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ISOTHERMAL CHANGE OF THE SPECTRUM OF LOCALIZED ELECTRONS IN GLASSY 1-PROPANOL IRRADIATED AT 4 K

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An isothermal change at 77 K of the absorption spectrum of electron localized at 4 K in glassy 1-propanol revealed the elementary steps responsible for the spectral shift from IR to the visible region: the rapid shift (from 1800 to 1650 nm) and decay of the IR peak were followed by a gradual shift (from 800 to 580 nm) and an increase of the visible peak. The results support the two-trapping site model previously proposed for alcoholic matrices.

The apparent spectral shift from IR to the visible region of localized electrons generated by ionizing radiations in glassy alcohols has been attributed either to the orientation of molecular dipoles around the localized electrons, which results in the deeper potential wells,$^{1)}$ or to the migration of electrons from shallow to deeper trapping sites.$^{2)}$ Recently we have proposed a new interpretation which says that the initial electron spectra are principally the superposition of the component spectra due to IR- and visible-absorbing electrons, and that the spectral shift is primarily due to the lesser stability of the former electrons.$^{3,4)}$ Using the 4 K γ-irradiation technique, this interpretation was based on the appearance of the initial visible absorption peak together with the IR peak when the alcohols were frozen slowly$^{3)}$ and on the selective scavenging of two kinds of electrons by toluene.$^{4)}$ Recently Buxton et al.$^{5)}$ have reported on the localized electron spectra from glassy 1-propanol pulse-irradiated at 6-115 K, and have proposed that the shape of the end-of-pulse spectra is determined by the temperature-dependent initial distribution of electrons among the various pre-existing trapping sites.

Up to now, there has been no satisfactory correlation between the data obtained by the low temperature pulse radiolysis$^{5-7)}$ and by the steady-state spectral measurements obtained by means of the 4 K-irradiation technique.$^{3,4)}$ The diverse proposals on the spectral shift may be attributed to the difference in experimental methods. A shortcoming of the steady-state measurements is the difficulty of monitoring the time-evolution of the spectra due to the relaxation (and decay) of the localized electrons.

To shed light on these problems, we have attempted to observe at 77 K the spectral evolution of the localized electrons generated in glassy alcohols at 4 K. The change of the electron spectrum was followed in detail for 1-propanol and found to be essentially consistent with the pulse radiolysis result reported by

Buxton *et al.*.5) The change supported strongly the existence of the IR- and visible-absorbing electrons which we had proposed previously.3)

1-propanol was purified and dried, sealed in a Suprasil quartz cell (0.2 cm optical path), and frozen rapidly as described elsewhere.3) γ-irradiation and optical absorption measurements were carried out at 4 K as described previously.3,8)

The time-evolution of the spectrum was recorded by transferring an irradiated sample quickly in complete darkness from a liquid He cryostat to a liquid N_2 Dewar set in a recording spectrophotometer (Shimadzu, MPS-5000) and by scanning it repeatedly in a limited wavelength range as shown in Fig. 1. The time-resolved spectral shapes were deduced from the recorded spectra in several wavelength ranges after subtracting the background absorption obrained by the complete photobleaching. Each scan took less than thirty seconds depending on the wavelength range and the first scan could be started two minutes after the sample transfer. The temperature of the sample monitored by a thermocouple reached 77 K within seconds.

The time-resolved spectral shapes after warming the sample to 77 K are shown in Fig. 2, where the initial spectrum recorded at 4 K is also shown for comparison. The IR peak initially lying at 1800 nm shifted to 1650 nm before the first scan at 77 K. Its intensity decreased rapidly to about one third during the first three minutes and up to two thirds during the next three minutes. During these periods the visible part of the absorption spectrum increased by only 20% of the ultimate amount of the intensity increment when the visible ab-

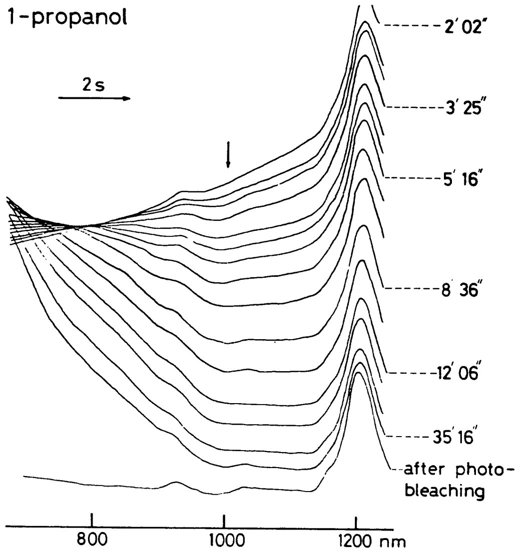

Fig. 1. Spectrophotometer traces of spectra from 1-propanol irradiated to a dose of 1.7x10^{19} eV·g^{-1} at 4 K recorded at 77 K. The numbers in the figure indicate the time when the scanning passed a wavelength of 1000 nm (shown by the vertical arrow) after the transfer of the sample into liquid N_2. The horizontal arrow shows the rate and direction of the scanning.

