Electron Trapping in Irradiated NaOH Ices. Electrons Stabilized at 4 K in Shallow Traps Associated with Na^+ Cations

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Studies on electron trapping in 8 and 18 mol·dm^{-3} NaOH glassy ices were performed by means of 4 K γ-irradiation technique. The optical absorption spectra of e^-_t were found to be considerably red-shifted and broader compared with the spectra in the ices irradiated and examined at 77 K. This trend was more pronounced for the concentrated sample. The red part of the broad spectra was removed either by photobleaching with light of $\lambda > 800$ nm at 4 K or by thermally annealing at 77 K. These results, combined with electron spin resonance data, lead to the conclusion that the shallow electron traps responsible for the red part of the spectra are formed with the participation of Na^+ cations in the alkaline ices.

Electron stabilization in irradiated glassy alkaline ices has been commonly interpreted in terms of solvation of excess electrons by dipoles of H_2O molecules ("dipolar trap"), and the role of alkali metal cations has been ignored in most models.[1] However, taking into account the relatively high concentration of the cations in most experiments (usually *ca.* 20 mol%), such picture is hardly acceptable and does not appeal to chemical intuition. In 1964, Kevan, who examined the electron spin resonance (ESR) spectra of γ-irradiated 2—5 mol·dm^{-3} LiOH, NaOH, and KOH ices, indicated a contribution of the alkali metal cation interaction to the ESR line width and suggested that "the charge density of trapped electrons in alkaline ices encompasses several water molecules and one or more cations".[2]

Recently, Polewoj and one of the present authors (J. K.) reported optical absorption spectra of electrons trapped at 77 K in highly concentrated (up to 20 mol·dm^{-3}) NaOH ice.[3,4] The properties of the spectra were tentatively explained by the existence of relatively shallow and unstable traps due to the formation of a cation-electron pair ("cationic trap"), $(Na^+\cdots e^-)_t$, whose absorption maximum lay at *ca.* 750 nm, as compared with the maximum at 585 nm in 10 mol·dm^{-3} NaOH ice. Here we provide further data, based mainly on optical absorption measurements at 4 K, which demonstrate the increasing variety of trap depths at high NaOH concentrations.

Experimental

Glassy NaOH ice samples of two concentrations, 8 and 18 mol·dm^{-3}, of NaOH were prepared in the form of windowless discs, 0.2 cm thick, by rapid cooling in liquid nitrogen. A modified version of the liquid helium cryostat described previously[5] was used for measurements at 4 K. The irradiations were carried out in dark with ^{60}Co γ-rays at a dose rate of *ca.* 0.9 Mrad/h at 77 K or at *ca.* 0.25 Mrad/h at 4 K. The total dose applied was *ca.* 0.2 Mrad.

The optical absorption spectra were recorded using a double-beam recording spectrophotometer with a twin photodetection system (Shimadzu, Model MPS-5000). ESR experiments were carried out with a conventional X-band spectrometer (JEOL, Model JES-3M) for the ice sample sealed in thin quartz tubes.

The irradiated samples were photobleached with light from a 500 W Xe lamp through a 420±50 nm band-pass filter or an 800 nm cut-off filter. Typically the samples were photobleached for 3 min for optical absorption measurements and for 15 min for ESR measurements.

Results and Discussion

Effect of Temperature on Optical Absorption Spectra. The optical absorption spectra due to trapped electrons are presented in Figs. 1 and 2 for 18 M and 8 M ice samples (containing 18 mol·dm^{-3} and 8 mol·dm^{-3} NaOH) irradiated and also examined at 4 and 77 K. In each case, the spectrum at 4 K is wider and red-shifted compared with the spectrum at 77 K. At 4 K the 8 M sample displays the absorption maximum at 650 nm and the spectral halfwidth is 1.4 eV. The former value is in complete agreement with that reported by Hase *et al.*,[6] whereas the latter value is somewhat lower. The 18 M sample at 4 K has a maximum at 690 nm and a halfwidth of 1.65 eV. The halfwidths at 4 K are *ca.* 1.3 times larger than those at 77 K for both samples. On the other hand, however, no dependence on the temperature of measurement, when examined at 77 and 4 K, is seen in the spectra of the samples irradiated at 77 K. This con-

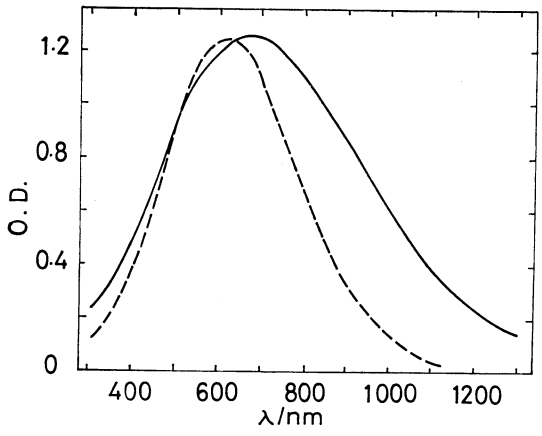

Fig. 1. Optical absorption spectra of trapped electrons in 18 M NaOH ices γ-irradiated and recorded at 4 K, —— and at 77 K, ----. The 77 K spectrum is normalized with the 4 K spectrum at peak height.

