

Dynamics of excited electronic states of polyatomic molecules: study by picosecond coherent anti-Stokes Raman spectroscopy

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The vibrational structure and dynamics of an excited electronic state of a polyatomic molecule, nickel octaethylporphyrine, have been measured at a picosecond time resolution for the first time. The experimental method was coherent anti-Stokes Raman spectroscopy. The decay time of the population of a lower-lying excited electronic state T_d of this molecule in tetrahydrofuran has been determined from the kinetics of the coherent Raman spectra: 290 ± 50 ps.

1. In this letter we report a study of the vibrational structure and picosecond-range relaxation processes in excited electronic states of a polyatomic molecule on the basis of the time evolution of its vibrational spectra. We used the technique of coherent anti-Stokes Raman spectroscopy (CARS), combined with a preliminary picosecond pulsed photoexcitation of the electronic subsystem of the nickel octaethylporphyrine (Ni-OEP) molecule. This method has made it possible to follow the temporal dynamics of the changes in the Raman-scattering spectra of the longest-lived excited state of this molecule (the triplet state T_d , which is characterized by a predominant excitation of the Ni atom, while the π -electron system remains essentially unperturbed) and to measure its lifetime ($\tau = 290 \pm 50$ ps). The method which has been developed can be used to study the picosecond dynamics of structural changes in a long list of polyatomic molecules (including biologically active molecules) and to study the electronic-vibrational interaction in excited states of such molecules in a condensed phase.

It has not previously been found possible to experimentally detect the picosecond kinetics of the photoinduced changes in the vibrational spectra of polyatomic molecules in a condensed medium, despite the obvious importance of such measurements and the great amount of information which they would furnish. Several attempts have been made.¹⁻³

2. The present experiments were carried out on a CARS spectrometer with a time resolution⁴ ~ 50 ps. The spectrometer is based on a Nd:YAG laser with acousto-optic mode locking and Q switching and a tunable, synchronously pumped dye laser. These lasers generate trains of picosecond pulses ($\tau_p \approx 80$ ps) with a repetition frequency up to 5 kHz. An electrooptic modulator is used to select a single pulse from the train in the second harmonic of the laser oscillator. The CARS signal is recorded by a photon-counting technique. Fast photomultipliers and a strobing system make it possible to measure the signal in a temporal window of 0.8 ns, with the result that the level of

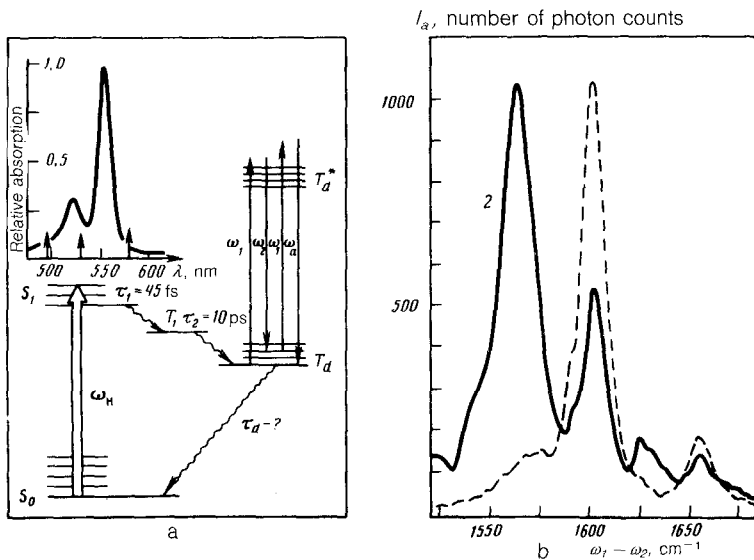


FIG. 1. a: Low-lying energy levels of the nickel octaethylporphyrine (Ni-OEP) molecule and the Q absorption band of Ni-OEP in tetrahydrofuran. The wavy arrows are characteristic pathways of radiationless relaxation between the singlet S_0 , S_1 and triplet T_1 , T_d electronic levels. b: Resonant CARS spectra of a tetrahydrofuran solution of Ni-OEP recorded in the absence of a pump pulse. 1—Weak focusing (lens with $F = 17$ cm), with a peak power $P_1 \approx 1$ kW of the light at the frequency ω_1 ; 2—hard focusing ($F = 10$ cm), $P_1 \approx 10$ kW. The pulse repetition frequency is $f = 1$ kHz.

noise and parasitic illumination is low. The experiment is controlled, and the results processed, by a microcomputer.

The solution studied, Ni-OEP in tetrahydrofuran, has a concentration no higher than 10^{-4} M. The measurements are carried out at room temperature.

