

DOUBLE EXCITATION SPECTROSCOPY
BY ELECTRON AND LASER-LIGHT PULSES

Katsumi Tanimura, Kazuo Soda and Noriaki Itoh

Department of Crystalline Materials Science, Faculty of Engineering,
Nagoya University, Nagoya, Japan

The studies of the photochemical processes in alkali halides by means of the double excitation spectroscopy, using an electron pulse from an accelerator and a light pulse from a tunable dye laser, are reported. The advantages of the double excitation spectroscopy over the single excitation spectroscopy and the implication of the obtained results are discussed.

In order to understand the photochemical processes in solids and molecules it is important to make clear the dissociative states at which the reaction products are evolved. For this purpose the studies of the wavelength dependent reaction using intense uv and visible light have been made extensively. We have undertaken studies of the wavelength dependent reaction induced by the double excitation: by an electron pulse and by a light pulse from a tunable dye-laser. In this method, the lowest triplet excited states are populated by the excitation with an electron pulse and are subsequently excited into higher states with a light pulse, which is delayed by 10^{-6} - 10^{-3} s from the electron pulse.

Advantages of the double excitation spectroscopy over the single excitation spectroscopy are as follows: (1) The triplet excited states can be surveyed directly; and (2) in the system in which some of the degeneracy in ground state is removed by the Jahn-Teller distortion at the lowest excited states, the double excitation can resolve the chemical reactions induced at the sublevel split by the Jahn-Teller distortion of the lowest excited states. In this paper we report the studies of the double excitation spectroscopy in alkali halide crystals. In alkali halide crystals with NaCl structure the self-trapping of the excitons is known to reduce the symmetry from O_h to D_{2h} .

The experimental apparatus¹⁾ for the double excitation spectroscopy is shown in Fig. 1. The amount of the chemical reaction products at the incidence of the electron and light pulses was determined by means of optical absorption spectroscopy.

One-electron orbitals of the self-trapped excitons in alkali halides is shown in Fig. 2. The lowest four orbitals are originated from the halogen p-orbitals, and the others are for a trapped electron in a D_{2h} potential. The electron occupation shown in the figure is for the lowest self-trapped excitons.

The optical absorption from the lowest triplet excitons to the higher state (T-T absorption) has been measured by Williams and Kabler.²⁾ The direction of the transition dipole for each transition is determined using the double-excitation technique: The change in the T-T absorption induced by polarized laser light is measured using polarized light either parallel or perpendicular to the laser light.³⁾ The order of the excited states are shown in Fig. 2 in accordance with the results of the polarization measurements.

The F center creation yield in KCl by the excitation of the lowest self-trapped excitons was obtained as a function of the excitation energy.¹⁾ The result is shown in Fig. 3, in which the T-T absorption curve is also shown. Evidently the excitation within the lowest optical absorption band which has been ascribed to the $a_{1g} \rightarrow b_{2u}$ electron transition produces the F-centers. Moreover the excitation into the next higher state is seen to produce the F centers at the same yield. This result means that no additional creation of the F centers takes place at the next excited state, namely at the state in which the electron is excited into the b_{3u} orbital. The result has been interpreted on the basis of the configurational mixing between the electron-excited states and the hole-excited states.

We have already used the double excitation spectroscopy for several other studies, such as the orientational correlation between the self-trapped excitons and the evolved interstitial centers³⁾ and the intersystem crossing from the electron-excited and hole-excited states in KI ⁴⁾ and in $NaCl$.⁵⁾ These results appear to yield very detailed information not only on the photochemical processes but also on the non-radiative processes in the self-trapped excitons.

References.

- 1) K. Soda and N. Itoh, J. Phys. Soc. Japan **46**, 1618 (1980).
- 2) R. T. Williams and M. N. Kabler, Phys. Rev. **B9**, 1897 (1974).
- 3) K. Tanimura, K. Soda and N. Itoh, to be published.
- 4) Y. Ban, K. Tanimura and N. Itoh, to be published.
- 5) K. Soda and N. Itoh, Physics Letters **73A**, 45 (1979).

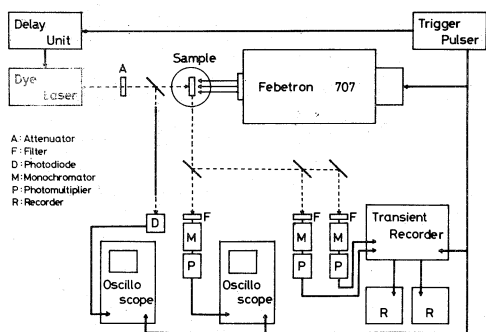


Fig. 1

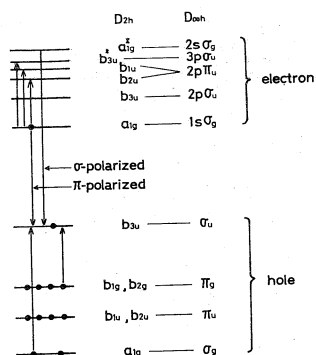


Fig. 2

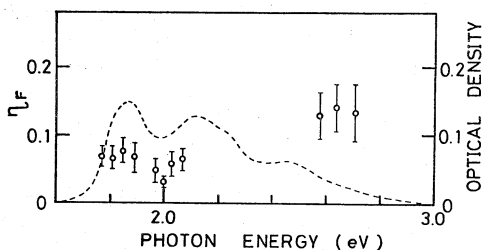


Fig. 3