Trapped Electrons and Free Radicals in γ-Irradiated Ethanol Glasses

By A. BERNAS* and D. GRAND
(*Laboratoire de Chimie Physique de la Faculté des Sciences de Paris, 91-Orsay, France*)
and C. CHACHATY
(*Service de Chimie Physique-C.E.N. de Saclay, B.P. no 2, 91-Gif-sur-Yvette, France*)

Summary The absorption spectrum and extinction coefficients of trapped electrons and $CH_3\dot{C}HOH$ in γ-irradiated glassy ethanol have been determined down to 210 nm and, by optical bleaching, the photodetachment threshold of the electrons is found to be about 2·3 ev.

THE optical absorption spectrum of trapped electrons in alcoholic glasses is very well known in the visible region; however their extinction coefficient has not been previously determined in an EtOH matrix. We now report such a determination, and also results on the optical bleaching of trapped electrons which allow an estimation of their photodetachment threshold.

Degassed and purified ethanol was irradiated in cylindrical Suprasil cells at 77K with ^{60}Co γ-rays. The absorption spectra were determined at 78K with a Zeiss PM QII spectrophotometer, modified for measurements at low temperatures as described.[1] Spectra were taken against blanks of unirradiated ethanol glasses.

The optical bleaching was carried out *in situ* with a 500 W Xe lamp in conjunction with a Bausch and Lomb monochromator. The concentrations of paramagnetic species were estimated from the radiochemical yields: $G(e_t^-) = 2{\cdot}5$, $G(CH_3\dot{C}HOH) = 5$.[2]

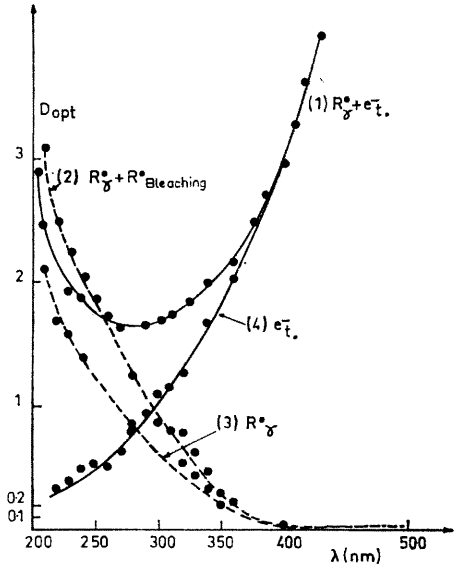

FIGURE 1. *Absorption spectra of irradiated glassy ethanol before photobleaching* (1) *and after photobleaching* (2). *Respective absorption spectra, after γ-irradiation, of* $CH_3\dot{C}HOH$ *radicals* (3) *and trapped electrons* (4).

In Figure 1, curve 1 corresponds to the trapped electrons e_t^- and to the $CH_3\dot{C}HOH$ radicals produced by γ-irradiation; curve 2 represents the absorption of the $CH_3\dot{C}HOH$, produced both by the γ-irradiation and by a subsequent electron optical bleaching. These curves are analogous to the absorption spectra already published by Dainton[3] for methanol, and by Teply[4] for the C_1—C_6 alcohols.

A calibration has now been performed by means of e.s.r. measurements of the separate e_t^- and $CH_3\dot{C}HOH$ signals on the same irradiated sample. Knowing from the e.s.r. results that one bleached electron gives rise to one $CH_3\dot{C}HOH$ radical and assuming that no other u.v.-absorbing species results from the dissociative electron attachment on the ethanol molecule, the respective extinction coefficients of e_t^- and $CH_3\dot{C}HOH$ can be deduced. These are given in

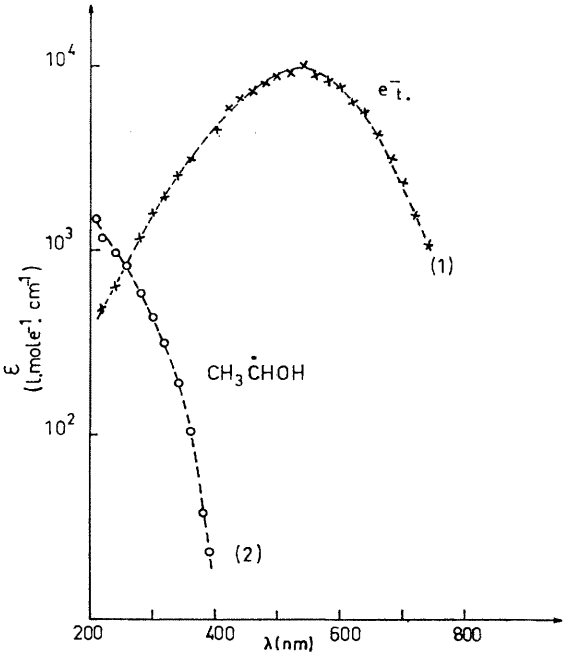

FIGURE 2. *Extinction coefficients of* e_t^- (1) *and* $CH_3\dot{C}HOH$ *radicals* (2).

