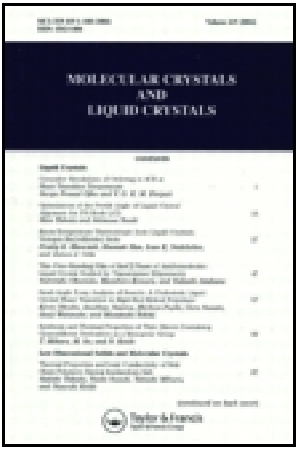

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Pulsed Dye Laser Induced Photoconduction in Single Crystals of α-Phenazine†

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Pulsed photoconductivity measurements have been performed on crystals of phenazine using a dye laser tuned in the range 500–630 nm. Within this wavelength range the magnitude of generated charges is proportional to the second power of the light intensity indicating a two-photon generation pathway. Wavelength, temperature and electric field dependences of the photogeneration efficiency have been studied. The spectral dependence is almost flat between 510 and 600 nm. Activation energies of the photogeneration process are found to be *ca.* 0.11 eV and wavelength independent. It is concluded that the photogeneration pathway involves a two photon absorption to a singlet state, a radiationless decay and an interaction between the mobile lowest singlet state and a charge carrier trap. The process leads to the production of a free electron and a trapped hole.

1. INTRODUCTION

Understanding the processes leading to the photogeneration of charges in molecular solids is a problem of major importance both from the theoretical point of view and because of the potential applications of these materials in electrophotography and solar energy devices. There are however, numerous unsolved problems. For example, although the validity of the description of the dissociation of the geminate pair of charges in terms of the Onsager model[1-3] seems to be well established

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for some organic substances (e.g. anthracene[4-6]) other existing experimental results indicate that the model is by no means generally applicable.[7-9] Recent theoretical calculations by Bounds and Siebrand[10] point out that the initial step of the intrinsic photogeneration in anthracene crystals may be a direct absorption of light by crystal charge-transfer states. This hypothesis sheds a new light on the pathways of photogeneration and it is worthwhile considering other materials in a similar manner.

Interpretation of numerous earlier reports on photoconduction of organic solids is difficult because the results reported are often influenced to an undesirable extent by surface effects, trapping of charge carriers and space charge effects. Therefore, attempts to confirm or disprove the validity of theoretical approaches to the problem of photogeneration may only be undertaken if the importance of various side effects is clearly understood.

Some of the experimental difficulties with avoiding surface and space charge effects may be overcome by studying photocurrents induced by a multiphoton absorption.[11-12] Such experiments have been performed to date for only a few photoconductors. Extension of these studies seems to be necessary to obtain more data on various generation pathways involved.

We have undertaken a study of various organic photoconductors using as the excitation source a tunable pulsed dye laser. The present communication deals with the photoconduction process in single crystals of α-phenazine. Charge generation processes in this compound have been studied by Itoh and Anzai,[13] and, later by us.[14] The results presented in Ref. [14] indicate that, independently of the excitation wavelength, the charge generation process involves the ionization of a $^1n\pi^*$ exciton in the vicinity of a molecule acting as a deep hole trap. This has been concluded, in part, from the fact that the photocurrent activation energy is wavelength independent. The results presented in Ref. [14] are supplemented now by data on wavelength, electric field and temperature dependences of the photogeneration yield employing a tunable pulsed eye laser.

2. EXPERIMENTAL

Single-crystalline platelets of α-phenazine parallel to the *bc* crystallographic face were cut from Bridgman-grown boules of highly purified material. Thicknesses of specimens ranged between 0.4 and 2 mm and areas were around 30–100 mm^2. Samples were mounted in a nitrogen dewar. Depending on the way the samples were mounted either irradiation through one of the electrodes [indium-tin oxide covered quartz] or through the side of a sample could be performed.

The excitation was with single pulses of a pumped dye laser (Molectron). The output pulses delivered up to 500 μJ in *ca.* 10 ns. The dye laser beam power was monitored using a beam splitter and a calibrated photodiode. The main beam was focused on the sample with a lens. A FET source follower with the input resistance of 10 MΩ provided the integrated photocurrent signal (see e.g. Ref. [15]) which was displayed on a scope together with the photodiode output.

