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INVESTIGATIONS IN THE WORLD OF ULTRAFAST EVENTS WITH FEMTOSECOND OPTICAL PULSES

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ABSTRACT

Rapid progress has taken place in the generation and application of femtosecond optical pulses. The impact of these developments is being felt in a broad range of scientific fields including physics, chemistry, and biology. This paper reviews the state of the art and describes the application of femtosecond techniques to the examination of nonequilibrium phenomena.

INTRODUCTION

Progress in gaining new understanding of the world of ultrafast events has dramatically increased with the development of new optical pulse generation and measurement techniques. Recently optical pulses with a duration of 6 femtoseconds (1 femtosecond = 10^{-15} second) have been measured and used for experimental investigations [1]. A 6 femtosecond optical pulse contains spectral components that cover a good portion of the visible spectrum and are ideal for obtaining high-resolution time-resolved spectra.

The impact of measurements in the femtosecond time domain covers a broad range of scientific activity. Femtosecond-pulse techniques have contributed significantly to the study of the dynamical properties of molecules and solids. Femtosecond optical pulses have been used to create nonequilibrium, nonthermal population distributions in semiconductors and large molecules. With optical pulses short compared to polarization dephasing times it has been possible to directly observe the process of dynamic spectral hole burning.

PROGRESS IN PULSE GENERATION

The large frequency bandwidth required to generate a short optical pulse has been a major source of difficulty in the generation of ultrashort optical pulses. A fixed-phase relationship must be maintained among all the frequencies oscillating in a mode-locked laser to generate a bandwidth-limited short optical pulse. Until recently, the group velocity dispersion in a laser cavity, due to mirrors, gain medium, and the saturable absorber, limited pulse generation in a dye laser cavity. However, a new device for compensating group velocity dispersion in an optical cavity was invented by Fork et al. [2]. The device consists of two pairs of prisms inserted into the optical cavity of a dye laser. Although the prism is typically made of a positively dispersive material, the prism pair arrangement can produce an adjustable amount of negative dispersion. With this cavity configuration, Valdmanis et al. were able to generate optical pulses as short as 27 fsec [3].

To generate even shorter pulses the bandwidth of the dye gain medium ultimately becomes limiting. A method of overcoming this limitation was first suggested by Gires and Tournois [4] and Giordmaine et al. [5] who proposed that optical pulses be shortened by adapting microwave pulse compression techniques to the visible spectrum.

The process of optical pulse compression is accomplished in two steps. In the first step a "chirp" or frequency sweep is imposed on the pulse. Then the pulse is compressed by using a dispersive delay line.

The pulse "chirp" is achieved by passing the optical pulse through a nonlinear medium; an experimentally convenient medium is a short piece of optical fiber. The intense optical field rapidly changes the index of refraction seen by the optical pulse and impresses the frequency sweep on the optical pulse. The chirped pulse is then passed through a "compressor" which provides the appropriate delay required to remove the frequency sweep and produce a compressed optical pulse.
The pulse compressor is usually a pair of gratings [6] which form a dispersive delay line. Each frequency component is diffracted by the gratings at a different angle and hence makes a different geometrical path through a set of parallel gratings. This type of compressor is adequate when the pulse frequency bandwidth is a small fraction of the carrier frequency. For very short pulses the grating compressor introduces phase distortions across the pulse spectrum and provides a limitation on the achievable pulse width that can be generated. A pair of prisms can also form a dispersive delay line in much the same way as a pair of gratings. By an accident of nature the unwanted phase distortion induced by the grating pair is of the opposite sign as that for a prism pair. The result is that a grating pair followed by a prism pair can correct phase distortions to third order in the phase [1]. Using such an arrangement an optical pulse of 6 femtoseconds in duration has been generated and measured using the second harmonic autocorrelation technique. An interferometric autocorrelation measurement is shown in Figure 1. For purposes of comparison crosses have been used to indicate the calculated maxima and minima for an interferometric trace of a hyperbolic secant squared pulse having zero phase distortion over the bandwidth of the pulse. The well resolved interference maxima also provide a rigorous calibration of the relative delay.