Figure 2 on a semi-log scale. Contrary to previous findings,[5] no structures appear on the radical absorption curve, which, on the other hand, is found not to extend into the visible region, as previously reported.[4] As for the trapped electron band, there is no indication of an absorption rise in the 540—210 nm region. Such a rise seems, however, to appear below 380 nm for trapped electrons produced by the deposition of alkali-metal atoms on solid alcohols.[6]

If the electrons are photodetached from their traps by excitation with light of varying wavelength, a relative quantum efficiency for the electron bleaching can be determined. The experimental results are given in Figure 3, and Figure 4 illustrates that a partial bleaching by

400 nm light modifies only slightly the general shape of the electron absorption spectrum. The full curve of Figure 3 indicates the onset of a complete photodetachment of the electron around 2·3 ev. Such an observation, also made for methanol glasses,[4] suggests that the first excited bound state of the electron lies very close to its ionization potential value in the two alcohols.

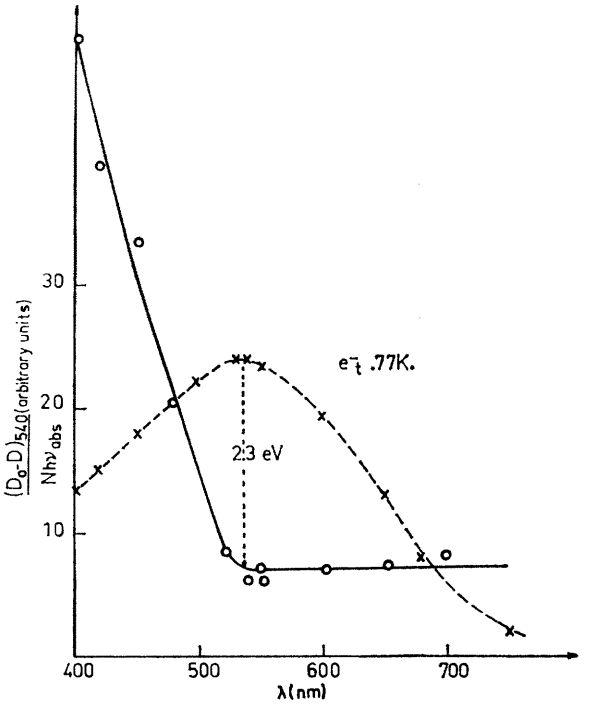

FIGURE 3. *Relative quantum efficiency for electron bleaching.*

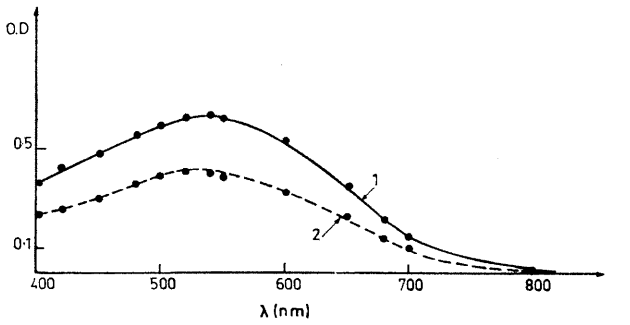

FIGURE 4. *Absorption spectrum of trapped electrons after γ-irradiation* (1), *and after partial bleaching at* 400 *nm* (2).

As already pointed out,[6] the absence of an absorption rise in the electron optical spectrum (540—210 nm) does not seem to be consistent with an unquantized ionization in this energy region. The bleaching curves obtained from methanol,[4] ethanol (present report), and methyltetrahydrofuran[7] glasses seem, however, to imply the existence of such an ionization continuum.

(*Received, October* 14*th*, 1970; *Com.* 1770.)

[1] A. Bernas and D. Grand, *J. Chim. Phys.*, 1970, **67**, 566.
[2] C. Chachaty, *J. Chim. Phys.*, 1967, **64**, 614.
[3] F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc.*, 1969, *A*, **313**, 1.
[4] A. Habersbergerova, Lj. Josimović, and J. Teply, *Trans. Faraday Soc.*, 1970, **66**, 656, 669.
[5] I. A. Taub and L. M. Dorfman, *J. Amer. Chem. Soc.*, 1962, **84**, 4053.
[6] J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc.* (*A*), 1967, 1393.
[7] P. J. Dyne and O. A. Miller, *Canad. J. Chem.*, 1965, **43**, 2695.