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Femtosecond laser studies of ultrafast processes in semiconductors and large molecules

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Résumé. — Les considérations fondamentales sous-jacentes à la technique de transmission-corrélation optique basée sur le système laser 40 fs à haute cadence de répétition sont passées en revue. Des résultats récents sur la dynamique de relaxation des porteurs non équilibrés dans GaAs ainsi que dans des composés et structures apparentés et des molécules de colorants photoexcitées sont résumés.

Abstract. — The basic considerations underlying the optical transmission-correlation technique based upon the high-repetition-rate 40 fs laser system are reviewed. Recent results on the relaxation dynamics of nonequilibrium carriers in GaAs and related compounds and structures and photoexcited dye molecules are summarized.

1. Introduction.

As the articles in this special issue clearly indicate, experimentally there are two basic approaches in the use of the recently developed femtosecond lasers to study ultrafast processes in optical materials. One is to use the pulses from the femtosecond lasers directly to do experiments [1-5]. The other is to further compress [6, 7] such pulses in order to get even shorter pulses or use the pulses from the laser to generate a continuum of other wavelengths to do the experiments. On the surface, the second approach being more versatile offers great appeal. However, the trade-off is in the pulse repetition rate, which is important if high signal-to-noise ratio in the experiments and, hence, accurate quantitative information are to be obtained. Coming directly from a femtosecond dye laser, at the present time, typically 2 eV photons with 40 fs width at 10^8 Hz rate can be routinely achieved for experimental purposes. Followed by pulse compression schemes, pulses as short as 6 fs have been achieved. Short pulse broad band continuum generation can also be achieved through self-phase modulation of the laser pulses in water or ethylene glycol [8]. Both schemes require amplifying the pulses from the femtosecond dye laser which drastically reduces the pulse repetition and, hence, data acquisition rate (at the present time, by 4 to 5 orders of magnitude), which translates into poorer experimental signal-to-noise ratio. In the

case of continuum generation, it is also often done at the expense of pulse width and repetition rate (with a few exceptions, typically 150 fs or longer and at a rate of a few kHz or less). Since accuracy in the final experimental results depends on both the time resolution and amplitude stability, whether the increased time resolution of compressed pulses actually translates into more accurate data will depend upon the type of data being collected and the signal processing scheme used in the experiment. There are many papers in this issue discussing the short pulse low-repetition-rate approach. In this paper, we review our work based on the 40-fs high-repetition-rate optical correlation spectroscopic approach to obtaining quantitative information on the ultrafast relaxation dynamics of hot carriers in semiconductors [2-4] and photo-excited large organic dye molecules [5]. In both types of materials, because multiple relaxation processes as fast as 40-fs or less are present simultaneously, there is no choice at the present time but to use the high-repetition 40 fs laser system to obtain usable quantitative information.

Since each pulse can be used to obtain information on the relaxation dynamics, the high-repetition-rate system allows a much higher data acquisition rate. This is important for obtaining a high signal-to-noise ratio through signal averaging. The high pulse rate makes it possible to signal average over many scans per data trace within a reasonable time frame. For example, in the experiments to be discussed below,

signal-to-noise ratio well over 60 dB (peak signal to background noise ratio of 1000) or more are made possible because each data trace is averaged over 10^4 scans at the rate of 10 scans per second with a total amount of time required on the order of 10 to 20 minutes. It is not possible to signal-average to the same extent within a reasonable time period with the kHz system. The details of the experimental setup and signal processing scheme are discussed in the following section.

The basic optical technique most commonly used is the pump-probe technique. In this technique, the material system to be studied is first perturbed or excited by a « pump » pulse. The response of the system to the pump pulse is then measured by observing the effects of perturbed system on the probe pulse. Experimentally, the problem is often complicated because the response of the system often consists of processes with relaxation times ranging from as short as the optical pulse widths to much longer than the scanning time of the experiment. Also, the data from pump-probe experiments require extensive processing before they can be analysed. Thus, separation of the slow process from the fast processes in the material response function can be quite difficult. The use of the optical correlation technique experimentally and automatically removes the signature of the slow process from the data and, thus, allows the data which contain only the effects of the fast processes to be analysed directly without preprocessing.

