

## OPTICAL DYNAMICS OF CONDENSED MOLECULAR AGGREGATES: AN ACCUMULATED PHOTON-ECHO AND HOLE-BURNING STUDY OF THE J-AGGREGATE

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Accumulated photon-echo and hole-burning experiments on the well-known J-bands of pseudoisocyanine bromide in an aqueous ethylene glycol glass are reported. From the low-temperature photon-echo decay of  $\approx 14$  ps and the assumption that this lifetime is purely radiative, the mean number of molecules in the aggregates is calculated to be about 500. It is shown that the temperature-activated optical dynamics of the excitonic J-bands can best be explained by invoking the presence of a pseudo-localized degree of freedom of  $\approx 9$  cm $^{-1}$ . It is concluded that photoionization is the primary process that causes hole burning of the J-bands and that the charge-separated state forms the bottleneck in the optical pumping cycle.

### 1. Introduction

Molecular aggregates play an important role in nature and technology. In many photosensitive protein-chromophore complexes, an aggregate of large organic molecules, firmly held together in a unique spatial arrangement by the surrounding protein matrix, is responsible either for transport of the captured photonic energy or, as in the case of the reaction centre, for a charge separation reaction within the aggregate [1]. Aggregates of dye molecules bound to silver halide grains play an important role in photographic science as film sensitizers. Here the aggregate also captures light after which an electron-hole pair is generated. The electron is then transferred to the conduction band of the silver halide and the hole is trapped in the aggregate [2]. It has been shown that aggregates of dye molecules with large non-linear optical coefficients can be formed in polymers and that thin films of such polymers exhibit significantly non-linear optical properties [3]. Waveguides of these materials may therefore become of great importance in the field of integrated optics. Finally, from a purely scientific point of view, aggregates are of interest as they bridge the gap between a single molecule and a crystalline lattice. Inter-

esting size effects on the spectroscopy and optical dynamics of aggregates are to be expected.

In view of the importance of aggregates in many branches of science we have initiated a study of the spectroscopy and optical dynamics of aggregates in the condensed phase.

Our initial study is on the well-known aggregate of the pseudoisocyanine (PIC) halide dye. In 1936 Jelly [4] and independently Scheibe [5] reported that concentrated aqueous solutions of PIC exhibited an extremely narrow absorption line at 573 nm which was assigned to PIC aggregates. In honour of Jelly this band has been named the J-band. Since the early observations of Jelly and Scheibe, numerous investigators have been involved with the spectroscopy and dynamics of these aggregates. Unfortunately, few of the obvious questions such as the number of molecules forming an aggregate, the structure or the excited-state lifetime of the aggregate have yet to find definitive answers. From optical [6], NMR [7] and EPR [8] experiments it is clear that the aggregate has a well-defined structure and that the number of molecules in the aggregate can be manipulated by varying the concentration and/or temperature of the solution.

In this Letter we report the results of photon-echo

and hole-burning experiments on aggregates of PIC Br in an ethylene glycol/water glass in the temperature range 1.5 to 100 K. At the lowest temperature the photon-echo decay is non-exponential which is considered as being due to the occurrence of a distribution of aggregate lengths. From the echo decay constant we infer that the average aggregate length is about 500 molecules. We further conclude from the temperature dependence of the echo decay that the optical excitation of the aggregate most likely dephases by coupling to a low-frequency (librational) mode of the aggregate. Finally, it is concluded that hole burning is due to photoionization of the aggregate and that the ionized aggregate plus the temporarily trapped electron forms a bottleneck in the optical pumping cycle.

## 2. Experimental

Samples were made from  $5 \times 10^{-3}$  mol/l solutions of PIC Br (Exciton) in a 50/50% mixture of ethylene glycol and water by placing a drop of this solution between 0.1 mm glass plates and then lightly pressing the plates. The samples were cooled at a rate of 0.5 K/s to liquid nitrogen temperature where the ethylene glycol/water mixture forms a glass. They were then cooled down to 1.5 K over a period of  $\approx 1$  h. The samples were mounted on a copper sample holder which was surrounded by helium gas. The temperature of the sample was measured by a rhodium-iron resistor situated close to the sample and could be read with an accuracy of at least 0.1 K. The accumulated photon-echo experiments were performed in the usual way [9] using stochastic excitation [10] with a bandwidth of 25 Å and a measured correlation time of 200 fs or by using mode-locked pulses of  $\approx 3$  ps which were close to transform limited. Echo decays at higher temperatures were measured by slowly warming the cryostat. This procedure ensured that the measurements were made in a situation where the sample temperature was at equilibrium with its environment. The echo decays were digitized by a computer and digitally stored for further data handling and fitting. The echo decay was stored as an array of  $\approx 200$  points and a typical echo scan was completed in about 2 min. The hole-burning experiments were performed using long pulses

