PHOTON-ECHO SPECTROSCOPY OF ORGANIC MIXED CRYSTALS

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We report the first observation of photon echoes in an organic mixed crystal. The echo was observed after excitation with a nitrogen-laser–pumped dye laser in the $^1B_{2u} \leftarrow {}^1A_g$ electronic transition at 3739.9 Å of pyrene in biphenyl at 2 K. The photon–echo excitation spectrum of the origin (zero-phonon line) region shows that drastic variations occur in the coherence lifetime of sites which, qua incoherent (fluorescent) decay, are indistinguishable.

Recently de Vries and Wiersma showed[1] that, at low temperature, the coherence lifetime in the vibrationless excited state of molecules in mixed crystals can well be in the nanosecond time range. This result suggested the interesting possibility of performing photon-echo measurements,[2] on this time scale, in organic mixed crystals.

In this Letter we report the first observation of photon echoes in an organic mixed crystal. The echo was obtained in the $^1B_{2u} \leftarrow {}^1A_g$ electronic transition at 3739.9 Å of pyrene in biphenyl[3] at 2 K. We further show that the coherence lifetime of different pyrene sites in the biphenyl crystal varies drastically.

The experimental setup, used to generate the photon echo, was similar to one recently described by Takeuchi and Szabo,[4] who for the first time successfully used a nitrogen-laser–pumped dye laser to obtain a photon echo in the $^3P_0 \leftarrow {}^3H_4$ transition of Pr^{3+} in LaF_3. A Molectron 1-MW nitrogen laser at a repetition rate of 10 Hz was used to pump a dye laser equipped with a beam-expanding telescope and constructed in the Hänsch configuration.[5] As lasing dye we used 2-phenyl-5-(4-biphenylyl)-1, 3, 4-oxadiazole (PBD) at a concentration (mole fraction) of 5 $\times 10^{-3}$ in a 50/50 ethanol-toluene mixture (Molectron dye No. 70350). This system produced 5-nsec pulses of 0.05 Å spectral width and a power of 20 kW at 3740 Å. The dye-laser beam was split in two and both beams were independently delayed by a White cell. The beams were then collinearly recombined and focused with a 10-cm–focal-length lens into the sample. The detection system consisted of a 10-cm–focal length collimating lens, a three-stage Pockels-cell optical shutter system (theoretical contrast ratio 10^9), and a $\frac{1}{2}$-m Jarrel–Ash monochromator equipped with a Philips UVP-150 photomultiplier. The use of the monochromator proved essential

as otherwise the echo was completely obscured by the incoherent emission occurring in the 10-nsec shutter-open time. Finally a Tektronix 454 oscilloscope was used to display the signals, while a Princeton Applied Research boxcar integrator, equipped with a digital storage option, was used for time-resolved intensity measurements.

The mixed crystal of pyrene in biphenyl (concentration $\sim 10^{-2}$ mol %) was grown from a Bridgeman furnace and cleaved with a sharp razor blade. In a 1.5-mm-thick crystal, for light polarized parallel to the crystal b axis, about 70% absorption was obtained. Since the natural a-b cleavage plane of biphenyl[6] is of the best optical quality the laser beam propagation direction was chosen perpendicular to it.

Figure 1 contains a typical echo signal of pyrene in biphenyl which showed considerable amplitude jitter, unless an intracavity polarizer was used in the dye laser.

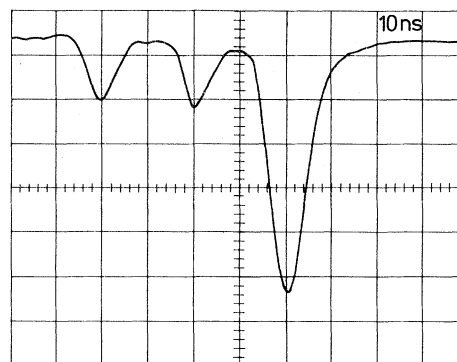The experimental setup was tested and optimized (especially the position of the focusing

FIG. 1. Typical photon-echo signal (third from the left) obtained from the $^1B_{2u} \leftarrow {}^1A_g$ electronic transition (3739.9 Å) of pyrene in biphenyl at 2 K. The first two pulses are the excitation pulses optically attenuated prior to detection.