The optical correlation technique is a variation of the pump and probe technique in the sense that it is a time-delay symmetrized version of the latter. In this case the pump and probe pulses are symmetrized and not distinguished. In the transmission-correlation technique, for example, two equal trains of pulses with a variable delay between the two are sent through the sample. The total transmission of both trains of pulses are measured as a function of delay between the two. If the delay between the pulses is far longer than the relaxation time being measured, the excitations of the two are independent of each other and the total is independent of the delay. Otherwise, the excitations of the two influence each other and they are « correlated ». Thus, the total transmission of the two contains information on the dynamics of the system. On a time scale short compared to the relaxation time corresponding to the slow process, the slow process will just provide a constant background in the transmission-correlation trace and can, thus, be ignored. It avoids, therefore, the necessity of removing the effects of the slow process from the data before analysis. The basic rationale and theory for transmission-correlation spectroscopy including the effect of quantum beats [5, 10] have been discussed extensively in the past. The main idea will be summarized in section 2.1.

This is the technique we used for the bulk of our experiments.

In order to produce quantitative information, it is equally important to be able to extract the relaxation time constants from the data accurately. This requires a reliable data reduction procedure as well as high quality data. The problem is complicated by the fact that often the time dependence of the measured parameter is a manifestation of several competing relaxation processes. In addition, there may be other time-dependent experimental artifacts (e.g. coherent artifact) present in the data. The conventional approach is to plot the data on a semi-log scale and then fit it by the best straight lines. This approach is reasonable if the data have little noise, no coherent artifact, and only one or at most two exponential components. This is not the case for the relaxation dynamics of hot carriers in semiconductors or large molecules. Conventional nonlinear fitting procedures are not practical when the number of exponential or damped sinusoidal components are not known and if this number is large. This is because four parameters are required to characterize each damped sinusoidal component and the nonlinear fitting procedure depends upon the initial trial values ; anything more than one or two components makes it practically impossible to carry out. A recently developed linear-prediction least-square fitting procedure is shown [11] to be a powerful numerical tool for quantitative analysis of optical correlation and pump-probe type of experiments. The main considerations of this method in the context of optical experiments are discussed in section 3.

Femtosecond optical correlation spectroscopy has been applied mainly to two types of problems in our laboratory. The first is to the study of the initial relaxation of photoexcited nonequilibrium carriers in III-V compounds and structures [1-4] and the second category is to the study of the relaxation dynamics of photoexcited dye molecules [5]. In the latter connection, we have observed for the first time quantum beats on a femtosecond time scale. Recent results in both topics are summarized in section 4.

A fact not always clearly appreciated in connection with femtosecond laser studies of the relaxation dynamics of hot carriers in semiconductors is the following. The qualitative picture of the relaxation dynamics is quite well known based on years of extensive studies of the transport properties of the carriers in various semiconductors and device structures carried out by workers in electronic device research. If optical studies are to have anything to contribute beyond confirming earlier known results, they must produce more reliable quantitative results. This is the motivation of our work at Cornell and has dictated our choice of these particular experimental and data analysis methods. The task is a promising but very difficult one.

2. Experimental.

2.1 OPTICAL CORRELATION SPECTROSCOPY. — In optical correlation spectroscopy, two pulses with a variable delay between them are applied to the sample and the reaction on the pulses is measured as a function of the delay. In the cases of optical transmission or reflection-correlation spectroscopy, for example, the total transmission or reflection, respectively, of the two pulses is measured as a function of the delay.