In order to obtain reproducible results of wavelength, temperature, and especially electric field dependences of the photogeneration yield, it was necessary to limit the amount of accumulated photogenerated charge in a given sample to values well below 10^{-10} C per square centimeter of the crystal surface (see e.g. Ref. [6]). When possible, results for a fresh, "virgin" sample are referred to.

It has been found in the course of preliminary measurements that for a given field strength the amount of generated charge depends linearly on the crystal dimension along which the laser beam propagates (i.e. thickness in the case of surface irradiation and the sample diameter in the case of side irradiation). Therefore, to maximize weak signals, most measurements were taken with side irradiation.

3. RESULTS

The photogeneration yield has been measured with the exciting light wavelength between 505 and 630 nm. Due to the variation of the dye laser output with wavelength, the construction of the spectral dependence of the normalized yield (Figure 1) was only possible after ascertaining the intensity dependence of charge generation. It was found that within almost the whole spectral region studied, and for the light intensities employed, the magnitude of the generated charge was proportional to the square of the light intensity (see Figure 2). Only at the shortest wavelength could a branch showing a linear charge-intensity dependence be observed. The existence of this branch is obviously due to the absorption within the tail of the nearby lying $^1n\pi^*$ state (peaking at *ca.* 440 nm[16]) and subsequent ionization of the singlet exciton.[14]

The square power dependence indicate that within the studied wavelength range a two-photon process is necessary to create charge carri-

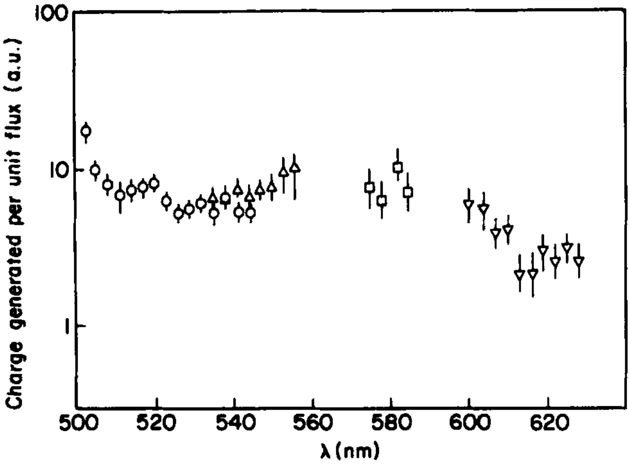

FIGURE 1 Wavelength dependence of the generation yield (normalized to a constant output power of the laser). Each point and an error bar represent the mean and variance from at least five determinations (the same applies to all subsequent figures save for Figure 2).

ers. This is readily understood since the energy gap in crystalline phenazine may be estimated to be *ca.* 4.1 eV and the energy of a photon between 500 and 630 nm is not sufficient to create any stable intermediate state in large densities which could eventually lead to the formation of charge carriers. One can suppose that triplet excitons formed by direct (forbidden) absorption may give rise to some photocurrent signal through detrapping of charges as has been observed in Ref. [14], however, these effects seem to be negligible in this study. Similarly one can exclude a direct photon-charge carrier detrapping process.

The nature of the two-photon process involved in the generation of charges may be deduced by looking at spectral and temperature dependences. Contrary to results reported by Bergmann and Jortner[11] for anthracene, there is no sharp structure in the two-photon generation coefficient vs. wavelength plot (Figure 1) which would suggest absorption into conduction subbands. Instead, the wavelength dependence exhibits a maximum at *ca.* 580 nm. The existence of this maximum may, however be put in doubt because of the relatively large spread of experimental values and possibilities of systematic errors in the determination of photogeneration efficiencies when different dyes are used in the laser. Thus, the dependence may be considered almost completely flat between 500 and 600 nm.