lens) to obtain maximally intense echoes in the $^3P_0 \leftarrow {}^3H_4$ transition at 4777.6 Å of Pr^{3+} in LaF_3.[4] Under optimum conditions the echo of this transition was easily observed by eye. We note here that echo signals, but orders of magnitude less intense, were also obtained in the $^1D_2 \leftarrow {}^3H_4$ transition at 5925 Å of Pr^{3+} in LaF_3.[7]

A rough estimate of the pyrene echo decay time at 2 K (assuming exponential decay) was obtained by measuring the echo amplitude, using a boxcar integrator, at pulse separations of 22 and 28.6 nsec. An echo decay time of about 8 nsec was measured which is an order of magnitude shorter than the echo decay times reported for the ions Cr^{3+}, Pr^{3+}, and Nd^{3+}.[2,4,8] The echo amplitude was also measured below 4.2 K and was found to increase drastically (factor of 5) when lowering the temperature from 3 to 2 K. The temperature dependence of the pyrene echo and its decay is presently being studied in greater detail.

We now proceed by presenting the relationship between the echo intensity and the absorption spectrum. Figure 2(a) shows the absorption spectrum of pyrene in biphenyl in the origin re-
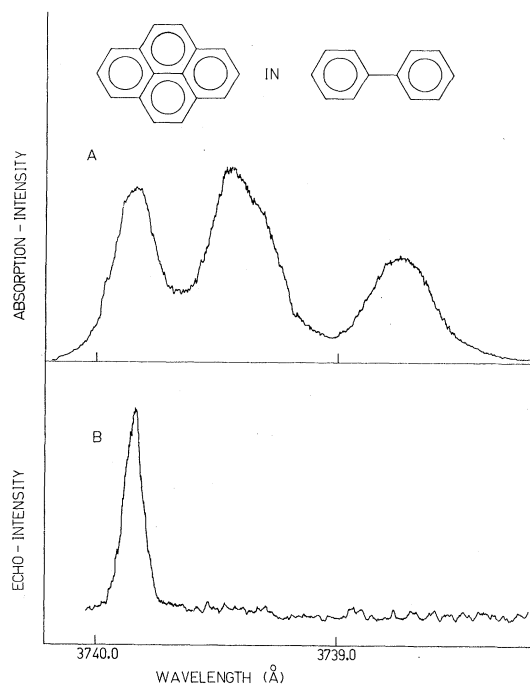

FIG. 2. (a) Absorption spectrum and (b) photon-echo excitation spectrum of the origin region of the $^1B_{2u} \leftarrow {}^1A_g$ electronic transition of pyrene in biphenyl at 2 K. The laser bandwidth (resolution) in these excitation experiments was about 0.05 Å.

gion of the $^1B_{2u} \leftarrow {}^1A_g$ transition at 2 K. The spectrum was obtained by broad-band (5 Å) detection of the fluorescence intensity at 3945 Å, using a boxcar integrator, while slowly scanning (0.08 Å/min) the laser (0.05 Å bandwidth) through the absorption region. The structure in the origin region is presumably due to pyrene sites that differ by rotation around the long axis of the molecule.[9]

The idea of the structure being due to sites is consistent with our observation that the emission band at 3945 Å, which is tripled under broad-band excitation conditions,[9] becomes single after laser excitation in any of the "three" sites. Further support for this pyrene-site hypothesis comes from the fact that a 75-nsec fluorescence lifetime was measured after laser excitation in any of the three sites.[10]

It then came as a surprise to us that the photon-echo excitation spectrum of this site structure, shown in Fig. 2(b), is so drastically different from the absorption spectrum. This spectrum was obtained by broad-band (5 Å) detection of the echo intensity using the boxcar integrator with a 10-nsec time gate. The laser again was slowly (0.08 Å/min) scanned through the absorption region while the boxcar integrator was read out into a recorder.

Figure 2(b) shows that the photon echo is only observed for excitation in the energetically lowest pyrene site. The coherence lifetime of the other sites thus must be at least a factor of 2 shorter, implying, most likely, a more efficient electron-phonon coupling process at these sites. A closer look at the onset region in Fig. 2(b) further shows that the spectral width (0.11 Å) in the photon-echo excitation spectrum is also sharper than expected, through the N^2 dependence of the echo, from the observed 0.21-Å inhomogeneous width in the absorption spectrum. This suggests that only part of the inhomogeneous width of that "particular site" contributes to the echo formation. These features are also presently being studied in greater detail.