from the same mode-locked dye laser which was equipped with a thin (FSR 900 GHz) and thick (FSR 30 GHz) etalon. The measured bandwidth of a typical 120 ps pulse from this system was  $0.2 \text{ cm}^{-1}$ . In these experiments the burning laser and the probing light beam (from the lamp) were both focused to spot sizes slightly larger than the area of the hole ( $1 \text{ mm}^2$ ) on which the sample was mounted. The lamp used was a 150 W halogen lamp and to avoid heating of the sample only a spectral window of 10 nm was used by filtering of the output. A Spex 1402 double monochromator at a spectral resolution of  $0.4 \text{ cm}^{-1}$  was used in all hole-burning and fluorescence experiments.

## 3. Results and discussion

### 3.1. Low-temperature absorption spectrum of the J-bands

Fig. 1 shows the absorption spectrum of the origin region (J-bands) of the PIC Br aggregate at 1.5 K. This spectrum is very similar to the one reported by Cooper [11] and reveals two lines with maxima at 571 and 576 nm. We note that these two bands must be due to *different* aggregates as their relative intensity changes with the rate of cooling; in fact when the samples are cooled very slowly, only the "blue" J-

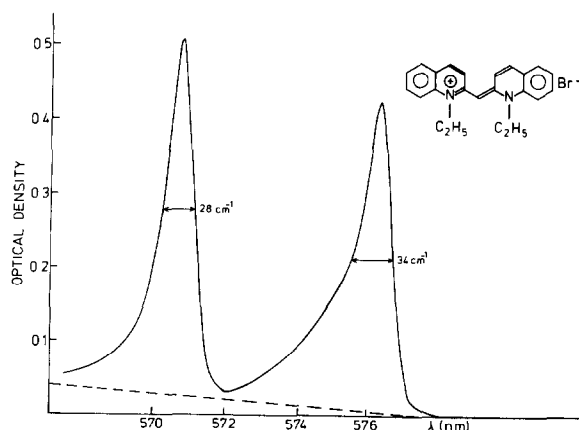


Fig. 1. Origin absorption spectrum of the J-bands of aggregates of pseudoisocyanine bromide in an ethylene glycol/water (50/50 vol%) glass at 1.5 K. Note that these J-bands at room temperature coalesce into one band, known as "the J-band".

band survives. In the accumulated photon-echo and hole-burning studies we have found only slight differences in the optical dynamics of these two bands which indicates that the structures of the aggregates absorbing at these different wavelengths must be very similar. One possibility is that these aggregates have basically the same structure with in one case the hydrophilic edges all appearing to one side and in the other case alternating on either side of the aggregate [12]. Packing calculations could possibly predict the thermodynamically more stable of the two forms. Note that most of the experiments reported in this Letter concern the red site.

Irrespective of the precise structure of the aggregated dye, the narrow ( $30\text{ cm}^{-1}$ ) linewidth of its absorption spectrum is intriguing. Study of the PIC Br monomer in the same glass shows that the origin absorption has an inhomogeneous bandwidth of  $\approx 1200\text{ cm}^{-1}$  [13]. Thus there has been a reduction of the inhomogeneous linewidth by a factor of 40! Before discussing this narrowing effect, we note that part of the inhomogeneity in the monomer case is possibly due to small rotations of the quinoline ring systems with respect to one another. This possibility no longer exists in the aggregate (except at the ends), where the molecules are firmly held in a specific conformation. We therefore suggest that the intrinsic inhomogeneous broadening of the PIC monomer optical transition is probably closer to  $300\text{ cm}^{-1}$ , a typical value found for other dye molecules in a glass [14]. The actual narrowing of the aggregate absorption is therefore probably closer to a factor of 10 than 40. The phenomenon of line narrowing is a direct consequence of the delocalization of the optical excitation over the molecules in the aggregate. The process of line narrowing in optical transitions of molecular aggregates has recently been described in detail by Knapp [15]. He showed that in the absence of spatial correlations of the inhomogeneity, the aggregate exhibits a linewidth which is a factor of  $N^{1/2}$  narrower than the monomer, where  $N$  is the number of molecules forming the aggregate. Use of this relation leads us to the conclusion that in our samples the aggregate length is about 100 molecules (for a narrowing of a factor of 10) up to 1600 molecules for the, less likely, narrowing factor of 40. In the next section we show that photon-echo experiments lead to a more accurate determination of this length.

