

Nanosecond Electron Transfer Dynamics between Traps in Zeolites Studied by Double-Pulse Excitation Diffuse Reflectance Spectroscopy

Shuichi Takatani, Hiroshi Fukumura,* and Hiroshi Masuhara*

Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan

Shuichi Hashimoto*

Chemistry Department, Gunma College of Technology, Maebashi, Gunma 371, Japan

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The 248 nm excitation of zeolites results in the formation of trapped electrons which are very sensitive to photoexcitation and the amount of water contained in zeolites. Na_4^{3+} , Na_3^{2+} , and Na_2^+ , which are prepared by 248 nm single-photon excitation, are directly confirmed as electron trapping states by nanosecond diffuse reflectance spectroscopy. Their stability decreases in the order of $\text{Na}_4^{3+} > \text{Na}_3^{2+} < \text{Na}_2^+$ in terms of the observed lifetimes of these trapped species. Water accelerates recombination between trapped electrons and the electron-ejected sites in the zeolite frameworks. Photoinduced conversion processes between these ion clusters were measured directly by double-pulse excitation experiments.

Introduction

Zeolites have received much attention because of their interesting structural elements, such as cavities and channels, and of their catalytic properties.^{1–4} Zeolites are crystalline aluminosilicates, and large pore faujasitic zeolites consist of three-dimensional network of nearly spherical supercages of about 1.3 nm in diameter connected tetrahedrally through 0.74 nm windows. Although there is no chemical bond between two reactant molecules embedded in large cavities, chemical reactions arising from specific orientation, as well as characteristic intermolecular interactions, were observed.^{1–4} This observation is ascribed to the events characteristic of confined geometry. It is expected that zeolites, which are very important catalysts, provide novel reaction fields.

Photochemical and photophysical primary processes in zeolites can be directly followed by diffuse reflectance spectroscopy, because zeolites are opaque and scattering powders and transmittance mode laser photolysis cannot be applied. Indeed, photoprimary processes of molecules adsorbed in zeolites have been the subject of interest, since Wilkinson et al. proposed nanosecond diffuse reflectance spectroscopy in 1981.⁵ Transient absorption spectra of aromatic molecules in zeolites have revealed normal processes like intersystem crossing and ionization, as well as electron transfer processes,^{6–9} and some of the results have shown transient species characteristic of zeolites. For example, an anthracene excimer is formed through a cation–anion ion pair as in 1,2-di(9-anthryl)ethane in solution,¹⁰ although anthracene undergoing dimerization gives no emission in solution. Other types of photochemical reactions in zeolites also have been clarified.^{11–19}

Radiation effects upon zeolites without adsorbates have also received much attention in photochemistry and radiation chemistry, since they are expected to provide useful information on the catalytic nature of zeolites and also may contribute to improve their properties. Of these, radiation- and photoinduced generation of trapped electrons is a representative process studied by many research groups,^{20–26} because this is one of the important processes to understand dynamic behavior occurring in zeolites. Production of trapped electrons means that

the effective polarity inside zeolites is high. The physicochemical nature of the medium in zeolite cages depends upon component ratio of Si to Al, acid–base properties, hydrogen-bonding abilities, water content, and loading level if molecules are incorporated.¹⁹ Thus, the dynamics of trapped electrons in zeolites is very complex and constitutes a subject of fundamental importance; however, it has not been clarified in detail, although many investigations are being carried out, particularly on photochemical reactions of adsorbed species.^{1–4}

In the present work, dynamics of trapped electrons produced by 248 nm excitation has been studied in representative zeolites by nanosecond diffuse reflectance spectroscopy. A technique of double-pulse excitation was also applied, and Na_4^{3+} and Na_3^{2+} , produced by excitation with the first pulse, were interconverted by the second pulse. This method has a potential to promote the understanding of the photoprimary processes with ease and reliability.