Consider for example the application of the transmission-correlation technique in the context of measuring the ultrafast relaxation dynamics of nonequilibrium carriers in GaAs and related compounds and structures. If the carriers generated by both pulses see each other, there is a mutual saturation effect leading to an increased transmission of the two pulses. Thus, the total transmission of both pulses as a function of delay between the two, which is called the transmission-correlation peak (TCP) measures the relaxation dynamics of the photo-excited carriers. In fact, the TCP is the convolution of the autocorrelation of the optical pulses with the response function of the photo-excited carriers plus whatever coherent artifact there may be. Comparison of the TCP with the pulse auto-correlation trace gives the relaxation times of the photo-excited carriers. Any slow decay process with a relaxation time constant much longer than the total scan time will just give a constant shift in the base line. Processes fast compared to the scan time will appear as symmetric peaks above this base line. Experimentally, the symmetry of the peaks is a valuable indication of satisfactory alignment.

In contrast, in conventional pump-probe measurements only the transmitted probe pulse is measured. The slow process gives rise to something like a step function, which is the convolution of the intensity autocorrelation of the optical pulses with an abrupt step plus whatever coherent artifact there may be. The fast processes modify the shape of this step function around zero delay. To determine the relaxation times of the fast processes, the part of the step function due to the slow process must first be subtracted. The part to be subtracted often can be a very large fraction of the total signal and a separate experiment is needed to determine the zero-delay position; these contribute uncertainties to this procedure. In addition, the lack of a quick experimental indication, such as the symmetry of the TCP, of whether proper alignment is achieved is another drawback.

The theory of the transmission-correlation technique is discussed in detail in reference [1]. A full density-matrix theory for the transmission-correlation signal including finite homogeneous and inhomogeneous dephasing and possible quantum beats

is given in references [10] and [16]. Applications of this technique to various semiconductor and molecular problems are discussed in references [2-5].

2.2 EXPERIMENTAL SETUP AND PROCEDURE. — All of the measurements discussed in this paper were made with the experimental arrangement which is diagrammed schematically in figure 1. The colliding-pulse modelocked ring dye laser [12] produces very clean 40 fs pulses at a pulse repetition frequency of 10^8 Hz, with an average power of 10 mW per arm. The SF10 glass prisms external to the laser resonator compensate for the dispersion of transmitting optics (mainly the focusing objective) and are adjusted so that all experiments are performed with minimally chirped pulses. The intensity autocorrelation is measured after the pulse traverses optics which are identical to those in the experiment. Two collinear beams of equal intensity are produced in a standard Michelson interferometer and are focused onto the sample by a microscope objective. The average power transmitted by the sample is detected by a slow photodiode and recorded as a function of delay between the pulses. In the experiments described here the sample was either an optically thin semiconductor membrane (mounted in a cryostat when low temperatures were required) or a 30- μ m thick jet of organic dye in solution.

Fig. 1. — Schematic of the experiment. CPM-colliding pulse modelocked ring dye laser; SF10-SF10 glass prisms; CC-corner cubes; $\lambda/2$ -1/2 wave plate; MO-microscope objective, S-sample; PD1, PD2-photodiodes; PZT-piezoelectric transducer; CA-current amplifier, DSO-digital storage oscilloscope.

The achievement of exceptionally high signal-to-noise ratios depends on two key observations. First, in experiments which measure transmitted light, the noise which accompanies the desired signal is temporally correlated with the fluctuations of the laser source. In addition, the fluctuations of the passively modelocked source tend to be clustered at low frequencies. When the nonlinearity which is respons-

ible for generating the correlation signal is small, as is the case in semiconductors and molecules, noise can be reduced significantly by detecting the difference between the transmitted and incident powers. This offers the additional advantage of increased dynamic range for the nonlinear portion of the signal. In virtually all pump-probe experiments, delay is controlled by a stepping motor, and synchronous detection is employed for noise reduction. Guided by the noise spectrum of the dye laser source, we have found that higher signal-to-noise ratios can be obtained by varying the delay as rapidly as possible and simply averaging the separate scans. A piezoelectric transducer controls delay in our interferometer, and the full range of delay values (up to 6 ps) is covered in 50 ms. 2×10^4 independent scans are acquired in 15 min, and this is generally sufficient for the measurement of nonlinear transmission $\Delta T/T = 10^{-3}$ with a signal-to-noise ratio on the nonlinear signal of 60 dB. With rapid scanning, fluctuations appear as overall shifts of the transmission-correlation baseline; these average to zero quickly, and in any case do not affect the nonlinear signal.