We note that the lineshapes of both aggregate transitions are somewhat asymmetric. While part of this asymmetry may be due to the occurrence of short chains, we have evidence from fluorescence experiments that in the blue wings of these lines other, structurally different, aggregate species may be present. We will return to this point in a future paper.

### 3.2. Accumulated photon-echo decay measurements

#### 3.2.1. Preliminaries

In view of recent misgivings as to the applicability of the accumulated photon echo to the study of condensed phase optical dynamics [14], it is appropriate to discuss the accumulated photon-echo [9] method and compare it with the two-pulse photon-echo and hole-burning methods. First we note that all three methods can yield information on the optical dynamics on the time scale of the excited state lifetime. Furthermore both the regular two-pulse and accumulated photon echo are echo phenomena and as such do not suffer from saturation effects as occurs in the case of hole burning. The only difference between the methods concerns the *time scale* on which the information is gathered. In the two-pulse photon-echo method this can be as short as the excited state lifetime; in the accumulated photon echo this is the lifetime of the bottleneck state (typically 1 ms) while in cw hole-burning experiments this can be minutes. These methods therefore will only yield the same information if, on the relevant time scale, the inhomogeneity is static. This is obviously an important prerequisite if the optical dynamics data obtained by the different methods is to be compared. With regard to the comparison between the two-pulse and accumulated photon echo we have not found a single case, either in molecular solids [16] or in a doped semiconductor [17], where the results of the two methods were different. Recently, however, there has been a report [18] of a hole-burning study on pentacene in a polymer which led to a narrower hole than predicted from an accumulated photon-echo study on this system [19]. We believe that this discrepancy is due either to an error in measurement of the temperature at the sample or to spatial inhomogeneity of the amorphous sample.

We now summarize the specific advantages of the accumulated photon echo compared to the regular

two-pulse echo. Firstly, accumulated photon-echo experiments can be performed with an extremely simple apparatus [9]. Secondly, the accumulated photon echo, in contrast to the two-pulse photon echo [20,21], is insensitive to optical density effects [22]. Thirdly, the accumulated photon echo is generated using low-intensity pulses. This is a particular advantage in the study of photo-biological systems and aggregates, where intense pulses, often needed in the two-pulse photon echo, can easily cause excitation-annihilation effects. Fourthly, the accumulated photon echo can be heterodyne detected which takes maximum advantage of the "echo polarization" in the sample. Finally, the time resolution in the accumulated photon-echo experiment is determined by the correlation time of the exciting radiation [10] which can be made sub-picosecond. These features make the accumulated photon echo an attractive alternative to the regular two-pulse photon echo for the study of optical dynamics in systems with a static inhomogeneity and a bottleneck in the optical pumping cycle. As stated previously the inhomogeneity has to be static only on the time scale of the lifetime of the bottleneck.

### 3.2.2. Low-temperature echo decay

Fig. 2 shows the low-temperature accumulated photon-echo decay with stochastic excitation of the J-band at 576 nm. The bandwidth of the exciting radiation was 2.5 nm. This exceeds the inhomogeneous width of the red J-band which implies that the echo samples the dynamics of all aggregates in the absorption line. First we note that with prolonged excitation of the sample the absolute echo intensity decreases, which is indicative of hole burning of the optical transition. This phenomenon is discussed in section 3.3. The important point to note here is that it was verified that this hole-burning process, which occurred on a time scale much longer than the time of a typical echo decay measurement, had no effect on the echo decay function that was measured. When instead of stochastic excitation, mode-locked pulses of 3 ps were used, the effect of hole burning on the echo intensity was obviously much more pronounced, but again the photon-echo decay remained unchanged. Mode-locked pulses were also used to probe whether the echo decay was dependent on the excitation wavelength in the inhomogeneous absorp-