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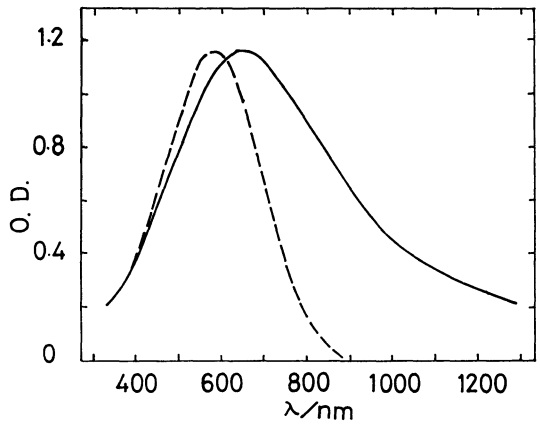

Fig. 2. Optical absorption spectra of trapped electrons in 8 M NaOH ices γ-irradiated and recorded at 4 K, —— and at 77 K, ----. The 77 K spectrum is normalized with the 4 K spectrum at peak height.

trast with blue-shift of the spectrum of trapped electrons in an ethanol glass observed upon cooling form 77 to 4 K after the irradiation at 77 K.[7]

Thermal bleaching, accomplished by transfer of the samples irradiated at 4 K into liquid nitrogen for 2 min and recording the spectra again at liquid helium temperature, led to the blue-shift and narrowing of the spectra. Thus, for the 18 M sample the absorption maximum shifts from 690 to 630 nm and the half-width decreases 1.1 times, whereas the 8 M sample shows the shift from 650 to 580 nm and the decrease in halfwidth of nearly 1.3 times. The effect of the thermal bleaching is more pronounced for the dilute sample than for the concentrated one.

Photobleaching of the Optical Absorption Spectra. The longer wavelength regions of the 4 K spectra are readily bleached by red light of $\lambda > 800$ nm, so that the absorption maxima effectively shift to the blue. The subsequent photo-bleaching with blue light of $\lambda \sim 420$ nm partially restores the longer wavelength regions and results in the red-shift of the maxima. The observed wavelength (transition energy) changes of the absorption maxima during the selective photo-bleaching for the 8 and 18 M samples are

$$\underset{(1.91\text{ eV})}{650\text{ nm}} \xrightarrow{\text{red light}} \underset{(2.16\text{ eV})}{575\text{ nm}} \xrightarrow{\text{blue light}} \underset{(1.98\text{ eV})}{625\text{ nm}}$$

and

$$\underset{(1.81\text{ eV})}{685\text{ nm}} \xrightarrow{\text{red light}} \underset{(2.10\text{ eV})}{590\text{ nm}} \xrightarrow{\text{blue light}} \underset{(1.77\text{ eV})}{700\text{ nm}}$$

respectively, and the shifts are more pronounced for the concentrated sample, whose recorded spectra are given in Fig. 3.

The changes of the spectral shape caused by photobleaching were first reported by Ershov *et al.*,[8] but they are not very distinct at 77 K. For 10 M NaOH ice, the shifts of the absortion maxima reported by Hase and Kevan do not exceed 35 nm.[9] For the 8 M sample at 77 K, photobleaching under the present experimental conditions did not change the spectral shape, though the total intensity decreased.

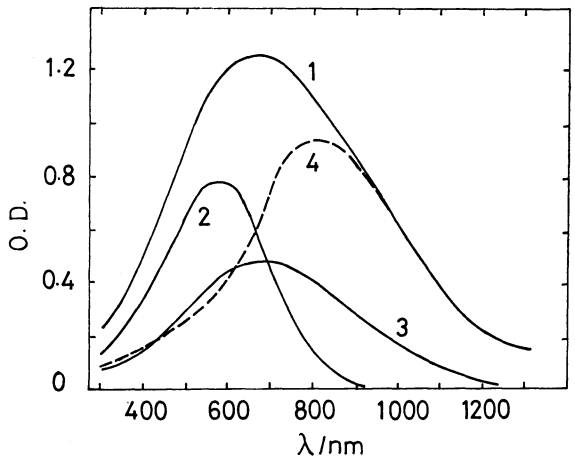

Fig. 3. The effects of selective photobleaching on the optical absorption spectrum of trapped electrons in 18 M NaOH ice irradiated and recorded at 4 K: 1, after γ-irradiation; 2, after photobleaching with 800 nm light; 3, after consecutive photobleaching with 400 nm light; 4, the spectrum bleached with the red light (1—2).