Experimental Section

Materials. Zeolites X ($\text{Na}_{85}\text{Al}_{85}\text{Si}_{107}\text{O}_{384} \cdot n\text{H}_2\text{O}$; Tosoh Co. Zeolum F-9 powder) and A ($\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot n\text{H}_2\text{O}$; Tosoh Co. Zeolum A-4 powder) were first heated at 500 °C in air for 6 h. Then, they were evacuated at 0.3 Pa under two conditions; for 7 h at 300 °C and for 4–6 h at room temperature. The samples prepared in the former way have less than 0.1 wt % of water, while the samples prepared in the latter way contain approximately 2 wt % (ca. 1×10^{-3} mol/g) of water molecules. These are abbreviated hereafter as NaX/300 °C, NaA/300 °C, NaX/RT, and NaA/RT. The zeolite samples were kept in a Suprasil cell with a 2 mm optical path length, and all the measurements were carried out at room temperature.

Conventional Diffuse Reflectance Spectroscopy. A diffuse reflectance spectroscopy for ground state absorption was performed by a UV spectrophotometer (Shimadzu UV-3100PC) with an integration sphere. Barium sulfate powder (Kodak white standard) was used as a reference scattering material. Absorption spectra of the ground state of zeolites were obtained by analyzing the Kubelka–Munk function.

Double Pulse Excitation Nanosecond Diffuse Reflectance Spectroscopy. Our nanosecond spectroscopic system is already reported elsewhere,^{27–31} and the fundamental points are briefly

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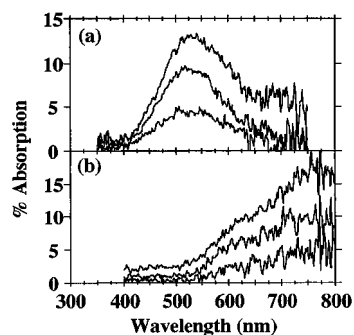


Figure 1. Transient absorption spectra of zeolites excited with a 248 nm excimer laser. (a) NaX/300 °C at excitation intensity of 20 mJ/cm² and (b) NaA/300 °C at excitation intensity of 27 mJ/cm². Delay times from upper to lower are (a) 10 μs, 10 ms, and 1 s and (b) 10 μs, 500 ms, and 2 s.

summarized here. A 248 nm excimer laser (Lambda Physik, LEXTRA 200, 30 ns) was used as an excitation light source. For double-pulse excitation experiment, the second harmonics (532 nm) of an Nd:YAG laser (Continuum, Surelite I, 20 ns) was additionally applied. A monitoring flash lamp for absorption spectral measurement was a Xe flash lamp (Hamamatsu Photonics, L 2359, 1 μs fwhm). The diffusely reflected light from the powder samples was collected and led to a polychromator (Jovin Yvon, 100 grooves/mm with blaze at 450 nm) combined with an intensifier-equipped multichannel photodiode array (Otsuka Electronics, IMUC-7000). The wavelength resolution was 1.8 nm. The origin of time axis (0 μs) was set to the time at which the T–T absorption of benzophenone microcrystal reaches the maximum value. Absorption intensity is displayed as percent absorption, which is proposed by Wilkinson et al.^{5,32,33}

For measurement of percent absorption decay curves, a Xe lamp pulsed by a homemade circuit (Wacom, KXL-300F, 200 μs fwhm) was used,^{27,28} and its steady-state mode was also used for the measurement in the sub-microsecond to 10 s range. The diffusely reflected light was led to a monochromator (Oriol 77250) with a photomultiplier (Hamamatsu R3896) and detected by an oscilloscope (Hewlett Packard 5410A or 54522A). This system is controlled by a personal computer (Epson PC-286V). The linearity of the output signal was carefully checked.

Results and Discussion

Absorption Spectra of Trapped Electrons in Zeolites. The ground state absorption spectra of NaX/300 °C and NaA/300 °C have a peak around 230 nm and its tail extends over 300 nm, which was confirmed by analyzing their Kubelka–Munk function. It is reported that the absorption band is due to charge transfer along the Al–O bond and, consequently, sensitive to the content ratio of Al to Si.³⁴ The ratio of NaX and NaA is 0.8 and 1.0, but the absorption intensity is not proportional to the ratio. This is because Al concentration is sometimes changed by thermal treatment and so on. The absorption intensity at 248 nm where laser pulse excites the sample powders is appreciable.