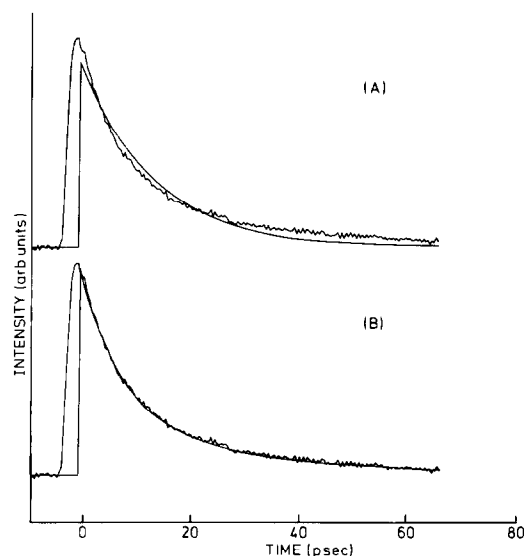


Fig. 2. Accumulated photon-echo decay trace obtained at 1.5 K. In (A) the best single-exponential fit, with a decay time of 14 ps, is shown. (B) shows a double-exponential fit with decay parameters of 6 ps (weight 0.75) and 27 ps (weight 0.25).

tion, but no such dependence was found. Independent of the mode of excitation a quasi steady-state situation was reached in which the echo decay function was identical to the initially measured one. Fig. 2 presents a typical decay and it is evident that this decay is non-exponential. This is clearly shown in fig. 2A where the solid line presents the best single-exponential fit to the data with a decay time of 14 ps. An excellent (mathematical) fit to the echo decay function can be obtained by a sum of two exponentials which is given as the solid line in fig. 2B. The fast component in this fit has a decay time of 6 ps and the slow one a lifetime of 27 ps. The most likely explanation of the observed non-exponential echo decay is that the echo probes an optical-dynamics parameter of the aggregate which is dependent on the aggregate length. As one expects a distribution of chain lengths for the aggregate it seems feasible that this could lead to a non-exponential decay of the photon echo. In order to analyze the data further we assumed that the low-temperature photon-echo decay is purely determined by population relaxation processes, i.e. that  $T_2 = 2T_1$ . Such an assumption is generally not warranted for monomers in glasses where  $T_1$  is in the range of nanoseconds and the measured  $T_2$  at low temperature is  $\approx 100$  ps. The echo lifetime

reported here is an order of magnitude shorter and, moreover, close to the fluorescence lifetime measured for these aggregates in solution [23].

The analysis of the data assumes that the PIC aggregates can be described by the following Frenkel-type Hamiltonian [24] of a linear chain with two molecules in the unit cell:

$$H = \sum_n |n\rangle \omega_n \langle n| + V \sum_n (|n\rangle \langle n+1| + |n+1\rangle \langle n|). \quad (1)$$

Here  $\omega_n$  is the transition frequency of a local PIC excitation at site  $n$ , and  $V$  is the nearest-neighbour intermolecular coupling. On the basis of this Hamiltonian it can be shown [15] that, if  $V$  greatly exceeds the width of the inhomogeneous distribution of site energies as is the case here, the excitation is delocalized over the aggregate and the optical excitation should be described in terms of excitation of allowed  $k$  states of a linear chain. In the optical exciton picture the J-band can then be described as the energetically lowest  $k=0$  transition of a linear chain with a transition dipole of length  $N^{1/2}\mu_m \cos \alpha$  [24]. Here  $N$  is the number of molecules forming the aggregate,  $\mu_m$  the transition dipole of the monomer and  $\alpha$  the angle between the transition dipole and the long axis of the aggregate. In the following  $\alpha$  is taken to be  $45^\circ$  as calculated by Scherer and Fischer [25] on the basis of measurements by Scheibe [26] and Kaiser and co-workers [13]. Using the Strickler-Berg relation [27] we then conclude that the radiative lifetime of the J-band is a factor of  $N \cos^2 \alpha$  shorter than that of the monomer, which was recently calculated to be 3.7 ns [28]. Using the fact that in the J-aggregate non-radiative processes involving the triplet and ground state are negligible [28,29], we conclude that the fluorescence lifetime of the aggregate must be very close to the purely radiative lifetime! On the basis of the best single-exponential fit of 14 ps to the echo decay and the 3.7 ns radiative lifetime of the monomer, we calculate the number of molecules per aggregate as 520. Assuming a Gaussian distribution for the chain lengths, we can go further and calculate this distribution by simulating the measured non-exponential echo decay. The result of this calculation is that a Gaussian distribution of chain lengths with a mean of 520 molecules and a spread of 400 (sigma value),