Of course, the elimination of random noise is only valuable if systematic errors can be reduced to the same level. Imperfect optical alignment is the primary source of systematic errors in these experiments. The transmission-correlation measurement provides a direct evaluation of the alignment through the required symmetry of the observed signal about zero delay. In practice, the signal is adjusted for perfect symmetry before a trace is recorded. Without this « real-time » feedback, it is doubtful that precision measurements could be made. With imperfect alignment the two halves of the data produce completely different quantitative results.

The signal-to-noise ratio of the data acquired using this system can be exceptionally high. Figure 2 shows a typical transmission-correlation trace obtained for a relatively thick ($\sim 1 \mu\text{m}$) GaAs sample. This trace is an average of 10^4 scans. The signal-to-noise ratio is 80 dB. Because the sample is optically thick and the light intensity varies significantly through the sample, the interpretation of the data is quite complicated. Typically, we use optically thin semiconductor samples for data analysis. In such cases, the signal-to-noise is not quite as good, typically 60 dB.

3. Data analysis. Linear prediction least squares fitting procedure.

It is shown in the previous section that the high-repetition-rate femtosecond laser system is capable of yielding exceptionally good TCP data, although with the currently available laser it is restricted to a photon energy of 2 eV. Extracting the relaxation

Fig. 2. — Transmission-correlation results for thick ($\sim 1 \mu\text{m}$) GaAs sample and carrier density of 10^{18} cm^{-3} . Only the positive-delay half of the symmetric trace is shown.

time constants from such data is a difficult problem. The complication is due to the fact that there are usually an unknown but large number of competing relaxation processes present. Without a systematic and reliable procedure, totally erroneous relaxation times may result. To give a clear example, a set of simulated data is shown in figure 3. This curve is the sum of three decaying exponential terms, with time constants of 40 fs, 150 fs and 1.5 ps. If one were to qualitatively fit straight lines through the data in this semi-log plot, it is easy to conclude that the long-time asymptote seems to give a long relaxation time of 1.5 ps. The short-time asymptote seems to give a relaxation time constant of 70 fs. The curved region in between is just the transition region and could be ignored. These results are incorrect, however, since the curved transition region contains an intermediate relaxation process that is not obvious in such a fitting procedure. Neglecting this intermediate process significantly affects the prediction of the short time constant. On the other hand, application of the linear-prediction procedure to the data shown in figure 3 to be described below did produce the three correct time constants (40 fs, 150 fs, and 1.5 ps). In general, an incorrect choice of the number of components produces time constants which may not coincide with any of the correct values. Of course, the analysis of experimental data is further complicated by the fact that the trace is a convolution and by the presence of the coherent artifact.

Fig. 3. — Simulated carrier response function, illustrating the difficulty of extracting multiple exponential decay components reliably. The solid lines represent exponential decays with time constants of 70 fs and 1.5 ps. The actual values are 40 fs, 150 fs and 1.5 ps.

To circumvent this data analysis problem, we carried out an extensive evaluation [11] of a recently developed linear-prediction least-squares fitting procedure [13]. The basic idea is the following. Assume the data $y(t)$ is to be fitted to an unknown number of exponentials and damped sinusoids :

$$y(t) = \sum_{i=1}^N a_i \exp(-t/T_i) \cos(2\pi\nu_i t + \phi_i).$$

The usual nonlinear numerical fitting procedure would first of all arbitrarily pick a number N . After that one would start from a set of initial trial values of the amplitude, damping constant, frequency and phase angle for each component and calculate $y(t)$ and then iterate. Because the relationship between the unknown parameters and the data to be fitted is nonlinear, the convergence of the iterative procedure depend highly on the initially chosen trial values. It may take a long time to or it may never converge. Even if it does, a wrong choice of N may render the results totally meaningless as the example discussed in the previous paragraph shows.