It is also interesting to note that the original 4 K spectrum can be generally reconstructed with respect to both absorption maximum and width by photobleaching at 4 K with the blue light the smaple which had been thermally bleached at 77 K.

The Nature of Shallow Electron Traps. All the above results of optical absortpion experiments seem to be consistent with the following picture: the trap depth distribution in NaOH ice shifts in favor of the shallow traps, responsible for the longer wavelength regions of the spectra, (a) with increasing NaOH concentration and (b) with decreasing temperature of irradiation. Point (a) suggests that the shallow traps may be of a cationic nature.

Electrons in the shallow traps are comparatively unstable and, in 18 M ice, were previously found to decay at 77 K.[3] It was suggested that about 15% of the trapped electrons generated in 18 M NaOH ice irradiated at 77 K are in "cationic" traps and are easily bleached.[4] At 4 K, the contribution of shallow traps significantly increases both for the 8 and 18 M samples. In contrast, the stable dipolar traps are responsible, in the 8 M sample irradiated at 77 K, for most trapped electrons, whose absorption spectra show very small shifts upon photobleaching.

Taking into account the fact that, at 77 K, the shallow trapped electrons still remain in the 18 M sample but not in the 8 M sample, it seems reasonable to expect that the thermal bleaching (4→77 K) effect may be larger for the dilute than for the concentrated sample. This has been found for both the shift of the absorption maxima and the narrowing of the spectral widths. It is suggested that no significant molecular rearrangements are required to allocate electrons in cationic traps and, therefore, they are more primary in nature. In the very early stage of electron trapping, probably in both the 8 and 18 M ices, a large number of electrons is stabilized by cations. The stabilization is

effective at 4 K, whereas it is short-lived at 77 K particularly in the 8 M ice.

Assuming that the spectral component bleached with red light at 4 K (curve 4 in Fig. 3) represents the electrons in the shallow, cationic traps, these electrons also have a very wide energy distribution. This may result from a variety of ion pairs more or less solvent separated, or more or less loose or tight, using the terminology of Seddon *et al.*[10] Their pulse radiolysis study indicated that the optical absorption bands of solvated electrons in amines and tetrahydrofuran are blue-shifted in the presence of alkali metal cations compared with those in neat solvents. Although the above results concerning liquid solutions bear a rather distant relation to the present work, they suggest that the cation-electon pairs form traps of intermediate depths between solvation wells in strongly (*e. g.* water) and weakly (*e. g.* tetrahydrofuran) polar media. It is also interesting to note that the solvated electron band in liquid ammonia shows a red-shift in the presence of metal ions, though this shift is not ascribed to the formation of a (M^+, e^-_s) pair.

The existence of two kinds of electron traps, the dipolar traps and the cationic ones, in the NaOH ice is also supported by more careful examination of the shape of the absorption spectra. None of the red parts of the spectra at 4 K fits a Gaussian distribution and all of them appear to be a superposition of two Gaussian components, as shown in Fig. 4. However, the spectral component in the longer wavelength region photobleached with red light at 4 K (curve 4 in Fig. 3) fits a single Gaussian shape (see curve 2 in Fig. 4) in agreement with the data reported for 77 K. The Gaussian form of the spectrum representing the ion-pairs should be also expected, judging from the results of Shubin *et al.*[11]

Electrons both in the shallow traps and in the deep ones are readily removable from their traps by photobleaching with light of a suitable wavelength (see Fig. 3). It is however worth noting that bleaching of the electrons in the shallow traps is not accompanied by any significant increase in the intensity of the shorter wavelength region of the spectra, corresponding to the electrons in the deep dipolar traps. The photobleached electrons probably disappear by reactions with O^- ions and impurities. On the other hand, the deep electrons are partially transformed into the shallow electrons by blue light. These results imply that an abundance of the shallow traps is available in the NaOH ice at 4 K.