under the given assumptions, generates a photon-echo decay which is close to the experimentally observed one.

### 3.2.3. Temperature dependence of the photon-echo decay

The temperature-dependent dephasing of the excitonic J-band was probed by measurement of the photon-echo decay as a function of temperature in the range 1.5 to 100 K. It was noted that the absolute intensity of the echo slowly decreases with increasing temperature. This is indicative of a less efficient bottleneck at higher temperature. To analyze the echo data we have made the following assumptions:

(1) The low-temperature (1.5 K) photon-echo decay is determined only by population relaxation ( $T_1$ ) processes.

(2) This population relaxation process is independent of temperature in the temperature range of the measurements.

(3) The pure dephasing constant ( $T_2^*$ ) is independent of the length of the aggregate. This implies that dephasing in these aggregates can be described in the statistical limit for aggregates of all lengths in the sample.

(4) The intrinsically multiple-exponential decay of the photon echo can be described (mathematically) by the sum of two exponents.

These assumptions allow us to express the amplitude of the accumulated photon echo ( $\mathcal{A}_{APE}$ ) as a function of pulse separation and temperature in the following form:

$$\begin{aligned} \mathcal{A}_{APE}(t_{12}, T_2^*(T)) &\propto \exp[-2t_{12}/T_2^*(T)] \\ &\times [\alpha \exp(-t_{12}/T_{1A}) \\ &+ (1-\alpha) \exp(-t_{12}/T_{1B})]. \end{aligned} \quad (2)$$

Here  $T_2^*(T)$  is the pure dephasing constant,  $T_{1A}$  and  $T_{1B}$  the fitted lifetimes of the short and long components in the low-temperature echo decay and  $\alpha$  is the weight factor of the two.

The procedure to determine  $T_2^*(T)$  from the data is to least-squares fit eq. (2) to the digitized form (200 points) of the echo decay curve at each temperature. The fact that this procedure leads to excellent fits with a single  $T_2^*$  supports the assumptions stated above.

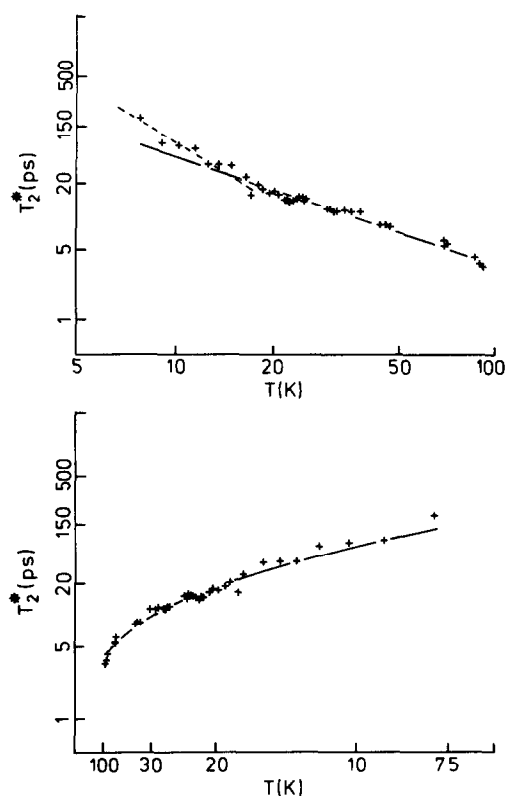


Fig. 3. Plots of measured pure dephasing times versus temperature. In the upper part fits are made to the power law  $T_2^*(T) = bT^\alpha$ . The solid line is the best fit to all data with  $b = 0.009 \text{ cm}^{-1}$  and  $\alpha = 1.24$ . The dashed line shows the low-temperature fit with  $b = 0.003 \text{ cm}^{-1}$  and  $\alpha = 1.6$  as parameters. In the lower part of the figure a fit is made to the relation  $T_2^* = \tau[\exp(-\hbar\omega/kT) - 1]^{-1}$  with the parameters  $\omega = 8.8 \text{ cm}^{-1}$  and  $\tau = 33 \text{ ps}$ .