On the other hand, invoking the principle of (autoregressive) linear prediction reduces the least-squares fit to a linear procedure, thus eliminating the difficulties inherent to the nonlinear iterative procedure. In the linear prediction procedure, expressing each element of the time series as a linear

combination of some number K of the previous elements,

$$x_n = \sum_{i=1}^K c_i x_{n-i}$$

produces an overdetermined set of linear equations (relating the data points x 's to the unknown coefficients c 's linearly) which can be solved with the aid of singular value decomposition and yield the desired values for the parameters, the a 's, T 's, ν 's, and ϕ 's. The mathematical details are discussed in reference 13 and the references therein. Significantly, the number of terms in the series (N) is not fixed, but is chosen after consideration of the singular value decomposition. Note that, with N not fixed, the terms in the series form a complete set and $y(t)$ can fit any arbitrary function. A detailed evaluation of the possible sources of error and the limits of applicability of this procedure is given in reference [11]. This procedure is found to produce reliable relaxation time constants from the experimental data. For values of fractional coherent artifact less than 0.5 and signal-to-noise ratio greater than 40 dB, the linear prediction routine can extract time constants as short as half the pulse duration from pump-probe data with approximately 10 % accuracy. In order to distinguish as many as three exponential terms, one of which has a time constant roughly equal to the pulse duration, a signal-to-noise ratio of greater than 60 dB is required. The beginning of the signal can be truncated at delay values larger than the autocorrelation fwhm without introducing an error in the time constants of more than 10 %. This is true even when the signal is dominated by a time constant less than the length of the pulse.

4. Results and discussions.

4.1 FEMTOSECOND RELAXATION OF NONEQUILIBRIUM CARRIERS IN SEMICONDUCTORS. —

The initial relaxation of carriers following photo-excitation by femtosecond laser pulses are studied using three types of semiconductor samples : (1) a thin (0.3 μm) layer of uncladded $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, (2) a thin (also 0.3 μm) layer of intrinsic GaAs cladded by 0.15 μm layers of transparent (to 630 nm light) $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$, and (3) a MQW structure made of seven 14.5 nm thick GaAs layers alternating between 36 nm thick $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$ barriers. The sample thickness is a crucial parameter. In general, because of the possibility of propagation effects and the strong variation of carrier density in the sample, interpretation of the results for optically thick ($> 0.3 \mu\text{m}$) samples is extremely difficult ; the samples used for transmission-correlation type of experiments must, therefore, be kept thin to obtain meaningful results.

Because the high-repetition rate femtosecond laser wavelength is fixed at about 1.97 eV, all our fem-

tosecond data refer to this photon excitation energy and at room temperature. Typical room-temperature transmission-correlation data obtained are shown in figure 4. Using the procedure discussed in the previous section, the relaxation times obtained from the type of data shown in figure 4 are given in table I.

Several special features are of particular interest : in all of the cases studied, there is a fast relaxation component on the order of 40 fs. In the cases of GaAs and AlGaAs bulk samples, but not the quantum well sample, there is an intermediate component with a relaxation time on the order of

Table I. — *Summary of the decay parameters for photoexcited electrons in semiconductors. Values are appropriate for carrier density of $3 \times 10^{18} \text{ cm}^{-3}$. Processes listed with negative amplitudes are « rising wings ». Amplitudes are normalized so that $y(t = 0) = 1$.*

$y(t) = \sum a_i \exp(-t/T_i)$			
Material	Polarization	a	T (fs)
$\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$	parallel	0.85	39
		0.10	140
		0.05	1 650
	orthogonal	0.81	46
		0.13	145
		0.06	1 750
GaAs	parallel	1.02	34
		0.09	160
		- 0.11	1 650
	orthogonal	1.04	40
		0.11	200
		- 0.15	1 700
MQW	parallel	1.67	45
		- 0.67	3 000

Fig. 4. — Typical transmission-correlation results (a) $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, (b) GaAs, and (c) GaAs/AlGaAs multiple quantum-well structure. Only the positive-delay halves of each trace are shown, and the pulse autocorrelation is shown (dashed lines) for delays greater than 80 fs.

