tion[14] of $P(\sigma, t)$ reduce after a single RG step ei-
ther to the form assumed in this work or to
terms of second order in the intercell interaction.
Of course, if the RG is performed to higher or-
ders in the cumulant expansion, more terms
must be used in $\varphi(\sigma, t)$ and the effective time-de-
pendent Hamiltonian and transition probability be-
come more complicated than the simple nearest-
neighbor form.

We have used this method in the second-order
cumulant approximation and confirmed dynamic
scaling to this order. The calculations are
lengthy and memory effects unavoidable. Details
will be published elsewhere.

(a)On leave from University of Birmingham, Birming-
ham B15 2TT, England.

[1]B. I. Halperin, P. C. Hohenberg, and S.-k. Ma,
Phys. Rev. Lett. 29, 1548 (1972), and Phys. Rev. B 10,
139 (1974); P. C. Hohenberg and B. I. Halperin, Rev.
Mod. Phys. 49, 435 (1977).

[2]C. de Dominicis, E. Brézin, and J. Zinn-Justin,
Phys. Rev. B 12, 4945 (1975).

[3]C. de Dominicis, S.-k. Ma, and L. Peliti, Phys. Rev.
B 15, 4313 (1977).

[4]S.-k. Ma, Modern Theory of Critical Phenomena
(Benjamin, New York, 1976).

[5]Y. Kuramoto, Prog. Theor. Phys. 51, 1712 (1974);
K. Kawasaki and J. Gunton, Phys. Rev. B 11, 4658
(1976).

[6]S.-k. Ma, Phys. Rev. Lett. 37, 461 (1976).

[7]T. Niemeijer and J. M. J. van Leeuwen, in Phase
Transitions and Critical Phenomena, edited by C. Domb
and M. S. Green (Academic, New York, 1976), Vol. 6.

[8]L. P. Kadanoff and A. Houghton, Phys. Rev. B 11,
377 (1975).

[9]H. Yahata and M. Suzuki, J. Phys. Soc. Jpn. 27,
1421 (1969).

[10]E. Stoll, K. Binder, and T. Schneider, Phys. Rev. B
8, 3266 (1973); H. C. Bolton and C. H. J. Johnson, Phys.
Rev. B 13, 3025 (1976).

[11]R. A. Ferrel, N. Menyhard, H. Schmidt, F. Schwabl,
and P. Szepfalusy, Ann. Phys. (N.Y.) 47, 565 (1968); B. I.
Halperin and P. C. Hohenberg, Phys. Rev. 177, 952
(1969).

[12]R. J. Glauber, J. Math. Phys. (N.Y.) 4, 294 (1963).

[13]K. Kawasaki, Phys. Rev. 148, 375 (1966); K. Kawasa-
ki, in Phase Transitions and Critical Phenomena, edited
by C. Domb and M. S. Green (Academic, New York,
1972), Vol. 2.

[14]Y. Achiam, to be published.

[15]M. N. Barber, J. Phys. A 10, 1187 (1978). There ap-
pears to be an error in this because our calculation of
$\Lambda_h = 4.43$ disagrees with the value quoted of 2.37.

[16]M. Suzuki, Prog. Theor. Phys. 43, 882 (1970).

[17]L. van Hove, Phys. Rev. 93, 1374 (1954).

Dynamics of Energy Transport in Molecular Crystals: The Picosecond Transient-Grating Method

J. R. Salcedo and A. E. Siegman
Department of Electrical Engineering, Stanford University, Stanford, California 94305

and

D. D. Dlott and M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305
(Received 23 May 1978)

Energy transport in molecular solids is investigated using a picosecond transient-grat-
ing technique. A model is presented which directly relates the rate of energy transport
to the experimental observable. The diffusion coefficient for singlet electronic excitation
transport is reported for pentacene in p-terphenyl. Acoustically induced optical absorp-
tion effects are also observed.

Intermolecular interactions in molecular crys-
tals give rise to electronic excited-state energy
migration. In pure crystals energy transport may
be excitonic[1] in nature, and in disorded or im-
pure crystals it may be due to long-range reso-
nant transfer.[2] In this paper we present the first
results from a new method which utilizes a pico-
second transient diffraction grating to directly
probe the time-dependent position of excited

states in the bulk of a crystal. As such, this
method allows determination of the rate of ener-
gy transfer along any crystallographic direction,
and thus the influence of intermolecular interac-
tions,[1] molecular orientation,[1] impurity effects,[3]
and exciton-phonon coupling[4] on the transport
process can be directly studied.