Transient absorption spectra of NaX/300 °C and NaA/300 °C are very broad and structureless, and have a peak around 530 nm and above 750 nm, respectively, as shown in Figure 1. Although a little faster decay component was observed above 650 nm for NaX/300 °C, the absorptions decayed monotonously and slowly. These bands are almost identical with the reference spectra of trapped electrons which are stabilized as Na₄³⁺, Na₃²⁺, or Na₂⁺ in zeolites.^{3,23,24} It is reported that the bands around 550 nm and above 750 nm are ascribed to Na₄³⁺ and Na₂⁺, respectively.^{3,23,24} Furthermore, it is known that Na₃²⁺ has an

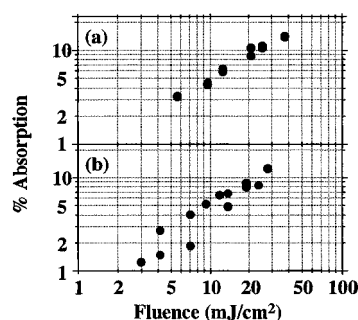
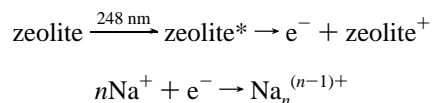


Figure 2. Excitation intensity dependence of transient percent absorption of zeolites at 10 μs. (a) NaX/300 °C monitored at 535–545 nm and (b) NaA/300 °C monitored at 695–705 nm.

absorption peak at about 680 nm. Therefore, the main species of NaX/300 °C and NaA/300 °C excited by 248 nm laser differ and the long wavelength component of NaX/300 °C may be related to the main species of NaA/300 °C. We consider that electrons liberated by laser irradiation cause rearrangement of Na⁺ ions and are eventually stabilized as trapped electrons. Usually Na⁺ clusters are involved to stabilize ejected electrons, which gives a characteristic band depending on the number of ions. Thus in NaX/300 °C, Na₄³⁺ and a minor amount of Na₃²⁺ are formed, while a little of Na₃²⁺ and mainly Na₂⁺ are formed in NaA/300 °C. Na₂⁺ has a shorter decay time than that of Na₃²⁺. It is important that even 248 nm (5.0 eV) laser excitation of zeolites induces efficient formation of trapped electrons, while the 193 nm (6.4 eV) ionization of zeolites was reported.^{24,25}

The photoionization here is not due to impurities, as considered in the following. By the treatment of the powders for longer 6 h at 500 °C, organic molecules should be completely vaporized or thermally decomposed. Furthermore, the used sample powders do not contain some other elements, which was confirmed by atomic absorption spectroscopy. If additional Na atoms are included, they would eject electrons and be converted to cations. This possibility is important, as zeolites exposed to Na vapor show formation of trapped electrons.^{22,35,36} We could not detect the absorption bands due to such an origin before laser excitation.

One important problem we have to point out here is whether 248 nm excitation energy is enough to ionize zeolites or not. As double-photon ionization is probable by the present excitation intensity, we examined an excitation intensity dependence of Na₄³⁺ formation in NaX/300 °C and Na₃²⁺ in NaA/300 °C. As shown in Figure 2, the slope in percent absorption–laser intensity plot was 0.82 and 0.97 for NaX/300 °C and NaA/300 °C, respectively. This means that single-photon ionization by 248 nm light is responsible for trapping of electrons in zeolites as follows:



where *n* is 2, 3, or 4. The photoionization of the zeolites can be regarded as electron transfer from the HOMO of zeolites, nonbonding O (2p) orbitals, to *n*Na⁺ sites. The Δ*G* of this electron transfer for the formation of Na₄³⁺ in NaX is estimated to be −0.64 eV under a 248 nm excitation condition. Here, ionization potential was measured to be 6.2 eV by UV photoelectron spectroscopy³⁷ and the stabilization energy (Na + zeolite → Na₄³⁺) was given to be −1.84 eV from the ab initio calculation.³⁸ Thus monophotonic ionization mechanism leading to formation of Na₄³⁺ can be well accepted. However, a similar explanation does not hold for formation of Na₃²⁺ in NaA, since Δ*G* of +0.28 eV is obtained. In this case, the accuracy of the

