathematical program package was developed based on the measurement of nonlinear absorption or nonlinear emission of light [3]. This program is the basis for a quantitative spectroscopy of excited states of organic molecules, especially of molecules with π -electron systems. This package contains: i) The creation of a start model for the molecular term scheme, which comes close to the real level scheme. This first part includes also the measured data [3]. ii) The second part turns the implicit

information about the molecule parameters into explicit data, e. g. the minimum number and the structure of the level scheme being involved as well as limits for the unknown parameters of the energy transfer like cross section, relaxation time and population density. This part is like a set of information based on an analytical treatment of the rate equations for phonons and population density of the molecular levels [4]. iii) This knowledge is the basis for the numeric calculation with a definite number of levels and a limited range of parameter values.

This code (PISA) calculates the expected measurement data and compares them with the experimental data. A procedure for minimization fits the curves. With the optimized parameters the population density of all levels involved will be calculated as a function of incoming intensity and time [5].

Measurement of the nonlinear absorption behaviour of organic molecules is carried out with the set-up TRANS-1. This equipment is a microcomputer based nonlinear absorption spectrometer for quantitative spectroscopy of excited molecular states [6]. It's main characteristics are given in Table I.

Table I
Trans-1: Microcomputer based nonlinear absorption spectrometer

Determination of the nonlinear absorption behaviour of liquid samples, solid samples, dye solution, biological objects, semiconductors

Techniquial parameters

Excitation: 337 nm; (400 ... 800) nm; $\Delta\lambda \leq 0.1$ nm

Photon flux: $(10^{21} \dots 10^{27})$ photons $\text{cm}^{-2} \text{s}^{-1}$

Pulse duration: 0,6 ns; 2,5 ns

Dynamic range: 6 orders of magnitude

Mode of operation: 2 channel energy measurement

Accuracy of transmission measurement: better than 1 %

At the beginning of our work the system for signal processing was the box-car integrator BCI-280, product of CSI, Ac. Sc. GDR. Now we developed the new system MFA-105, a microprocessor controlled signal analyzer. The main characteristics are given in Table II.

This apparatus was used to determine the relaxation rate constant k_{31} from the S_3 -state to the S_1 -state of chlorophyll-a in dioxane ([3] Leupold, Thesis).

Because of the complicated level structure of chlorophyll-a with the manifold of transitions at a given wavelength, the procedure is rather complex. Firstly, the nonlinear absorption measurement of chl-a in dioxane led to the result that there is a two-step absorption at 670 nm to a S_x -state followed by a nonradiative relaxation $S_x \rightarrow S_1$ with a rate of $7.7 \times 10^{+10} \text{s}^{-1}$.

Table II
 Boxcar-System MFA-105 - A microprocessor controlled signal analyzer (x)

Main Characteristics

- Recording of signals by sampling technique (improvement of SNR; 150, ps time resolution; 4 signal channels; 2 decay units)
 - Computer controlled, programmable (internal Z-80 microcomputer, incorporated graphic display, manual, interface to printer and plotter)
 - Extensive software for signal analysis
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(x) A joint project of CIOS and CSI of Ac. of Sci. of GDR

Now the question arises what the S_x -state is and whether the two-step absorption comes via the S_{10} -state or is interrupted by a S_{1v} to S_{10} relaxation. By variation of the solvent and the pulse duration of the exciting light it becomes clear that there is no S_{1v} to S_{10} relaxation at 670 nm.

In the next step the method of the nonlinear double resonance was used. Two wavelengths (670 nm and 435 nm) are interacting with the sample and the results we get from the 670 nm interaction are used. With help of the nonlinear program package all unknown parameters are determined and we get for the transition S_3 - S_1 the rate constant $k_{31} = 1.6 \times 10^9 \text{ s}^{-1}$, and $T_{31} = 600 \text{ ps}$. This is a rather unexpected value, hence up to now one believes that the relaxation time of higher excited electron states is shorter than 100 ps, mostly in the order of 1 ps. Therefore photochemistry from higher excited states was believed to be highly ineffective.

The presented method gives us more insight in the processes connected with higher excited energy states in complex molecules. Further work in this field is going on.

References

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