Detrapping Excitation Spectra and Optical Absorption of Matrix Trapped Electrons

By A. Bernas,* D. Grand, and T. B. Truong

(*Equipe C.N.R.S. n° 98, Laboratoire de chimie-Physique de l'Université de Paris VI, Centre d'Orsay* 91-*Orsay, France*)

Summary When the photorelease of trapped electrons is followed through photoconductivity, photobleaching efficiency, and neutralization luminescence, the three excitation spectra are found to coincide but, depending upon the solvent, are more or less shifted towards the blue with respect to the e^-_t absorption band; the corresponding energy separation cannot be correlated with the dielectric properties of the solvent.

It has been generally considered that the trapped electron (e^-_t) optical absorption band corresponds to a $2p \leftarrow 1s$ transition between two bound states of the electron. In particular, in all types of theoretical treatment of the hydrated electron,[1] the excited state has been regarded as a bound electronic state. It has also been suggested that the solvated electron transition might reflect a photodetachment process[2,3] and, quite recently, experimental observations have led to a similar interpretation for aqueous electrons, either solvated[1] or trapped in alkaline ice.[4] Another interpretation has also been put forward: that the e^-_t absorption spectrum in alkane relaxed glasses might be a composite of two transitions of the electron, one to a bound state, the other to the photoionization continuum.[5] However, recent photoconductivity measurements on a γ-irradiated MTHF glass have shown that electron photodetrapping efficiency and absorption curves are widely separated.[6]

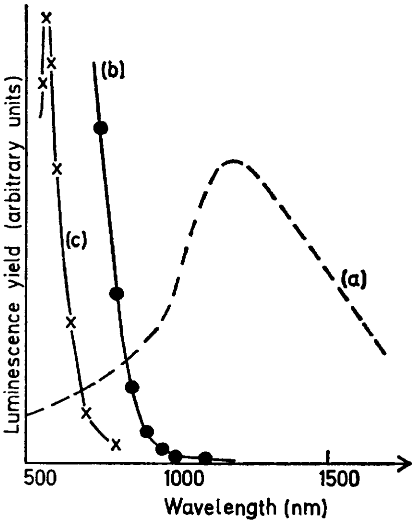

Figure 1. e^-_t *in MTHF glass.* (*a*) *Absorption spectrum;* (*b*) *stimulated luminescence spectrum from photoionized TMPD in MTHF* (λ_{an} = 480 nm); (*c*) *identical to* (*b*) *for DPPD in MTHF* (λ_{an} = 480 nm).

The present study, based on photoionized solid solutions, attempts to correlate the photoconductivity to the photobleaching efficiency curves and the neutralization luminescence excitation spectra. Comparison will be made with the e^-_t absorption spectrum in the relaxed matrix.

Tetramethyl-*p*-phenylenediamine (TMPD) and diphenyl-*p*-phenylenediamine (DPPD) have been photoionized at 77 K, under 313 nm, in methyl tetrahydrofuran (MTHF), methylcyclohexane (MCH), and 3-methylpentane (3MP) glasses (4×10^{-3}M solutions).

After the isothermal luminescence had become negligible, the photobleaching experiments were carried out at variable wavelengths λ_b, either in the cavity of the spectrophotometer (for measuring the decrease of d_{opt} at the maximum of the e^-_t band) or in the cavity of a Jobin Yvon Bearn spectrofluorimeter (for neutralization luminescence recordings at the analysing wavelength λ_{an}, maximum of the solute phosphorescence band).

In both cases, the curves refer to a constant number of absorbed photons; the luminescence curves are further corrected for the variation of light flux with λ_b and for the e^-_t depletion due to the successive bleachings.

Figure 1 gives the luminescence excitation or so called "stimulation" spectra obtained for TMPD(b) and DPPD(c) in a MTHF glass. For TMPD, when λ_b is smaller than 800 nm, the stimulation spectrum presents, besides an e^-_t band, some extra bands presumably originating from a molecular or radial anion of TMPD.[7] The DPPD stimulation spectrum clearly shows a maximum located at 580 ± 10 nm, which is precisely the wavelength position of the