In this experiment, two time-coincident, Gaus-
sian picosecond excitation pulses of wavelength

λ are crossed in the bulk of a molecular crystal at an angle θ. Optical absorption creates a spatially varying density of electronic excited states which follows the sinusoidal optical interference pattern, thus creating a transient diffraction grating. The strength of this excited-state grating is probed by Bragg diffraction of a third picosecond pulse. The diffracted intensity[5] is measured as a function of probe-pulse delay. The grating strength decays by two processess: The excited-state lifetime reduces the amplitude of the fringe peaks, and the transfer of electronic excitation reduces the peaks and fills in the nulls.

In these initial experiments, resonant singlet electronic energy transfer between substitutional impurities in a molecular crystal was studied. In this case a model employing purely diffusive energy transfer is adequate,[6] and is used throughout the analysis. Although only diffusive energy transfer between identical impurity molecules on a lattice is considered here, in general energy transport need not be diffusive. For example, exciton transport in pure crystals at low temperatures can be wavelike (coherent),[7] resulting in a distinct functional form for the time dependence of the grating signal. A detailed treatment of the application of the transient-grating technique to the general energy transport problem will be presented later.

The appropriate diffusion equation for the excited-state density N_{xt} is

$$\partial N_{xt}/\partial t = D\partial^2 N_{xt}/\partial x^2 - N_{xt}/\tau, \qquad (1)$$

with the Green's function

$$G_{xt,x_0 0} = (4\pi Dt)^{-1/2} \exp\left(\frac{-(x-x_0)^2}{4Dt} - \frac{t}{\tau}\right), \qquad (2)$$

with the initial condition imposed by the spatial grating

$$N_{x_0}t\big|_{t=0} = N_{x_0 0} = \tfrac{1}{2}(1 + \cos\Delta x_0). \qquad (3)$$

The solution to Eq. (1) is

$$N_{xt} = \exp(-t/\tau)[1 + \exp(-\Delta^2 Dt)\cos\Delta x]/2, \qquad (4)$$

where D is the diffusion coefficient for the energy-transport process along the grating direction x, $\Delta = 2\pi/d$ is the magnitude of the grating wave vector, $d = \lambda/2 \sin\tfrac{1}{2}\theta \approx \lambda/\theta$ is the fringe spacing with λ and θ measured in the same medium, and τ is the lifetime of the excited state. Equation (4) is the time impulse response function of the grating pattern. The grating depth is

$$\Delta N = N_{0t} - N_{d/2,t} = \exp(-\tfrac{1}{2}Kt), \qquad (5)$$

where K is the decay-rate parameter, $K = 2(\Delta^2 D + 1/\tau)$. The time dependence of the transient-grating signal, i.e., the time-dependent diffracted probe intensity is given by

$$S(t) = I_p * [I_e * \Delta N]^2, \qquad (6)$$

where the asterick denotes convolution and I_e and I_p are the Gaussian excitation and delayed probe pulse intensities, respectively. Thus, in terms of conveniently defined dimensionless parameters

$$S(\eta|\chi) = \exp(-2\chi\eta)\int_{-\infty}^{+\infty} \exp(-\xi^2)\exp(a\chi\xi) - [1 + \mathrm{erf}(2\eta/a - a\chi/4 - \xi)]^2 d\xi/4\pi^{1/2}, \qquad (7)$$

where $2\chi = K\tau_{FWHM}$ is the normalized decay rate (FWHM is full width at half-maximum), $\eta = t/\tau_{FWHM}$ is the normalized delay, $a = (2/\ln 2)^{1/2}$, and τ_{FWHM} is the pulse duration, in this case the same for both excitation and probe. Predicted decay curves obtained from Eq. (7) are shown in Fig. 1. The corresponding values of D are also shown for typical experimental condictions, $\tau_{FWHM} = 75$ ps, $\tau = 9.5$ ns, $d = 5$ μm, and $\lambda = 532$ nm. For short optical pulses the time dependence is essentially contained in the first exponential,

$$S(t) \propto \exp(-2\chi\eta) \equiv \exp[-2(\Delta^2 D + 1/\tau)t], \qquad (8)$$

and therefore the observed signal should have an exponential decay with a decay rate given by

$$K = 2/\tau + 2\Delta^2 D = 2/\tau + (8\pi^2 D/\lambda^2)\theta^2. \qquad (9)$$
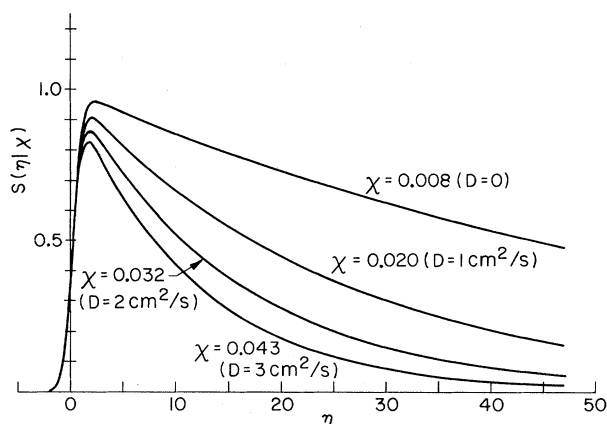

FIG. 1. Computed effect of energy-transport diffusion coefficient D on transient-grating time-dependence signal.