In conclusion we would say that the experiments reported in this paper show that photon-echo spectroscopy of organic mixed crystals may well become an important tool in the study of the dynamics of energy relaxation in these systems.

[1]H. de Vries and D. A. Wiersma, Phys. Rev. Lett. **36**, 91 (1976).

[2]I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. **141**, 391 (1966).

[3]A. Bree and V. V. B. Vilkos, Spectrochim. Acta **27A**, 2333 (1971).

[4]N. Takeuchi and A. Szabo, Phys. Lett. **50A**, 361 (1974).

[5]T. W. Hänsch, Appl. Opt. **11**, 895 (1968).

[6]J. Trotter, Acta Crystallogr. **14**, 1135 (1961).

[7]T. J. Aartsma and D. A. Wiersma, unpublished.

[8]S. Chandra, N. Takeuchi, and S. R. Hartmann, Phys. Lett., **41A**, 91 (1972).

[9]R. M. Hochstrasser and G. J. Small, J. Chem. Phys. **48**, 3612 (1968).

[10]The fluorescent decay of pyrene is markedly nonexponential. Next to a fast decay component of 75 nsec there is a weak underlying slow component of about 400 nsec. This was observed for all three sites and is as yet unexplained.

Parametric Decay of "Kinetic Alfvén Wave" and Its Application to Plasma Heating

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Because of its electrostatic properties, the rate of the parametric growth of the kinetic Alfvén wave [Alfvén wave with $\lambda \equiv k_\perp^2 c_s^2/\omega_{ci}^2 \sim O(1)$] is shown to be larger than that of the classic result by a factor of $\lambda \omega_{ci}/\omega_A$, where ω_{ci} and ω_A are the ion-cyclotron and the Alfvén frequencies, $k_\perp$ is the perpendicular wave number, and c_s is the ion sound speed. This fact can be utilized to heat a plasma with typical tokamak parameters.

In a previous report,[1] we have shown that a plasma with typical tokamak parameters can be heated by the kinetic Alfvén wave which can be excited in the plasma through resonant mode conversion. The Alfvén wave which is excited by the resonant mode conversion has a perpendicular wave length, $k_\perp^{-1}$, comparable to the ion gyroradius, ρ_i, and accompanies an electrostatic component. Hence it is called the kinetic Alfvén wave here. The dispersion relation of the kinetic Alfvén wave is given by[1]

$$\omega^2 = \begin{cases} k_\parallel^2 v_A^2 \left[1 + \left(\frac{3}{4} + \frac{T_e}{T_i}\right)k_\perp^2\rho_i^2\right], & k_\perp^2\rho_i^2 \ll 1, \\ k_\parallel^2 v_A^2 \left(1 + \frac{T_e}{T_i}\right)k_\perp^2\rho_i^2, & k_\perp^2\rho_i^2 \gg 1. \end{cases} \quad (1)$$

It was shown in the linear analysis that both electrons and ions are heated in a collisional regime, while only electrons are heated in a colli-

sionless regime by electron Landau damping.

In this report we show that, in a collisionless regime, ion heating is possible by utilizing either parametric decay to the ion acoustic wave if $T_e \gg T_i$, or ion nonlinear Landau damping if $T_e \lesssim 5T_i$.

Decay of a conventional Alfvén wave into another Alfvén wave and an ion acoustic wave has been studied by Sagdeev and Galeev[2] using the ideal magnetohydrodynamic (MHD) equations. Applications of this process for heating plasmas have been suggested by Vahala and Montgomery[3] and Rashmore-Davies and Ong.[4] However, because the growth rate is so small ($\sim \omega_0 B_p/B_0$; ω_0 is the pump frequency, B_p the pump amplitude, and B_0 the ambient magnetic field) the actual application is considered difficult. Furthermore, if $T_e \lesssim 5T_i$, the ion acoustic wave is heavily ion Landau damped and such a decay becomes practically absent.

We show here that the parametric decay of the kinetic Alfvén wave to the ion acoustic wave has