As stated earlier, aggregates are intermediate in size between the single molecule and the crystalline limit and it is therefore interesting to determine whether the dephasing dynamics are caused by modes of the amorphous glass or by pseudolocalized modes associated with the aggregate. In the former case it is to be expected that  $T_2^*(T)$  will follow a temperature power law [30], in the latter case a Bose-Einstein activation of  $T_2^*(T)$  should be observed [31]. In fig. 3 we show the results of fits to these expressions. In the upper frame the solid line presents the best (weighted) fit to all data with  $T_2^*(T) = bT^\alpha$  where  $b = 0.009 \text{ cm}^{-1}$  and  $\alpha = 1.24$ . Völker and co-workers [30,32] have shown that many molecules in glasses exhibit the same optical dephasing characteristics in

the temperature range below 10 K. Interestingly enough in this case the low-temperature regime is best described, using this power law, with a higher  $\alpha$  (1.6) and a smaller  $b$  (0.003). This fact points at a reduced interaction between the optical excitation at the aggregate and the glass modes compared to the single molecule case. This is related to the observed exchange narrowing of the absorption line in these aggregates. It therefore seems that both the static and dynamic interactions between the optical excitation at the aggregate and the glass structure are reduced by exchange narrowing. Irrespective of these arguments it remains puzzling that such an excellent fit to a power law is obtained over such an extended temperature range.

In the lower part of fig. 3 the data have been fitted to the Bose-Einstein expression for  $T_2^*(T) = \tau[\exp(-\hbar\omega/kT) - 1]^{-1}$ . Here  $\omega$  is the average energy of the pseudo-localized level in the ground and electronically excited states that acts as the doorway states in the dephasing process [33,34], and  $\tau$  the corresponding average lifetime. An excellent fit to all data over the whole temperature range is obtained for  $\omega = 8.8 \text{ cm}^{-1}$  and  $\tau = 33 \text{ ps}$ . Compared to the parameters obtained from optical dynamics studies of mixed molecular crystals [31] these numbers can perfectly reasonably be assigned to the energy and lifetime of a libration of the aggregate. Unfortunately, we have not been able, either in absorption or emission studies of the aggregate, to identify levels at  $\approx 9 \text{ cm}^{-1}$ . Additional experiments are needed on aggregates of the other halides to provide evidence for the existence of these states. Until such information is available we cannot exclude the possibility that optical dephasing in these aggregates is dominated by direct coupling of the excitation to modes of the amorphous host rather than to its own libration.

### 3.3. Hole burning

As already mentioned, even under conditions of stochastic excitation the intensity of the accumulated photon echo slowly diminishes in time. This points to hole burning of the transition. To study this, we have made some preliminary hole-burning experiments. A typical result of these experiments, performed in a sample held at 1.5 K, is shown in fig. 4.

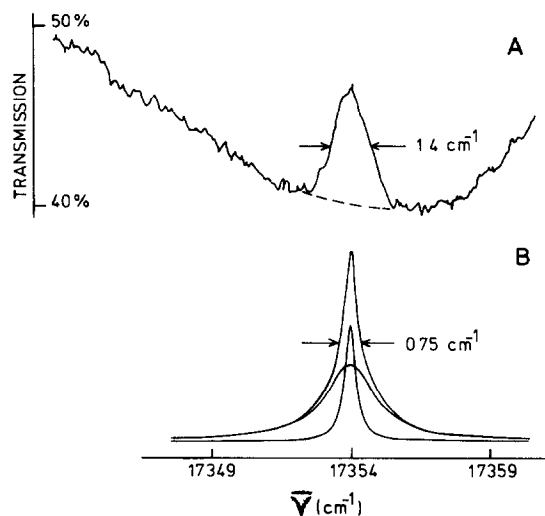


Fig. 4. Hole-burning for the J-band at 576 nm in aggregates of pseudoisocyanine bromide in an ethylene glycol/water glass (50/50 vol%) at 1.5 K. The upper curve (A) shows part of the unburned inhomogeneous absorption line profile (noisy and dotted curve) and the hole observed after burning, under conditions specified in the text. The lower traces (B) present the calculated hole widths due to the short and long components in the echo decay and their scaled sum.