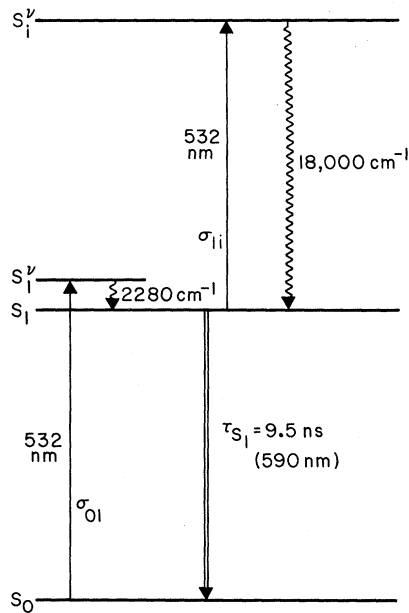FIG. 2. Pentacene energy-level diagram.

FIG. 3. Typical results for Bragg-diffracted probe-signal intensity versus probe-pulse delay relative to excitation pulse.

By performing the transient-grating experiment with different fringe spacings, i.e., by varying θ, a set of decay constants K will result which when plotted versus θ^2 should lie on a straight line with intercept $2/\tau$. The slope of the line yields directly the diffusion coefficient. Only if radiationless excited-state diffusion is the dominant process affecting the grating signal will this angular dependence be observed.

The experiments were performed using a high repetition rate, continuously pumped, actively modelocked, and repetitively Q-switched Nd:YAlG laser.[8] Single pulses are doubled to 532 nm and split into two excitation beams and a delayed probe beam. The samples are 1-mm-thick single crystals of p-terphenyl doped with $\sim 10^{-3}$ mol/mol concentration of pentacene. The p-terphenyl acts as a transparent host for the pentacene molecules. In Fig. 2 the energy-level diagram for pentacene is given. Excitation to S_1^ν is followed by rapid radiationless relaxation to vibrationally unexcited S_1. The $S_1 \to S_i^\nu$ transition was found to be significantly stronger than the $S_0 \to S_1^\nu$ transition at 532 nm. Thus the sample becomes more absorbing upon excitation. This difference in cross section gives rise to strong transient-grating signals.

A typical result is shown in Fig. 3, together with a semilog plot of the decay. The decay time $\tau_{1/e} \approx 1.5$ ns is much shorter than 4.75 ns which
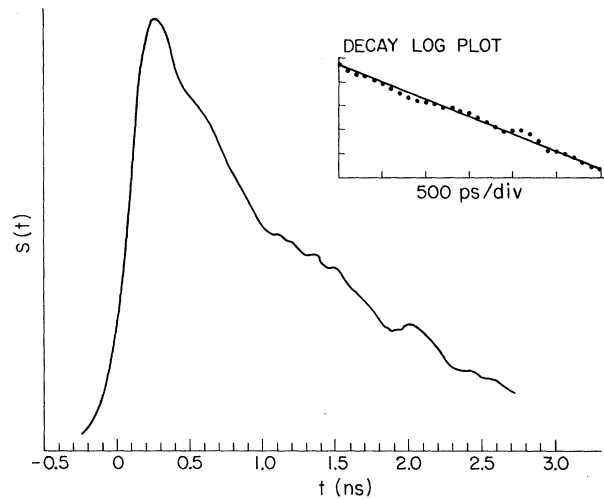
would be produced by the excited-state lifetime along, since the lifetime at room temperature was measured by conventional means to be $\tau = 9.5 \pm 0.3$ ns. Figure 4 displays a series of measurements on one crystal, for different fringe spacings. The fit to a straight line is good and has the predicted intercept showing that the data are in agreement with the diffusive energy transport model. Using Eq. (9), we obtain a direct measurement of the diffusion coefficient $D = 2 \pm 0.1$ cm^2/s, along the crystallographic b axis for this sample which contained a concentration of 1.6×10^{-3} mol/
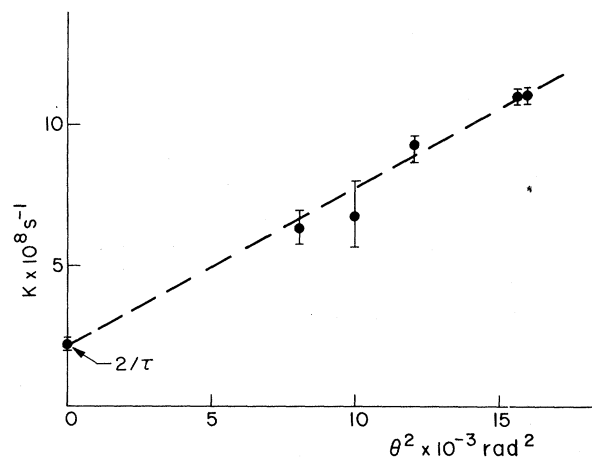
FIG. 4. Transient-grating decay constant K vs θ^2. From the slope, the diffusion coefficient is $D = 2$ cm^2/s. The predicted intercept $2/\tau$ is observed. τ is the independently measured lifetime.
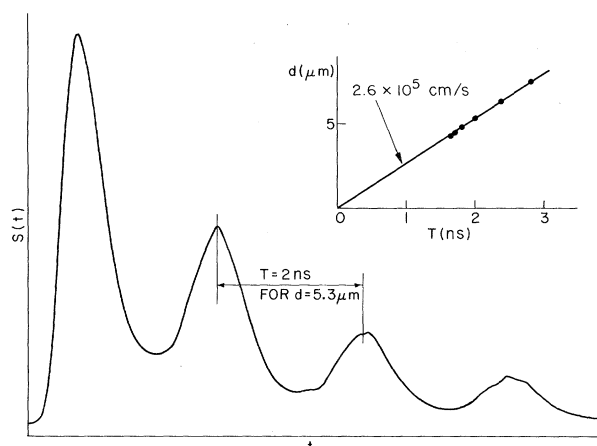
FIG. 5. Oscillatory transient-grating signal under high-power excitation. Thermally produced acoustic waves modulate the amplitude grating depth.