A feeling of the absolute values of the generation efficiencies may be given by first defining, viz Bergmann and Jortner[11] the two-photon generation coefficient K_2 which relates the concentration of generated

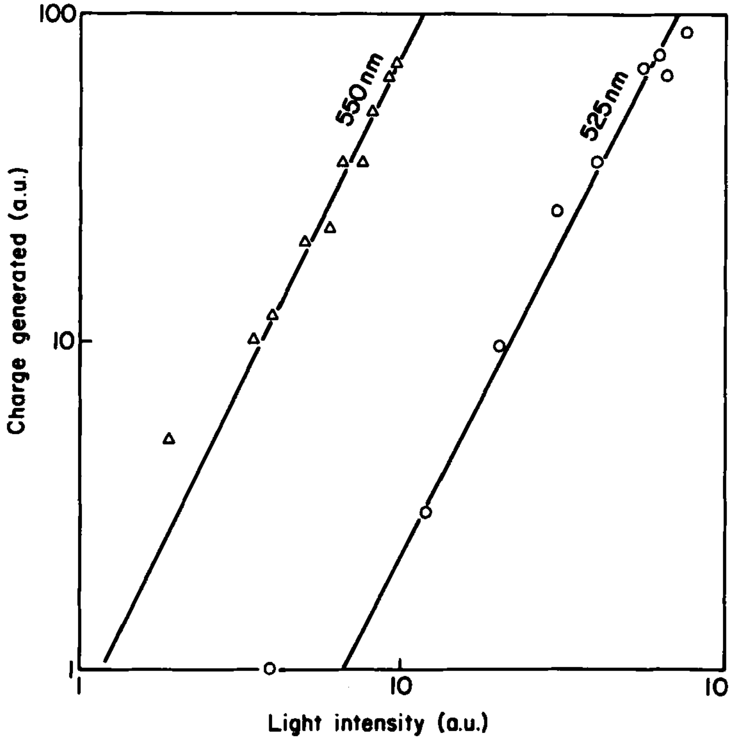

FIGURE 2 Typical intensity dependences of the charge generated by laser pulses. Wavelengths are marked in the figure.

charges m (cm^{-3}) to the light intensity I (quanta/cm^2 s)

$$m = K_2 I^2 \tag{1}$$

It should be noted that this definition is not very convenient because the K_2 value involves the duration time of the light pulse. More generally, one can define a coefficient relating the generation rate rather than the total charge to the light intensity. For comparison sake, however, it suffices to remember that in both Bergmann and Jortner's work and in this study *ca.* 10 ns pulses were used. An estimate of the K_2 value for phenazine yields *ca.* 3×10^{-41} cm s^2 at 520 nm for an electric field strength of 1.2×10^4 V/cm. This is more than an order of magnitude lower than values given for anthracene[11,17] which is consistent with our observation that photocurrent signals produced in phenazine were as a rule *ca.* 10–50 times lower than those obtained for anthracene under similar conditions in the same experimental set-up.

The measurements of electric field dependences of the photogeneration yield have been performed on a few phenazine samples and at dif-