ESR Evidence for the Shallow Traps Associated with Na^+ Cations. Additional evidence as to the wider variety of electron traps in the 18 M sample is provided by ESR measurements at 77 K. These results are shown in Fig. 5. The width of the initial trapped electron signal is 2.1 mT, in fairly good agreement with the data reported by Blandamer *et al.* for 20 M NaOH ice.[12] It decreases to 1.9 mT upon photobleaching with red light. The bleached component of the signal has the width of 2.4 mT, which is much broader than the width, 1.4 mT, of the ordinary trapped electrons in the dipolar traps in the alkaline ice

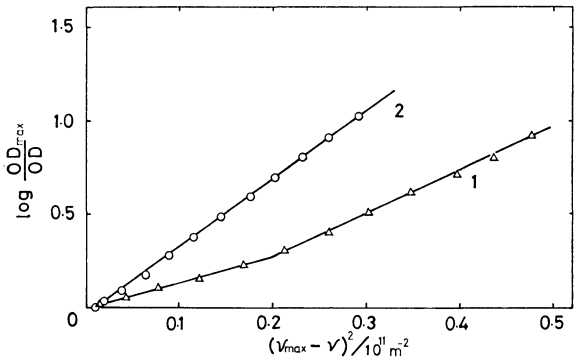

Fig. 4. The gaussian plots. The curve 1 for red parts of the spectrum of γ-irradiated 18 M NaOH ice at 4 K (Fig. 3, curve 1) and the curve 2 for the spectrum due to trapped electrons bleached with 800 nm light (Fig. 3, curve 4).

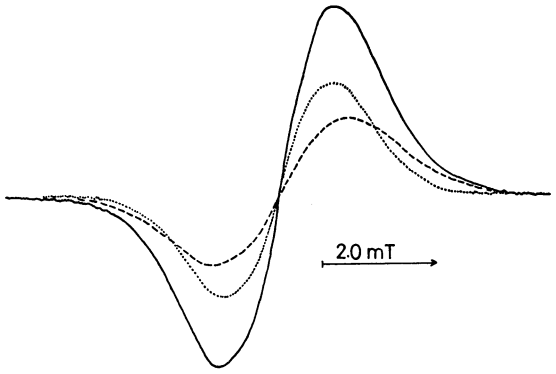

Fig. 5. ESR spectra of trapped electrons in γ-irradiated 18 M NaOH ice at 77 K: ——, after γ-irradiation; ·····, after photobleaching with 800 nm light; and ----, the spectrum bleached with the red light.

matrices of NaOH concentrations less than 10 M at 77 K.

It has been found that the ESR width of the trapped electrons in ethylene glycol–water mixed matrix is broadened from 0.3 to 1.4 mT when thermally annealed at 77 K after the irradiation at 4 K.[5] This change is accompanied by a tremendous blue-shift of the optical absorption spectrum of the trapped electrons.[5,6] This is interpreted in terms of the deepening of traps by the oriented matrix molecules with a polar hydroxyl group, which results in a closer distance between trapped electrons and neighboring protons and, therefore, a larger hyperfine broadening. However, the correlation between the ESR width and the optical absorption observed here is the reverse: when the absorption spectra effectively shift to the blue upon the photobleaching with red light, the ESR width becomes narrower. The present results strongly suggest that the deepening of traps (the blue-shift) in the 18 M sample is not due to the change in the orientational configuration of water molecular dipoles around the traps, but is due to the photorelease of electrons from the traps associated with Na^+ cations, leaving electrons in the dipolar traps.

The ESR width of 2.4 mT of the photobleached component of the signal can reasonably be under-

stood to be due to the hyperfine splitting of the Na nucleus, because it gives a non-negligible conctribution to the ESR width of electrons even in the ordinary dipolar traps in the NaOH ice of lower concentrations.[2] ESR spectra of 8 M and 18 M KOH glassy ice samples irradiated at 77 K have the same width of 1.2 mT. This is in good agreement with the reported data,[12] as reasonably expected from the small nuclear magnetic moment of the K nucleus.

Conclusion

The present data substantiate the results reported previously[3,4] and indicate the nature of shallow, cationic traps for excess electrons in irradiated NaOH ice. This kind of trap is abundant and contributes to the primary step in stabilizing and localizing the electrons.

In fact, the situation may be very complex. Dipolar traps themselves have a wide energy distribution and the contribution of shallow, unrelaxed dipolar traps probably increases at an early stage of the electron trapping process. Moreover, electrons in dipolar traps follow to some extent their own rearrangement pattern, when photo- or thermally bleached. The main purpose of the present work is to point out the possible importance of another type of electron stabilization, *i.e.*, by valence traps or in the form of ion pairs.

This work was performed by using the cryogenic facilities of the electron LINAC laboratory, Hokkaido University.

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