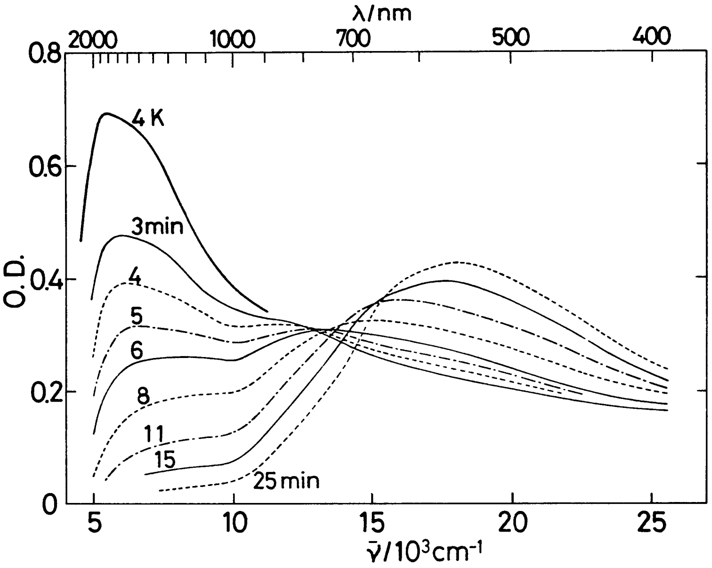

Fig. 2. The change of the electron spectrum at 77 K of glassy 1-propanol irradiated to a dose of 1.7x10^{19} eV·g^{-1} at 4 K. The times after transferring the sample into liquid N_2 are shown in the figure (in min/unit). The spectral shape indicated as 4 K was recorded before warming to 77 K.

sorption was measured at 580 nm.

When an appreciable amount of the IR absorption decayed out, a broad peak of the visible absorption became discernible at about 800 nm (see, for example, the spectrum for 5 min in Fig. 2). The visible peak gradually and continuously shifted to 580 nm and increased in intensity. The intensity increase occurred mostly during the later period of the spectral change after the IR absorption had almost disappeared. Therefore the change in the visible absorption did not synchronize with that in the IR absorption (the former occurred slowly).

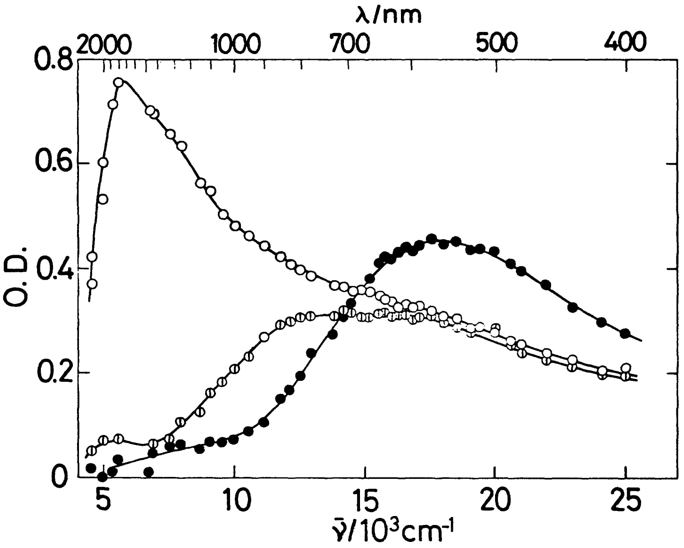

Fig. 3. The electron spectra observed (○) immediately after irradiation to a dose of 1.7x10^{19} eV·g^{-1} at 4 K, (⦶) after photobleaching at 4 K with light of 1100 nm, and (●) after warming the photobleached sample to 77 K for 20 min. All measurements were made at 4 K.

The two-site model appeared to be reliable for interpreting the observed spectral evolution. The decay of the IR peak was largely due to the simple disappearance of the IR-absorbing electrons. The growth of the visible peak was attributable to the narrowing of the component spectrum of the visible-absorbing electrons, although it may have been caused partly by the transformation of the IR-absorbing electrons into the visible-absorbing ones, especially in the later period.

The spectral narrowing of the visible-absorbing electrons was proved by another experiment shown in Fig. 3. Although the IR part of the initial spectrum had been removed by selective photobleaching with light of λ>1100 nm at 4 K, the remaining visible peak significantly increased in intensity and shifted to the blue side when warmed at 77 K for 20 min. This change was comparable to that which took place in the unbleached sample between 11 and 25 min after warming to 77 K (see Fig. 2). The intensity increase of the visible peak occurred in the absence of the IR-absorbing electrons, and it was caused by spectral narrowing due to the relaxation of the visible-absorbing electrons themselves at 77 K.

The time-evolution of the spectrum revealed the presence of localized electrons in two distinctly different trapping sites. It has been proposed that the IR-absorbing electrons are in the trapping sites in alkyl moiety and the visible-absorbing electrons are in the trapping sites associated with hydroxyl groups in glassy alcohols.[3,9,10] In our experiment both of the electrons exhibited the blue-shift in their component spectra when they were relaxed at a high temperature. The apparent tremendous blue-shift of the absorption peak from the IR to the visible region was, as suggested previously,[3] primarily due to the removal of the IR-absorbing electrons.

In the recent pulse radiolysis experiment,[5] it has been found that the wavelength of the IR peak of the end-of-pulse spectra moved to the blue side with increasing temperatures. This can be interpreted as that the relaxation of the IR-absorbing electrons proceeds during the pulse irradiation at a temperature-dependent rate. The relaxation of the visible-absorbing electrons was so slow that the growth of the visible peak did not occur within the time-scale of the pulse radiolysis experiments (up to 1.5 ms) conducted below 76 K.5) Thus, there was no essential difference between the present results and the previous pulse radiolysis results,5) except for the plasma spectra of delocalized electrons observed in the latter.

Klassen et al.6) have studied the pulse radiolysis of glassy ethanol at 77 K and have reported that the absorption intensity at an intermediate wavelength of 700 nm showed an increase followed by a decrease. They have taken this finding as an important indication that a single absorption peak continuously shifts from 1300 to 540 nm, and they have suggested the existence of a dipole orientation mechanism for the total change of the spectrum. However, our results have shown that the intensity change at 700 nm is better explained by the continuous shift of the visible peak due to the relaxation of the visible-absorbing electrons.

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