Transient Photobleaching of Trapped Electrons

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Summary Intense light pulses from a ruby laser have been used to saturate trapped electron absorptions in crystals (*viz.* KBr and KI) and low temperature glasses (*viz.* aqueous 10 M-OH^- and MTHF) and have shown that (*i*) the electron band is broadened homogeneously in the crystals and heterogeneously in the MTHF glasses, and (*ii*) the characteristics of transient and permanent photobleaching differ very markedly in each system.

TRAPPED electrons were produced by γ-irradiation in single crystals of pure KI(λ_{max} 685 nm) and KBr (λ_{max} 630 nm) at 295 K, in MTHF (2-methyltetrahydrofuran) glasses at 77 K (λ_{max} 1250 nm) and in 10 M-NaOH/KOH aqueous glasses at 77 K (λ_{max} 580 nm). The samples were illuminated at these temperatures by single 20 ns pulses of 694 nm light from a *Q*-switched ruby laser at light fluxes up to 2×10^{26} photon cm^{-2} s^{-1}, at which level there were typically several hundred times as many photons per cm^2 as there were absorbing species. Measurements were made concurrently of the absorbance at 694 nm during the ruby pulse, by monitoring the transmitted intensity as previously,[1,2] and the absorbance at 633 nm (He/Ne laser line) both during and after the ruby pulse.

The Figure shows the extent of bleaching, as measured by $(A^\circ - A)/A^\circ$, with incident ruby light intensity.

F-Centre electrons in KI crystals were completely bleached during the pulse peak for values of $I \geqslant 10^{26}$ photon cm^{-2} s^{-1}. Some of this transmission resulted from saturation of the optical transitions involved; but for all these intensities *ca.* 70% of the induced transparency persisted for a short time (μs) after the pulse. The original absorbance was then re-established ($A \rightarrow A^\circ$) according to a first-order kinetic rate with a half-life of 7·5 μs for KI and 0·4 μs for KBr. Permanent bleaching of the *F*-centres for all ruby light intensities was very small, <1% bleaching per pulse, which corresponds to a quantum yield of $<10^{-2}$. During the pulse peak the extents of transient bleaching at 694 and 633 nm were equivalent and analogous results were obtained for KI and KBr. *F*-Centre bands are evidently homogeneously broadened in line with theoretical work.[3] Another state, probably *F'*, which may be reached indirectly from the first excited state, readily undergoes saturation of optical transitions under a photostationary situation, and eventually decays to the *F*-centre at room temperature over a period of microseconds.

By contrast e_t^- in MTHF glasses showed transient bleaching during the pulse at the exciting wavelength but not at 633 nm. Thus the absorption band at 694 nm seems to be heterogeneously broadened despite expectations that that region represents an ionisation continuum.[4] Some net permanent bleaching "grew in" at 633 nm but only very slowly, some 10^{-2} to 10^{-1} s (variation from sample to sample) after the pulse.

For electrons trapped in 10 M-OH^- glasses bleaching occurred at both 694 and 633 nm during the pulse at the highest available intensities; but in addition a comparable amount of bleaching at 633 nm "grew in" after the pulse with a half-life of *ca.* 0·6 μs. Subsequently there was no further change in the transmission at 633 nm so that the permanent bleaching in OH^- glasses consisted of both the immediate and the fast delayed effects. Bleaching sets in only at much higher intensities per absorbing species for the OH^- glasses than for MTHF. The immediate bleaching at both wavelengths implies homogeneous broadening or very much stronger overlap of any substructure bands than in the case of MTHF. Furthermore, they differ markedly from *F*-centres in that permanent bleaching is observed to be comparable to transient bleaching. This suggests that the de-excitation is too rapid for any saturation of the transition (as with e_{aq}^-[1,2]) but that some loss by reaction occurs from the excited state.

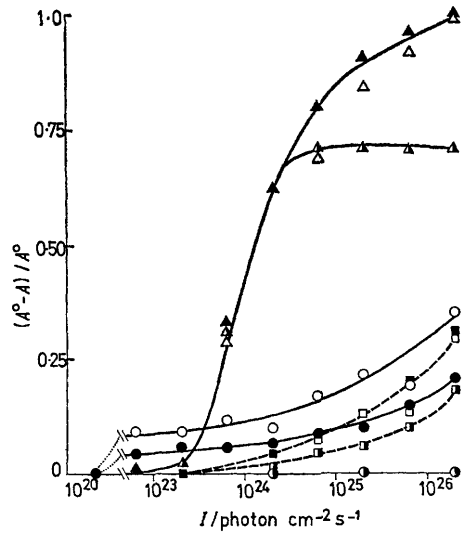

FIGURE. *Photobleaching of trapped electrons in three media as a function of laser peak intensity* (I) *at 694 nm. The ordinate shows the fraction bleached, where* A° *is the absorbance at 694 or 633 nm for low incident intensities* ($< 10^{20}$ *photon* cm^{-2} s^{-1}) *and* A *is the measured absorbance at 694 or 633 nm for intensity* I *of 694 nm light. Triangles refer to F-centre electrons in KI crystals at 295 K. Circles refer to electrons trapped in MTHF glasses at 77 K. Squares refer to electrons trapped in aqueous 10 M-OH^- glasses at 77 K.* ▲, ■, ●, *694 nm during the pulse peak.* ◭, ◨, ◑ *633 nm 10 ns after the end of the pulse.* △ *633 nm during the pulse peak.* ○, □ *633 nm 1 min after the end of the pulse.*

These transient flash photolysis effects are strikingly different to the permanent changes induced by low intensity illumination.[5]

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