This was obtained at the lowest excitation density feasible in our experiments (1 mW/cm<sup>2</sup> for 5 min burning time). The following observations were made:

- (i) A hole filling process occurs on the time scale of minutes that leaves the hole width unchanged.
- (ii) On the time scale of hours the hole width broadens significantly. The narrowest hole obtained in our experiments and shown in fig. 4 has a (deconvoluted) width of 1.4 cm<sup>-1</sup>.

For a static inhomogeneity one can predict [35] that the hole width is twice the width of the Fourier transform of the echo decay. Fig. 4 shows the Lorentzian lineshapes due to the short and long component in the echo decay and their sum. It is clear that the observed hole width in the hole-burning experiment exceeds the predicted width by almost a factor of 2. At this point we attach no significance to this discrepancy as our apparatus is not ideal. To improve these measurements we are reviving the apparatus used in ref. [36].

These preliminary hole-burning experiments do

show however that the hole lineshape is completely symmetric. This indicates that the non-exponential decay of the echo at low temperature is not due to asymmetry of the exciton lineshape.

With regard to the hole-burning mechanism we have come to the conclusion that the main photoproduct is the ionized aggregate, J<sup>+</sup>. This conclusion is based on nanosecond pulsed laser experiments on the aggregate which show that the absorption spectrum of the photoproduct looks very similar to that of the J-aggregate, except for a blue-shift of the pure electronic excitation of  $\approx 90$  cm<sup>-1</sup>. Furthermore it was shown using coherent Raman spectroscopy that the Raman spectra of the two species are indistinguishable [37] which lends support to the proposal that J<sup>+</sup> is the main photoproduct. This also explains the fast hole filling process as arising from electrons returning from deep traps to the aggregate. The more persistent hole is then possibly due to the fact that some of the ejected electrons have reduced the ethylene glycol and are permanently trapped.

A riddle concerning the nature of the bottleneck is also solved. From luminescence experiments it is clear [29] that the triplet state cannot function as a bottleneck in the aggregate. We propose that the bottleneck is formed by the ionized aggregate and the temporarily trapped electron. The dynamics of the returning electrons is a point for further study.

Finally we note that the quantum yield of photoionization can, in principle, be calculated from the relative intensity of the accumulated photon echo [9]. By noting that the lower limit of the lifetime of the bottleneck in this case is determined by the 4 kHz chopping rate of the pump beam, we calculate an ionization efficiency of less than 1%. This implies that the ionization process has a negligible effect on the fluorescence lifetime of the aggregate. Experiments are planned to directly measure the rate of this ionization process.

#### 4. Summary and conclusions

We have shown that the accumulated photon-echo technique can be successfully used to study the ultrafast optical dynamics of the J-band of aggregates of the dye pseudoisocyanine bromide in the condensed phase.

From the low temperature decay of the photon echo we deduce that the average number of molecules per aggregate in our samples is about 500. From the temperature dependence of the echo decay we conclude that the optical dynamics in these aggregates is most likely governed by phonon-scattering processes involving a libration. Finally, it is concluded that the observed hole burning is due to photoionization of the aggregate and that the charged aggregate plus temporally trapped electron forms a bottleneck in the optical pumping cycle of the J-band.