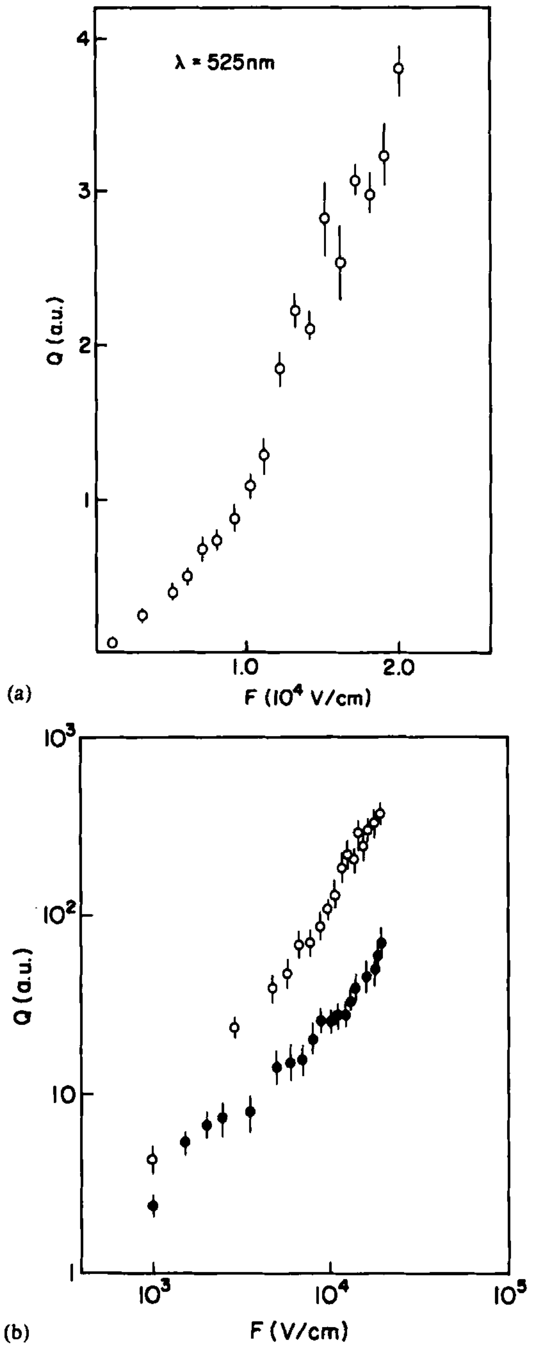

FIGURE 3 Typical electric field dependences of the photogeneration yield: (a) plotted on a linear scale ("virgin sample"), (b) double log plot of data from Figure 3a. Full points refer to the same sample but after a prolonged set of measurements during which large number of trapped charged carriers were produced.

ferent wavelengths. Figure 3 shows a typical field dependence plot obtained for a "virgin" sample of phenazine. Similar plots have been obtained for different wavelengths and for field up to 4 × 10^4 V/cm there is no evidence that the dependence exhibits a linear branch with a positive ordinate axis intercept which would justify invoking the Onsager model of field-dependent charge separation (cf. Refs. [2, 4, 5]). This is in contrast to similar results of field dependences obtained by two-photon absorption in anthracene.[12,18] When a sample with a substantial amount of charge accumulated during previous experiments is used, the dependence changes to some extent, the charges generated at given field strengths being lowered, and in many cases a straight line with a zero intercept on a linear Q vs. F scale could be observed.

The temperature dependences of the carrier generation obtained with different excitation wavelengths are shown in Figure 4. It is

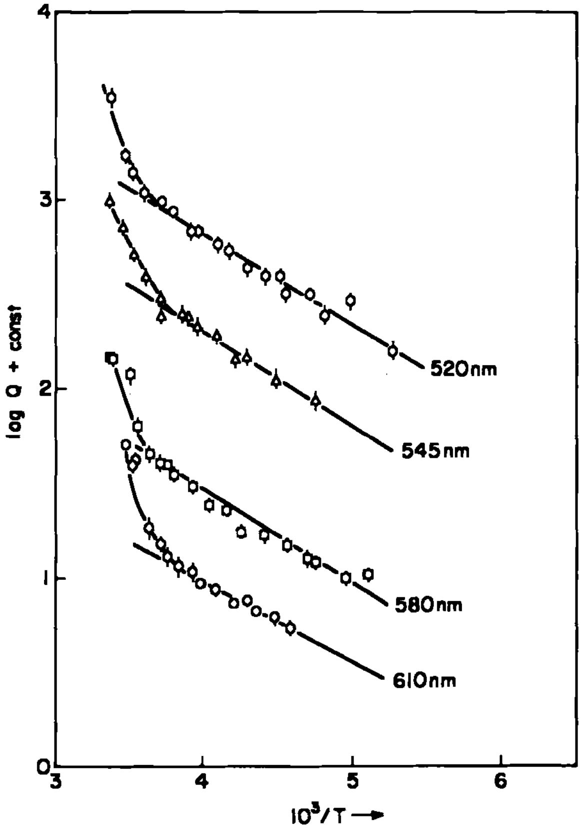

FIGURE 4 Temperature dependences of the photogeneration efficiency taken at wavelengths marked in the figure. To facilitate comparison plots have been vertically shifted.

clearly seen that, again, contrary to the case of anthracene,[12] the temperature dependences are identical for all wavelengths studied. Below 270 K the dependences may be described by an exponential function of the form $Q \sim \exp(-E_a/kT)$ with the activation energy E_a equal to *ca.* 0.11 eV. This value is in excellent agreement with the activation energy of the dc photoconductivity determined in Ref. [14]. Above 270 K a stronger temperature dependence branch is observed. The activation energy which would be necessary to explain this rather rapid increase would be at least 0.4 eV.

4. DISCUSSION

The results presented above, together with those given in Ref. [14], provide a more or less complete picture of photogeneration processes in phenazine. However, it is necessary to interpret the two-photon mechanism involved in the present study and then to compare it with the data on dc photoconductivity.

