

STUDIES OF HIGHLY EXCITED TRIPLET STATES IN SOLIDS BY MEANS OF  
CASCADE EXCITATION WITH FEBETRON AND DYE-LASER

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Pulsed electron beams have been used widely for studies of the dynamic processes of photochemical reactions. So far most of the studies are confined to the measurements of the optical absorption change induced by the irradiation and of the photo-emission arising from the lowest singlet or triplet excited states. It is known that many of the photochemical reactions take place when the system is excited into a dissociative state which may be located at higher energies than the lowest states. Therefore it is of primary importance to clarify the structure of the highly excited states which may be a mixture of vibronic states and dissociative states. An excitation from the lowest triplet states to a higher state by a dye-laser may allow populating a triplet excited state at a given energy. Measurements of the luminescence or the photochemical changes induced by such an excitation may be useful to derive information on the non-radiative processes from the highly excited states and to isolate a dissociative state out of the mixed states.

The purpose of the present paper is to report the measurements of the fluorescence induced by a cascade excitation using an electron pulse from a Febetron accelerator and a light pulse from a dye laser. The former populates the lowest triplet excited state, whereas the latter produces the highly excited states. From the result of the fluorescence measurements, the triplet-singlet conversion efficiencies in naphthalene doped with  $\beta$ -chloronaphthalene and in NaCl were obtained as a function of the photon energy of the exciting light.

The block diagram of the experimental arrangements for the measurement of the fluorescence induced by the cascade excitation is shown in Fig. 1. A trigger pulse from a pulser is fed into a Febetron accelerator and a nitrogen laser so that a specimen is irradiated successively with an electron pulse and a laser pulse at a separation of  $1 \sim 100$  ms. Each of the fast and slow components of the luminescence from the specimen is measured with an oscilloscope. Photo-emission from Rhodamin B dissolved in ethanol at a concentration of  $5 \times 10^{-3}$  mol was used for a monitor of the intensity of the laser light. The laser light and the fluorescence were recorded on the oscilloscope A and the phosphorescence and the timing signal were recorded on the oscilloscope B.

The relation between the fluorescence induced by the cascade excitation and the photon energy for a naphthalene crystal doped with  $\beta$ -chloronaphthalene obtained at 15K is shown in Fig. 2. The ordinate of the figure is the fluorescence intensity corrected for the fluctuation of the intensities of the light and electron pulses. The latter correction was made using the intensity of the phosphorescence. The responses for photons for 2.0~2.3 eV and above 2.9 eV were assigned to be due to the excitation from the lowest triplet exciton trapped by  $\beta$ -chloronaphthalene to the exciton formed by a

$^3A_{1g}^+$  states, and that formed by a  $^3B_{1g}^-$  state of the naphthalene molecule, respectively. The structure in the response curve are almost the same as those observed in the optical absorption curve.

The yield of the singlet exciton per high energy triplet state created by the cascade excitation was found to be  $2 \times 10^{-4}$  for the excitation to the  $^3A_{1g}^+$  state and  $8 \times 10^{-4}$  for the excitation to the  $^3B_{1g}^-$  state. The yield is independent of the photon energy from the dye laser except a linear increase between 2.3 eV and 2.5 eV. This increase may be related to the presence of the bottom of the conduction band at 2.3 eV above the lowest triplet exciton state. The fluorescence intensity induced by the cascade excitation was found to be proportional to the square of the concentration of the triplet exciton. This result indicates that the fluorescence is induced by the interaction between two triplet excitons: one detrapped by the excitation and the other trapped by the  $\beta$ -chloronaphthalene. The quantum yield of the detrapping was found to be nearly unity above 2.5 eV.

Similar experiments were made for NaCl. It was found that the excitation spectrum for the singlet emission by the cascade excitation is completely different from the optical absorption spectrum. This result appears to be due to the fact that the coupling between the electronic states and the lattice in alkali halides is very strong.

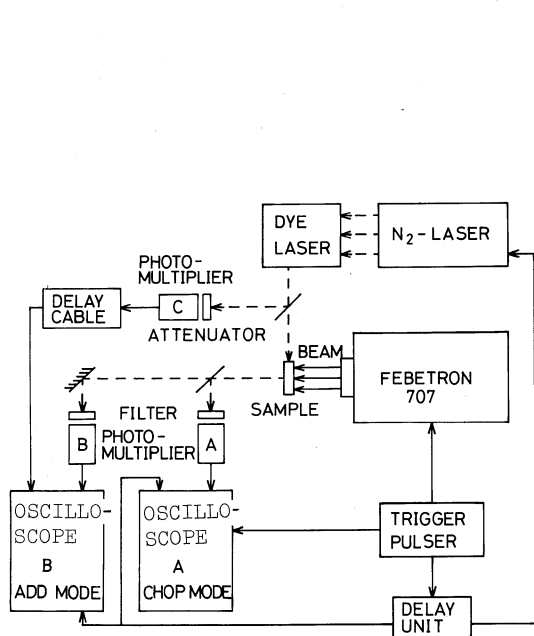


Fig. 1

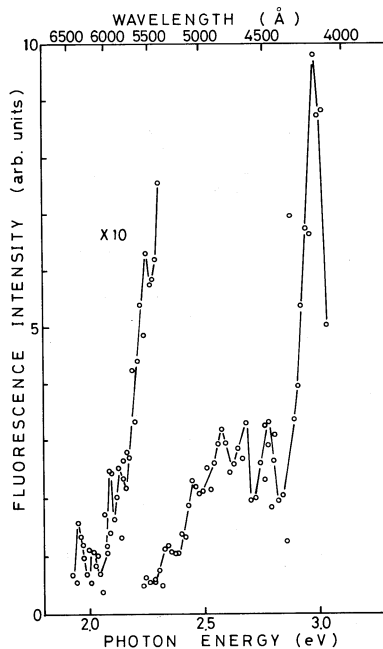


Fig. 2