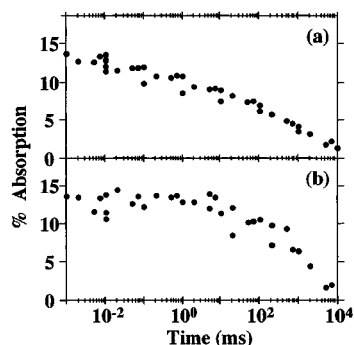


Figure 3. Semilog plot of percent absorption decay curves of zeolites. (a) NaX/300 °C monitored at 535–545 nm and (b) NaA/300 °C monitored at 695–705 nm. Excitation intensity is the same as that of Figure 1.

estimated stabilization energy of Na_3^{2+} in NaA remains questionable.

Decay Processes of Trapped Electrons. In NaX/300 °C, the band of Na_3^{2+} , which was clearly identified as 10 μs , disappeared in 10 ms. As Na_4^{3+} was observed even at 1 s, it is significantly stable. Na_3^{2+} and Na_2^+ are main species in NaA/300 °C, and Na_2^+ decayed a little faster. It is concluded that the trapped electrons involving more Na ions, namely larger clusters, are more stable. The conversions of Na_3^{2+} to Na_4^{3+} in NaX and of Na_2^+ to Na_3^{2+} in NaA are expected, but could not be directly observed in this experiment. The conversion rate may be comparable to or slower than that of the intrinsic decay of the converted species, so that a rising component via the conversion was not detected. For the direct measurement application of another method is required.

Usually trapped electrons in solution undergo unimolecular geminate recombination or homogeneous bimolecular recombination with a counter cation. However, the present decay curves are very complex and cannot be explained in terms of both the recombination processes. The percent absorption of trapped electrons was logarithmically plotted against time in Figure 3. Such an extremely slow decay is often observed for recombination of ejected electrons and generated cations in rigid glasses and polymer films. Miller et al.³⁹ found that trapped electrons in rigid matrices decay in the presence of electron acceptors over the wide time range covering nanoseconds to minutes, and showed that the decay processes of those electrons under various conditions can be interpreted in terms of a mechanism involving quantum mechanical tunneling. The effect of distance distributions between electron donor and acceptor, as well as the orientation of frozen solvent molecules surrounding the donor and acceptor, has been taken into account for a theoretical formulation of long-range electron transfer in rigid solution.⁴⁰ A similar slow charge recombination process was recently analyzed for amorphous poly(*N*-vinylcarbazole) film.⁴¹ However, in these systems the logarithmic plot gives a linear relationship, while curved ones were obtained here. This may be due in part to the different distribution of holes and trapped electrons characteristic of zeolites, while a random distribution could be assumed in the reported systems. At the moment we are working on the explanation of this deviation from the long range electron transfer mechanism.

Effect of Adsorbed Water. Water content in zeolites can be controlled to some extent by the method of preparation. NaX/300 °C and NaA/300 °C are considered to be dried samples, but NaX/RT and NaA/RT contain appreciable amounts of water. The ground state absorption intensity of NaX/RT and NaA/RT is slightly enhanced compared to NaX/300 °C and NaA/300 °C, their spectral shape being not changed appreciably. This may be ascribed to polarity effect upon the charge transfer

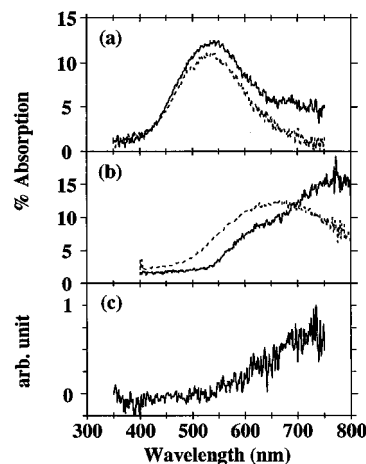


Figure 4. Effect of water adsorption on transient absorption spectra of zeolites at 10 μs . (a) NaX/RT (dotted line) excited at 94 mJ/cm^2 and NaX/300 °C (solid line) at 20 mJ/cm^2 . (b) NaA/RT (dotted line) excited at 200 mJ/cm^2 and NaA/300 °C (solid line) at 27 mJ/cm^2 . (c) A difference spectrum obtained by normalizing the spectra of NaX/RT and NaX/300 °C and subtracting the former from the latter.