In the experiments, the Ni-OEP molecules are excited by an intense picosecond pulse in the second harmonic from the Nd:YAG laser, with a subsequent probing by the resonant CARS method with substantially less intense pulses (Fig. 1a). A picosecond pulse containing more than 90% of the radiant energy at $\lambda = 532$ nm is used as a pump pulse (ω_{pump}). The remainder (10% in terms of the energy) of the second-harmonic (ω_1) pulse and also the pulse from the tunable dye laser (ω_2), after passage through a delay line, constitute the two waves used in the CARS probing. The pedestal is removed from the CARS spectrum (at the frequency $\omega_a = 2\omega_1 - \omega_2$) by a method of polarization suppression of the nonresonant background.⁵

3. Observation of resonant CARS spectra (with the help of nanosecond pulses) from an excited electronic state of Ni-OEP was reported first in Ref. 6, where the frequencies and symmetry of the vibrations were determined. The excitation profiles of several lines were also measured. We have observed the appearance of some additional lines, whose frequencies correlate well with the data of Ref. 6, in the CARS spectrum (Fig. 1b) with increasing intensity of the light at ω_1 and ω_2 in the absence of the pump pulse (ω_{pump}). In the case of low-intensity excitation, we detect a scattering only by

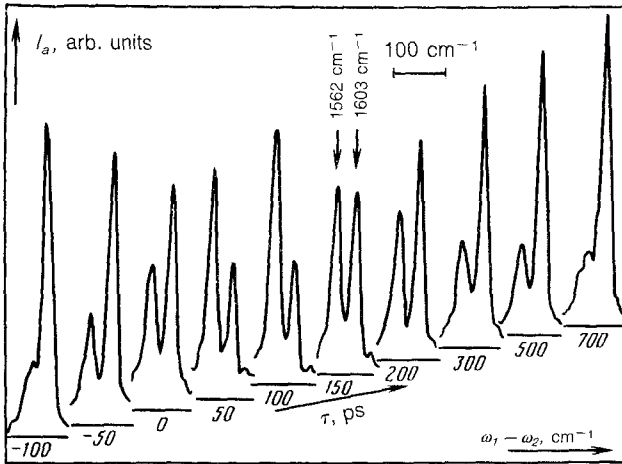


FIG. 2. CARS spectra of Ni-OEP in tetrahydrofuran for various time delays between the exciting and probing pulses. The average power levels of the light at the frequencies ω_{pump} , ω_1 , and ω_2 are 5, 0.5, and 0.4 mW, respectively ($f = 620$ Hz).

vibrations of the S_0 state. In the case of hard focusing, some new bands appear in the CARS spectrum. The high intensity of the “additional” lines at 1562 and 1627 cm^{-1} in the CARS spectra is evidence of an effective population of excited electronic states by picosecond pulses.

Preliminary excitation with subsequent CARS probing made it possible to study the temporal dynamics of the spectra of coherent Raman scattering (Fig. 2). On the spectra we can clearly see the “flare-up” and subsequent decay of the line of Raman scattering from an excited electronic state (1562 cm^{-1}) and synchronized changes in the intensity of a line of Raman scattering from the ground state (1603 cm^{-1}). The number of counts in the maximum of the line at 1603 cm^{-1} is typically more than 1000, while that for the line at 1562 cm^{-1} reaches 400 at delays in the interval $\tau = 0$ – 200 ps (with an accumulation time of 20 s). Under these conditions, there are only a few background counts. The pulses are synchronized on the basis of the level of a coherent signal in the cell holding the solvent. The full width at half-maximum of the autocorrelation function of the CARS signal is 80 ± 30 ps according to these measurements.

4. The resonant CARS spectra (Fig. 2) were simulated with allowance for the interference of the resonant susceptibilities of adjacent lines of Ni-OEP in the vibrational-frequency interval⁶ 1500 – 1700 cm^{-1} . For each delay time, the ratio $\chi_{T_d}^R / \chi_{S_0}^R \propto N_{T_d} / N_{S_0}$, was determined, where χ_{T_d, S_0}^R are the resonant cubic susceptibilities for states T_d and S_0 , respectively, and N_{T_d, S_0} are the populations of the corresponding states. The population ratio N_{T_d} / N_{S_0} was also determined through a numerical solution of the system of kinetic equations for the energy-level scheme in Fig. 2 (the result is shown in Fig. 3). The lifetime found for the T_d state is $\tau_d = 290 \pm 50$ ps, approximately equal to the value found^{7,8} by differential absorption spectroscopy for

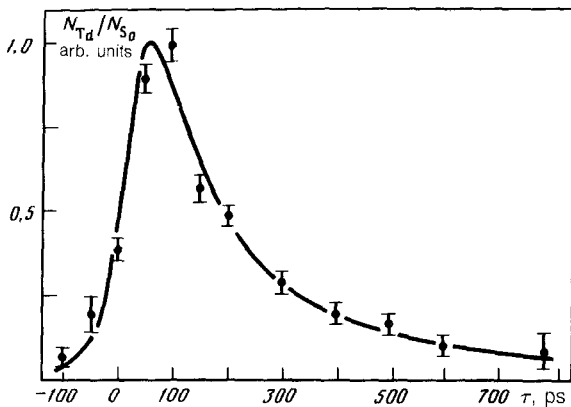


FIG. 3. Ratio of the populations of states T_d and S_0 versus the delay time τ . Points—results of a processing of the CARS spectra; solid line—results of a solution of the kinetic equations with $\tau_d = 290$ ps.

toluene solutions of nickel porphyrines. We can therefore attribute the additional lines observed in the spectra to specifically this excited state. The important difference in the observed vibrational frequencies of identical symmetry types in the electronic ground state and an excited electron state⁶ is evidence of a significant redistribution of the electron charge density upon excitation of the Ni-OEP molecule and of a change in the nature of the electronic-vibrational interaction.

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