![Figure 1. Plot of the interferometric autocorrelation of a 6 femtosecond optical pulse using the second harmonic technique.](image)

**SPECTRAL HOLE BURNING IN LARGE MOLECULES**

Ultrashort optical pulse techniques provide a unique means for investigating non-equilibrium energy distribution among vibronic levels in large organic molecules in solution. Using femtosecond pulse techniques it is possible to observe time-resolved hole burning and the process of equilibration to a thermalized population distribution.

The absorption spectrum of a large dye molecule is dominated by vibronic transitions from a thermalized ground state. Typically these large molecules, which have a molecular weight of 400 or more, have a correspondingly large number of degrees of freedom. The optical absorption coefficient may be written as a sum over transitions from occupied vibration levels in the ground state to vibrational levels in the excited state. The absorption coefficient is given by

\[
\alpha(\nu) = C \sum_{i} P_i M_i^2 x_{if} \nu g(\nu - \nu_{if})
\]

where \( C \) is a constant, \( P_i \) is the thermal probability of the initial state, \( M \) is the dipole moment of the electronic transition, \( x_{if} \) is the Franck-Condon factor and \( g \) is the lineshape profile for each transition. The above expression describes the molecular system in thermal...
equilibrium. With a short optical pulse it is possible to excite a band of states that are resonant with the pumping energy. Before the molecular system comes into equilibrium, bleaching is observed in a spectral range determined by the convolution of the pump spectrum with the line shape profile of the individual transitions. As time progresses the system relaxes to the thermal equilibrium due to interaction with the thermal bath. The thermal bath couples to the vibronic levels by both intramolecular and intermolecular processes.

Femtosecond pulse techniques make the experimental investigation of such nonequilibrium processes feasible [7]. The experimental apparatus is arranged to pump the sample with a 60 femtosecond optical pulse and a second shorter and weaker pulse of 10 femtoseconds in duration is used to probe the sample absorption. The shorter pulse is used to probe the absorption spectrum of the molecule by passing through the excited sample into a spectrometer and a diode array. The broad spectrum of the short probing pulse allows the measurement a good portion of the $S_1$ transition of the absorbing molecule.

In Figure 2 we have plotted the absorbance spectrum of the molecule cresyl violet near zero time delay between the pump and the probe before and after excitation. Note that a reduction in the absorbance is observed near the pumping wavelength with additional replica holes above and below the main hole.

![Figure 2. Plot of the absorbance spectrum of the molecule cresyl violet near zero time delay before (solid line) and after excitation (dashed line) with a 60 femtosecond optical pulse.](image)

The mechanism for the formation of the replica holes is readily understood. Measurements of the Raman spectra of cresyl violet [8] reveal the presence of a strong mode at 590 cm$^{-1}$. In a large molecule with a large number of degrees of freedom a correspondingly large number of modes can contribute to the absorption spectrum as was illustrated in equation (1). Usually only a few modes called active or system modes with energies larger than kT change their occupation number during a transition to the excited state. The strength of the absorption is determined by the Franck-Condon factor, $X_{if}$. The 590 cm$^{-1}$ mode appears to be the dominant mode in the absorption spectrum as evidence by bleaching both at the 0-0 transition, which is at the excitation energy, and the 0-1 and 1-0 positions of the Franck-Condon progression.

In Figure 3 we plot the differential absorbance spectra as a function of relative time delay between the pump and the probe. The holes broaden and relax to the quasiequilibrium spectrum within the first few hundred femtoseconds.
Figure 3. Differential absorbance spectra plotted as a function of relative time delay following excitation with a 60 fs optical pulse at 618 nm for the molecule cresyl violet.

REFERENCES