absorption along the Al–O bond. Studies on water adsorption to zeolites have a long history,⁴² but few investigations, as far as we know, on photophysical and photochemical processes have been performed, particularly on photoionization. In Figure 4 transient absorption spectra of NaX/RT and NaA/RT (water-rich zeolites) are compared with those of NaX/300 °C and NaA/300 °C (well-dried ones). In NaX powders, the absorption band in the long wavelength disappeared, namely, contained water-quenched Na_3^{2+} and Na_2^+ completely. Indeed, a difference spectrum between NaX/300 °C and NaX/RT is similar to that of NaA/300 °C. In the case of NaA zeolites, the water-rich sample gave a characteristic, broad, and structureless band around 650 nm, which is clearly assigned to Na_3^{2+} . The band of Na_2^+ was suppressed greatly. Thus, water molecules adsorbed in zeolites decompose rather labile trapping sites and leave the most stable site selectively. The results are consistent with decay behavior described above.

In order to investigate the ionization process in water-rich zeolites, excitation intensity dependence was examined at 535–545 nm. Their slope was 1.26 for NaX/RT and 1.30 for NaA/RT, namely, higher than that for dried samples but close to unity. Although some ambiguity is left, we suggest that the ionization in water-rich zeolites is also a single-photon process. It is worth noting that excitation intensity for obtaining appreciable absorption in water-containing sample is a few times higher than that in a well-dried one. The ground state absorption at 248 nm was increased as mentioned above but transient absorption was suppressed, indicating that the ionization efficiency in the time range investigated is extremely suppressed. Usually in homogeneous media water enhances ionization because of its high polarity. Hence it is likely that the mutual recombination immediately after excitation, which cannot be followed by the present instrument, is very fast. An alternative explanation is that water molecules receive ejected electrons competitively with Na ions. This process would give rise to hydrated electrons in zeolites; however, no absorption suggesting hydrated electrons was observed by our measurement system. Recently, using pulsed electron radiolysis technique, Liu et al. has found that trapping of electrons by water molecules is prior to that by cation clusters in fully hydrated NaX and NaY, which results in the formation of hydrated electrons.⁴³ The average lifetimes of the hydrated electrons are estimated to be 0.46 μs in NaX and 3.61 μs in NaY. This indicated that the time resolution of the measurement system we employed here would not be high enough for the detection of the hydrated electrons. Picosecond

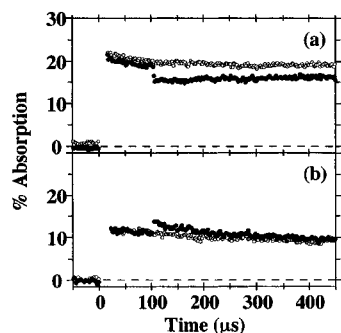


Figure 5. Decay curves of trapped electron in NaX/300 °C by 248 nm excitation with (closed circles) and without (open circles) the second excitation by 532 nm pulse. The time interval between the first and second pulses was adjusted to be 100 μ s. Monitoring wavelength is (a) 560 nm and (b) 650 nm.

and femtosecond diffuse reflectance spectroscopy⁴⁴ will be very helpful to detect hydrated electrons and/or to elucidate the fast ionization and recombination processes.

The trapped electron observed here should escape the very fast geminate recombination, and the decay observed here was also accelerated by water in the range of microseconds to 10 ms. The latter decay process was again very complex as shown in Figure 3 for NaX/300 °C and NaA/300 °C and cannot be analyzed at the moment. The role of water may diminish the energy barrier for charge recombination in the two time ranges; early time range whose substantial aspects are beyond our knowledge and the slow decay confirmed here.