150 fs. Finally, there is a « rising-wing » component (as indicated by a negative amplitude) with time constants of 1.7 ps and 3 ps, respectively, for GaAs bulk and quantum-well samples. Note that the appearance of a negative amplitude in the sum of decaying exponential components implies that the transmission increases with delay. This increase in transmission eventually becomes a decay component well beyond the scan range.

We believe that both the experimental data and the relaxation times extracted from the data are highly accurate and reliable. The interpretation of the physical origins of the relaxation components observed require additional considerations. First of all, we believe that the observed decay in all cases was due primarily to the relaxation of excited electrons, because of the large difference in effective masses of the electrons and holes and the expected very large hole-hole scattering rate. The fast component around 40 fs is due primarily to scattering to the satellite valleys (mainly L-valley) with about 30 % contribution due to carrier-carrier and plasmon scattering. This is ascertained on the basis of measurements carried out on $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ at cryogenic temperatures [3]. By temperature-tuning the band-gap of this material, it is possible to eliminate selectively various processes leading to the relaxation of hot electrons excited by 2 eV photons. From such results, the physical origins of the various observed relaxation components could be determined. In particular, the contributions due to intervalley and carrier-carrier scattering were determined by comparing the responses measured with and without the presence of intervalley scattering. In either case, a roughly 40-fs component is obtained; the relative amplitudes of this component in the two cases provide a direct measure of the carriers which leave the initial states by each process. Theoretical estimates [1] based upon the generally accepted indirectly determined deformation potential scattering constant ($D = 10^9$ eV/cm) do give a Γ to L valley scattering rate of this order. Recent Monte-Carlo calculations [14] confirm this assignment of the 40 fs component.

The intermediate component (approximately 150 fs) observed in both the GaAs and AlGaAs bulk samples is most probably due to polar-optical phonon scattering within the Γ valley. The temperature scanned results [3] and Monte-Carlo calculations [14] confirm this interpretation. The absence of the intermediate relaxation component in quantum wells is not well understood at this time.

The « rising-wing » component observed in GaAs and GaAs/AlGaAs quantum wells has been shown [4] to be due to a dynamic band-filling effect (or Burstein-Moss shift), which leads to the saturation of the transition from the split-off band. It is absent in the data for the $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ sample because, for

2 eV photons, direct transition from the split-off band is forbidden for AlGaAs of this composition. The rate of rise of the wings gives the return rate of scattering from the L-valley minimum to the central Γ -valley. It is 1.65 ps in bulk GaAs and on the order of 3 ps in the quantum well studied. A similar result on bulk GaAs based on mobility studies has more recently been reported [15]. The peak [4] of the rising-wing is at about 2 to 3 ps in bulk GaAs and 5 to 6 ps in the multiple quantum well studied. This is, therefore, approximately how long it takes for a quasi-equilibrium distribution to be established near the bottom of the conduction band at room temperature after the electrons scatter away from the initially photo-excited states.

It should be pointed out, however, that with the exception of the results on quantum wells most of the conclusions and results based on optical studies reported so far in the literature related to the relaxation dynamics of hot carriers in bulk III-V compounds basically confirm earlier known qualitative results based upon transport studies. The challenge remains in coming up with new information and better quantitative results.