Three different mechanisms of two-photon generation may be postulated to take place:

(i) a direct two-photon band-to-band transition[11,19] leading to the production of a pair of charge carriers,

(ii) absorption to a triplet state and subsequent photoionization of a triplet (cf. Refs. [14, 20]),

(iii) two-photon absorption to a higher singlet state and ionization of this state or that resulting from the internal conversion of excess energy (the lowest singlet state of the $n\pi^*$ type.).

Obviously, any higher-order processes, like photoionization of a singlet state (formed by two-photon absorption) which would involve a cubic or still higher intensity dependences need not to be considered, although one cannot exclude their existence at light intensities still higher than those used in the present work (up to 10^{24} quanta/cm^{2}s).

The first two of the processes outlined above are believed to be operative in single crystals of anthracene, although there is an uncertainty with respect to their relative importance.[14,17,19,20] It is believed that both should lead to the creation of a pair of charge carriers (a "CT exciton"[10]) the separation of which should depend on the energy of the exciting light. In terms of the Onsager theory this means that the initial separation r_0 is wavelength dependent and so is the photoconductivity activation energy. This is certainly not the case for phenazine and indeed in anthracene, r_0 was also found to be wavelength independent over a comparable energy range.

The independence of r_0 on the wavelength may be explained[8,9] assuming that prior to the Onsager type dissociation process the excess energy of an initially formed higher excited state is rapidly dissipated so that the state being the precursor of the initial charge carrier pair is independent of excitation energy. From results presented in Ref. [14] it is evident that absorption to a $n\pi^*$ singlet state suffices to generate charge carriers hence carrier pairs. It has been argued in Ref. [14] that the energy balance of the photogeneration process must involve interaction of the exciton with a deep hole trap which leaves a free electron and a deeply trapped hole (*ca.* 1 eV). Temperature dependences observed in this work confirm this point of view, the difference being that above 270 K a branch showing a higher activation energy is seen. This feature may be understood if one assumes that different sets of trapping levels may be operative in the process. At high exciton densities, such as produced by laser pulses, the number of deeper centers may not be sufficient and some shallower traps may contribute to some extent to the total photogeneration yield, their lower energy giving rise to a higher activation energy of the process.

If the explanation put forward here is correct the spectral dependence of the two-photon generation should simply reflect the changes of the two-photon absorption coefficient. Unfortunately, no results of two-photon absorption in phenazine are known to the authors and obtaining the spectra using the simplest method of monitoring the two-photon induced fluorescence is impossible since phenazine shows no fluorescence.

The charge-carrier generation electric field dependences presented in this work are the most difficult to explain. It is clear that the behavior of curves in Figure 3 are not interpretable in terms of the Onsager theory. It is not likely that the field range used in this work may be considered high enough to observe superlinear behavior predicted by the Onsager theory. On the other hand one can suppose that the observed dependences are obscured by trapping effects which diminish the collected charge at low fields. Although this explanation cannot be completely excluded on the basis of the present work only, it is necessary to mention that photocurrent signals which were obtained with pulses of dye laser lasing at 450 nm i.e. in the region of relatively strong absorption (one-photon generation taking place in the surface region) did not show the presence of excessive trapping of electrons whereas no detectable hole signal could be obtained.[18]

Superlinear field dependences of the photogeneration yield have been often observed for various organic materials and to date no consistent theory has been presented which could explain those data. One cannot attach much significance to the fact that the date fit occasionally to a Poole–Frenkel type formula since it is well known that any slightly superlinear dependence may resemble the Poole–Frenkel type plot, especially if taken within a narrow field range. The Poole–Frenkel concept of field induced lowering of a potential barrier around a Coulombic center, while being convenient to describe ionization of donor or acceptor type levels in semiconductors does not in itself describe the photogeneration process, since to calculate the photogeneration yield one has to assume a finite recombination rate at the center (cf. e.g. Ref. [21]). Moreover, it is not clear whether it is justified to treat the interaction between geminate charges in a molecular crystal as purely Coulombic.