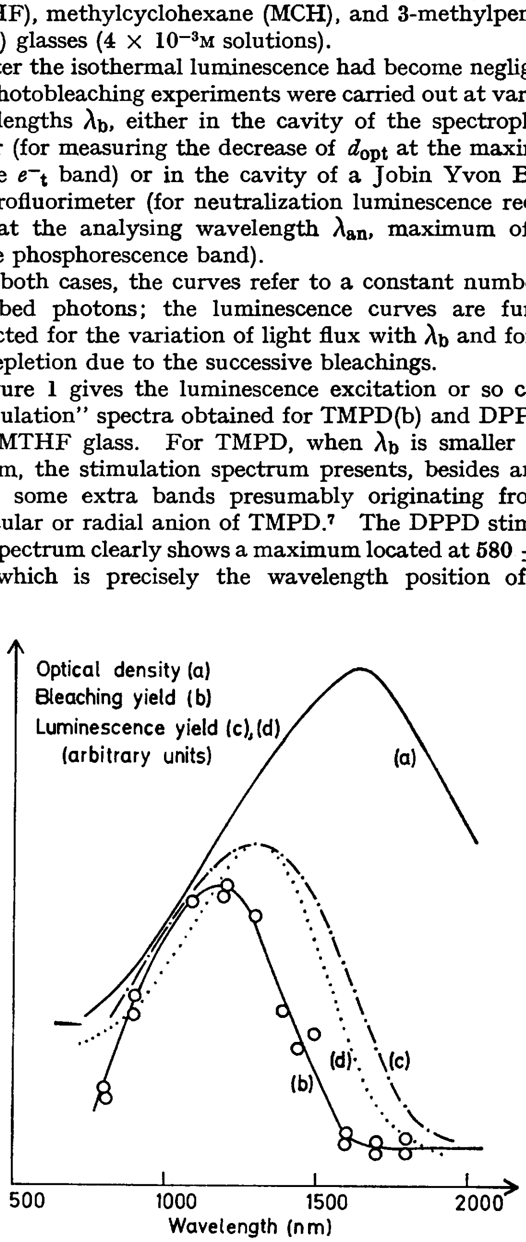

Figure 2. e^-_t *in MCH glass.* (*a*) *Absorption spectrum;* (*b*) *bleaching efficiency curve;* (*c*) *stimulated luminescence spectrum from TMPD in MCH* (λ_{an} = 480 nm); (*d*) *stimulated luminescence spectrum from γ-irradiated MCH* (λ_{an} = 430 nm).

maxima found for photoconductivity and photobleaching efficiency.[6] On the other hand, the e^-_t optical absorption peaks at 1200 nm.

Figure 2 shows the results obtained for a MCH matrix; to avoid its cracking, 10% 3MP was added. The absorption (a) and bleaching efficiency (b) curves refer to a γ-irradiated MCH sample ($2\cdot3 \times 10^{19}$ eV g^{-1}).

Two luminescence excitation spectra are presented; spectrum (c) corresponds to a u.v. ionized TMPD–MCH system, (d) refers to a γ-irradiated MCH glass; they are both envelopes of the experimental curves which display structures related to the solvent molecule stretching modes. The λ_{max} agrees satisfactorily with previous determinations.[8] Since the energy separation between the e^-_t absorption band and the luminescence spectra is small ($\Delta E \simeq 0\cdot2$ eV), it would be desirable that the luminescence excitation spectrum λ_{max} be more precisely located. However, two difficulties appear in this respect: for the γ-irradiated MCH, λ_{an} has been set at 430 nm but the nature of the emitter remains uncertain;[9] as to the u.v. ionized TMPD–MCH sample, λ_{max} has been found to decrease slightly on increasing irradiation time and TMPD concentration.[7] Curve (c) corresponds to a 20 min irradiation time and a solute concentration of 4×10^{-3}M.

For a TMPD-3MP glass, the luminescence stimulation spectrum looks very similar in shape and spectral position to the spectrum obtained from TMPD–MCH. However, from previous bleaching measurements[10] no bleaching efficiency maximum appears.

We conclude that the three curves: photocurrent versus λ_b, photo-bleaching efficiency, and neutralization luminescence excitation spectra present a threshold at the same frequency position and also a maximum at the same λ_{max}. Any of these curves represents an electron photodetrapping cross-section. Using Albrecht's terminology,[11] it follows that the optically excited electrons which recombine are not only "mobilized" but "ionized," that is they have been raised to the conduction band. Determination of the photoionization excitation spectrum for a few glasses shows that the e^-_t absorption spectrum in the fully relaxed matrix does not in general cover a transition to the ionization continuum. The energy separations ΔE between the maxima of the e^-_t absorption band and any one of the three detrapping curves amount to $0\cdot2 \pm 0\cdot1$ eV for MCH and 3MP, 1·1 eV for MTHF. For alkaline ice, $\Delta E = 0$[4] and for MeOH[12] or EtOH[13] glasses, $\Delta E > 0\cdot8$ eV.

Hence, just as the dielectric properties of the solvent do not suffice to account for the e^-_t transition energy from the ground to the first excited electronic state[14,15] it appears that the binding energy of the excited state cannot be correlated with the solvent polarity.

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