mol pentacene. Measurements on several other samples are consistent with these results. We are currently investigating the dependence on direction, concentration, and temperature of diffusion coefficient.

For excitation intensities above 500 MW/cm^2, an oscillatory behavior in the transient signal is observed, as shown in Fig. 5. The oscillations are periodic, and experiments at different fringe spacings yield a linear dependence between the oscillation period T and the fringe spacing d. At these intensities, significant heat is produced at the grating peaks by excited-state absorption of the excitation pulses to $S_i{}^{\nu}$ followed by rapid radiationless relaxation (see Fig. 2). For each photon absorbed in this manner, about 19 000 cm^{-1} of heat are essentially instantaneously deposited in the sample (a mechanism involving annihilation produces the same effect). Thus a thermal grating is superimposed on the excited-state grating. The temperature increase produces a nearly instantaneous pressure rise at the grating peaks which subsequently modulates the density. This modulation can be visualized as a "frozen" sinusoidal stress pattern plus two counterpropagating acoustic waves which interfere producing, in effect, an acoustic ringing The slope of the line in the inset in Fig. 5 yields a velocity of 2.63×10^5 cm/sec along the grating direction. The velocity of sound along the grating direction was independently measured by the ultrasonic pulse-echo overlap method and found to

be $V_s = 2.65 \times 10^5$ cm/sec. An analysis of the beating effects between the diffusing excited-state grating and moving acoustic waves shows that the observed pattern can occur only if the thermoacoustically generated grating is primarily an *amplitude* rather than a phase grating. We hypothesize that the excess pressure changes the optical absorption cross section of the transitions involved, thus changing the effective depth of modulation of the excited-state grating. This is consistent with the reported pressure dependence of the absorption spectrum of pentacene in *p*-terphenyl.[9] A detailed analysis of the acoustic ringing effect will be presented subsequently.

In conclusion, the picosecond transient-grating technique has been demonstrated to be a novel and powerful tool for the direct study of energy-transport processes in molecular crystals. The method gives directly energy-transport parameters, e.g., the components of the diffusion tensor. The method is also shown to be useful in the study of phonon processes in crystals. Temperature and concentration dependence as well as anisotropic energy transfer are presently being studied in detail in the pentacene system. A more general formalism will be presented at a later time and applied to exciton transport in pure crystals. This technique for the first time makes the rate of energy transport a direct experimental observable.

[1]A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
[2]I. Berlman, *Energy Transport Properties of Aromatic Compounds* (Academic, New York, 1973).
[3]R. D. Wieting, M. D. Fayer, and D. D. Dlott, to be published.
[4]M. Grover and R. Silbey, J. Chem. Phys. 52, 2099 (1974), and 54, 4843 (1971).
[5]A. E. Siegman, J. Opt. Soc. Am. 67, 545 (1977).
[6]Th. Förster, Ann. Phys. (Leipzig) 2, 55 (1948).
[7]D. M. Burland, D. E. Cooper, M. D. Fayer, and C. R. Gochanour, Chem. Phys. Lett. 52, 279 (1977).
[8]D. W. Phillion, D. J. Kuizenga, and A. E. Siegman, Appl. Phys. Lett. 27, 85 (1975).
[9]J. M. Vonnini, J. Chimie Phys. 71, 1543 (1974).