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### References

- [1] G. Feher and M.Y. Okamura, in: *The photosynthetic bacteria*, eds. R.K. Clayton and W.F. Siström (Plenum Press, New York, 1978) pp. 349–387.
- [2] P.B. Gilman, *Phot. Sci. Eng.* 18 (1974) 418.
- [3] Y. Wang, *Chem. Phys. Letters* 126 (1986) 209.
- [4] E.E. Jelly, *Nature* 138 (1936) 1009.
- [5] G. Scheibe, *Angew. Chem.* 49 (1936) 563.
- [6] E. Daltrozzi, G. Scheibe, K. Gschwind and F. Haimerl, *Phot. Sci. Eng.* 18 (1974) 441.
- [7] R.E. Graves and P.I. Rose, *J. Phys. Chem.* 79 (1975) 746.
- [8] H. Schmidt, H.D. Rödder and U. Dietzel, *Phot. Sci. Eng.* 25 (1981) 21.
- [9] W.H. Hesselink and D.A. Wiersma, *Phys. Rev. Letters* 43 (1979) 1991; *J. Chem. Phys.* 75 (1981) 4192.
- [10] S. Asaka, H. Nakatsuka, M. Fujiwara and M. Matsuoka, *Phys. Rev. A* 29 (1984) 2286.
- [11] W. Cooper, *Chem. Phys. Letters* 7 (1970) 73.
- [12] H.J. Nolte, *Chem. Phys. Letters* 31 (1975) 134.
- [13] B. Kopainsky, J.K. Hallermeier and W. Kaiser, *Chem. Phys. Letters* 83 (1981) 498.
- [14] C.A. Walsh, M. Berg, L.R. Narasimhan and M.D. Fayer, *J. Chem. Phys.* 86 (1987) 77.
- [15] E.W. Knapp, *Chem. Phys.* 85 (1984) 73.
- [16] W.H. Hesselink and D.A. Wiersma, *Chem. Phys. Letters* 65 (1979) 300; *J. Chem. Phys.* 73 (1980) 648.
- [17] L.W. Molenkamp and D.A. Wiersma, *Phys. Rev. B* 32 (1985) 8108.
- [18] R. van den Berg and S. Völker, *Chem. Phys. Letters* 127 (1986) 525.
- [19] L.W. Molenkamp and D.A. Wiersma, *J. Chem. Phys.* 83 (1985) 1.
- [20] D.E. Cooper, R.W. Olson and M.D. Fayer, *J. Chem. Phys.* 72 (1980) 2332.
- [21] R.W. Olson, H.W.H. Lee, F.G. Patterson and M.D. Fayer, *J. Chem. Phys.* 76 (1982) 31.
- [22] H. de Vries and D.A. Wiersma, *J. Chem. Phys.* 80 (1984) 657.
- [23] Z.X. Yu, P.Y. Lu and R.R. Alfano, *Chem. Phys. Letters* 79 (1983) 289.
- [24] M. Kasha, in: *Spectroscopy of the excited state*, ed. B. di Bartolo, *Nato ASI Series, Series B, Physics*, Vol. 12 (Plenum Press, New York, 1976) pp. 337–365.
- [25] P.O.J. Scherer and S.F. Fischer, *Chem. Phys.* 86 (1984) 269.
- [26] G. Scheibe, in: *Optische Anregungen organischer Systeme*, ed. W. Foerst (Verlag Chemie, Weinheim, 1966) p. 109.
- [27] S.J. Strickler and R.A. Berg, *J. Chem. Phys.* 37 (1962) 814.
- [28] H.P. Dorn and A. Müller, *Chem. Phys. Letters* 130 (1986) 426.
- [29] P.B. Gilman, *Phot. Sci. Eng.* 11 (1967) 222.
- [30] H.P. Thijssen and S. Völker, *J. Chem. Phys.* 85 (1986) 785.
- [31] W.H. Hesselink and D.A. Wiersma, in: *Spectroscopy and excitation dynamics of condensed molecular systems*, eds. V.M. Agranovich and R.M. Hochstrasser (North-Holland, Amsterdam, 1984).
- [32] S. Völker, *J. Luminescence* 36 (1987) 251.
- [33] M.A. Krivoglaz, *Soviet Phys. Solid State* 6 (1964) 1340.
- [34] P. de Bree and D.A. Wiersma, *J. Chem. Phys.* 70 (1979) 790.
- [35] H. de Vries and D.A. Wiersma, *J. Chem. Phys.* 72 (1980) 1871.
- [36] H. de Vries and D.A. Wiersma, *Phys. Rev. Letters* 36 (1976) 91.
- [37] S. Nakanishi, H. Bos and D.A. Wiersma, unpublished results.