4.2 RELAXATION DYNAMICS OF LARGE MOLECULES. — The problem of the relaxation dynamics of photoexcited dye molecules is somewhat analogous to the semiconductor problem, where the ground and excited vibronic bands of the molecule are the analogs of the valence and conduction bands, respectively, of the semiconductor. We are interested in relaxation of the molecule following photoexcitation by a femtosecond pulse well into the excited vibronic band. Experimentally, instead of the semiconductor samples, a thin dye jet, as typically used in dye lasers, is used in the experiment. On a femtosecond time scale, the molecule can be considered as isolated even though it is in a condensed phase because the collision frequency with the solvent molecules is typically in the picosecond time domain. A large number of dye molecules have been studied using the optical correlation spectroscopy approach described in this paper. Figure 5 shows a typical experimental trace, and the relaxation parameters obtained by fitting the data with the procedure described above are summarized in table 2.

The most interesting feature in these results is perhaps the damped oscillatory decay observed in several of the dyes. Malachite green, ethyl violet, methyl violet, and victoria blue are all triphenyl methane dyes, and each exhibits a single damped sinusoidal term. These are quantum beats [5, 10, 16] resulting from coherent excitation of split levels either in the excited or ground vibronic bands of the molecule. Work is underway to resolve definitively which is the case. Raman and infrared spectra of

Fig. 5. — Malachite Green transmission correlation. The symbols are the data points, and the solid line is the best fit to the data.

these molecules [17] indicate that quantum beats occur between different vibrational states of the same electronic level. This experiment thus constitutes a time-domain observation of molecular vibrations. The multiple oscillatory components observed in Nile Blue and DODCI dyes suggest the possibility of obtaining vibrational spectra in real time with this technique. Theoretical analysis [10] suggests that the decaying exponentials are due to intramolecular population relaxation from states not associated with the quantum beats.

5. Summary.

The experimental issues involved in the use of femtosecond lasers and related techniques for studying the relaxation dynamics in semiconductors and large molecules are discussed. In particular, the basic considerations underlying the optical transmission-correlation technique based upon the high-repetition-rate 40 fs laser system are reviewed. The key advantage of the high-repetition-rate system is that the high data-acquisition rate allows effective time-averaging to achieve high signal-to-noise ratio. In the case of semiconductors in particular, where the challenge is to produce better quantitative results than those possible from transport studies, good signal-to-noise is particularly important.

The initial relaxation dynamics of nonequilibrium carriers in GaAs and related compounds have been studied using the optical transmission-correlation

Table II. — Summary of the decay parameters for photoexcited organic dye molecules. The amplitudes are normalized so that $y(t = 0) = 1$.

$y(t) = \sum a_i \exp(-t/T_i) \cos(2\pi\nu_i t + \phi_i)$					
Molecule	a	T (fs)	ν (THz)	ϕ (deg)	
Malachite Green	0.58	75			
	0.36	4 800			
	0.06	205	6.60	11	
Ethyl Violet	0.60	120			
	0.33	1 700			
	0.07	380	6.45	7	
Methyl violet	0.55	39			
	0.23	2 650			
	0.19	150			
	0.03	280	6.40	7	
Victoria Blue	0.57	30			
	0.31	10 000			
	0.11	105			
	0.01	190	6.14	13	
Methylene Blue	0.98	27			
	0.01	1 470			
	0.002	380	7.7	2	
DODCI	0.47	185	0.87	5	
	0.32	1 050			
	0.09	370	6.35	3	
	0.07	300	2.61	9	
	0.03	180	8.17	93	
	0.02	500	5.00	8	
Nile Blue	0.72	43			
	0.20	400			
	0.04	180	4.86	140	
	0.02	490	3.06	87	
	0.006	560	5.00	12	
	0.005	405	8.39	144	
	0.005	4 300	2.16	21	
	0.0007	4 700	6.96	73	
	0.0004	3 900	9.12	93	
	0.0003	11 500	10.6	27	

technique. Quantitative results for the intervalley, intra-valley polar-optical phonon, and carrier-carrier scattering rates are determined.

In the case of dye molecules, in addition to ultrafast exponential relaxation components we have also observed damped oscillatory decay components in the femtosecond time domain. These are interpreted as quantum beats due to split-levels in either the excited or ground vibronic bands of the molecules.

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