The extrinsic process of interaction of a Frenkel exciton with an empty carrier trap suggested here to describe the photogeneration path in phenazine has not been treated in detail yet. One can envisage such a process as consisting of two steps: the interaction of a neutral exciton with an impurity or a defect center to give a CT state, in which charges are separated, and the dissociation of the CT state. The latter process bears a resemblance to the analogous process being described by the Onsager theory of the intrinsic generation. The difference between the two dissociation processes is in the character of the initial CT state which in the case of intrinsic generation consists of identical molecules and, as a rule is of a relatively large radius.[10] For the extrinsic process the initial state consists of different molecules (i.e. one of these is an impurity or at least a host molecule in a highly distorted position), and it is likely that the radius of the state is low i.e. of the order of a single lattice spacing.

It is also possible that the neutral exciton generated interacts with a trapped carrier, again a free carrier generation mechanism which would lead to wavelength independent generation efficiencies which are yield dependent. In materials such as phenazine, anthracene etc., the complex purification processes used are generally very efficient in removing materials of a different nature, i.e. non-molecular. Hence the majority of impurities remaining will be similar to the host [eg anthracene is very difficult to remove from phenazine] and these impurities are probably the source of the carrier generation site. The nature of the site is however unknown. In either case however, one cannot automatically apply the Onsager description to the process of the electric field enhanced dissociation of such a state. One can anticipate that both assumptions vital to the Onsager formalism i.e. that of the Coulombic interaction of geminate charges and that of the continuum-like diffusion process may break down.

The existence of a superlinear field effect may also be attributed to the superposition of the field dependence of the dissociation process onto a field dependent yield of initial charge-transfer pairs. Indeed, one can consider it likely that the process of interaction of a neutral exciton with a neutral impurity to form a partly ionized CT state may be field dependent. At the present time it is impossible to separate the contributions of both photogeneration steps to the total observed field dependence. It is hoped that investigations of charge generation in weak CT complexes may shed some light on the problem of the field dependences of the dissociation of a CT exciton.

References

1. L. Onsager, *Phys. Rev.*, **54**, 554 (1938).
2. (a) D. M. Pai in: Photoconductivity and related Phenomena. Ed. J. Most and D. M. Pai, Elsevier Scientific Pub. Co. 1976; (b) D. M. Pai and R. C. Enck, *Phys. Rev.*, **B11**, 5163 (1975).
3. R. H. Batt, C. L. Braun and J. F. Horning, *J. Chem. Phys.*, **49**, 1967, 1968: *Appl. Opt. Supl.*, **3**, 20 (1969).
4. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **59**, 2269 (1973). R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **64**, 3573 (1976).
5. L. E. Lyons and K. A. Milne, *J. Chem. Phys.*, **65**, 1474 (1976).
6. K. Kato and C. L. Braun, *J. Chem. Phys.*, **72**, 172 (1980).
7. Z. D. Popovic and E. R. Menzel, *J. Chem. Phys.*, **71**, 5909 (1979).
8. J. Noolandi and K. M. Hong, *J. Chem. Phys.*, **70**, 3230 (1979).
9. Z. D. Popovic and J. H. Sharp, *J. Chem. Phys.*, **66**, 5076 (1977).
10. P. Bounds and W. Siebrand, *Chem. Phys. Letters*, **75**, 414 (1980).
11. A. Bergmann and J. Jortner, *Phys. Rev.*, **B9**, 4560 (1974).
12. C. S. Ryan, J. B. Webb and D. F. Williams, *Mol. Cryst. Liq. Cryst.*, **56** (Letters), 69 (1979).
13. U. Itch and H. Anzai, *J. Phys. Soc. Japan*, **25**, 1198 (1968).
14. M. Samoc, J. B. Webb and D. F. Williams, *Mol. Cryst. Liq. Cryst.* **62**, 201 (1981).
15. Z. Burshtein and D. F. Williams, *Phys. Rev.*, **B15**, 5769 (1977).
16. R. M. Hochstrasser and C. Marzacco, *J. Chem. Phys.*, **49**, 971 (1968).
17. M. Samoc, W. Siebrand, J. B. Webb and D. F. Williams, *Mol. Cryst. Liq. Cryst. (Letters)*, **64**, 89 (1981).
18. J. B. Webb and D. F. Williams, in preparation.
19. G. Strome, *Phys. Rev. Letters*, **20**, 3 (1968).
20. P. Holtzman, R. Morris, R. C. Jarnagin and M. Silver, *Phys. Rev. Letters*, **19**, 506 (1967).
21. D. F. Blossey, *Phys. Rev., B9*, 5183 (1974).