Double-Pulse Excitation Experiment. During the experiments we found that the absorption spectral behavior is sensitive to the monitoring light intensity. This suggests that trapped electrons formed are unstable upon further irradiation or that temperature elevation attained by absorbing the IR part of the monitoring light enhances their degradation. It is well-known that trapped electrons in polymer matrices, rigid solvents, and inorganic glasses show a similar behavior. Furthermore, one report deals with temperature effect upon decay dynamics of trapped electron in zeolites.²⁷ We excluded a possible contribution of the photothermal effect due to the monitoring light by cutting near IR and IR light with an appropriate combination of filters. Thus, we felt that the absorption of the excitation pulse by the trapped electron is critical and conducted the following double-pulse excitation experiment.

Trapped electrons in NaX/300 °C were initially formed by 248 nm excimer laser irradiation, and at about 100 μ s later the second laser pulse of 532 nm was introduced to excite Na_4^{3+} whose absorption maximum is located at 540 nm. The monitoring light intensity was reduced to 7% of that in normal measurement by a neutral density filter for suppressing the bleaching effect by the monitoring light. Upon excitation with the second pulse, the percent absorption of Na_4^{3+} was diminished by 3%, and its small recovery was overlapped giving almost constant value between 100–300 μ s, as shown in Figure 5. This is possibly ascribed to an excited state of Na_4^{3+} with a long lifetime or conversion of Na_4^{3+} to some related species. Of course the former is improbable considering the very slow decay, so we examined the possibility of the latter process. Upon the second excitation, the percent absorption at 650 nm was increased and a slightly faster decay of the additional component was detected. At around 350 μ s delay time, the decay curves produced by the double-pulse excitation became similar to those produced by the conventional single-pulse excitation experiment. This indicates that Na_3^{2+} is produced from Na_4^{3+} and that some of the latter goes back to Na_4^{3+} again in 200 μ s leading to the initial quasi-equilibrium between Na_4^{3+} and Na_3^{2+} .

The present novel process was observed more clearly by

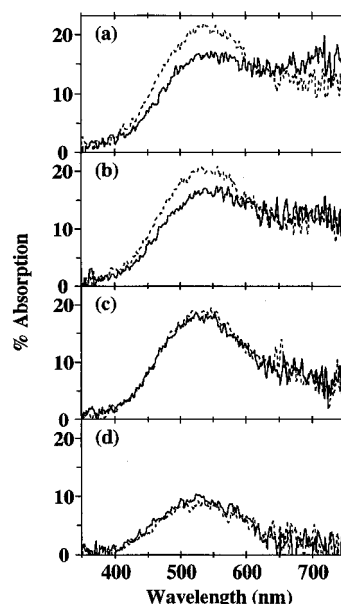


Figure 6. Transient absorption spectra of NaX/300 °C by double-pulse excitation (solid lines) where the first and second pulses are 248 nm (45 mJ/cm²) and 532 nm (22 mJ/cm²), respectively, and their time interval is 10 μ s. The delay time of the spectra after the first excitation is (a) 20 μ s, (b) 60 μ s, (c) 1 ms, and (d) 1 s. The reference transient absorption spectra without the second 532 nm excitation (dotted lines) are also included.

measuring transient absorption spectra upon double-pulse excitation. The results are summarized in Figure 6, where the time interval between the first 248 nm and second 532 nm pulses was fixed to 10 μ s and the delay time was counted from the first excitation. At a few tens of μ s, it was clearly demonstrated that the absorption of Na_3^{2+} is increased by 2.5% accompanied by the decrease of the Na_4^{3+} band. The spectral difference between single- and double-pulse excitation experiments was not identified within experimental errors after 1 ms, which is of course consistent with Figure 5.

The double-pulse excitation was also performed for NaX/RT where Na_3^{2+} was not identified as already demonstrated above. Upon the second 532 nm excitation, the percent absorption at 560 nm was decreased, while the increase at 650 nm was not detected, as shown in Figure 7. This is reasonable because Na_3^{2+} is unstable in water-rich zeolite. The excitation of Na_4^{3+} only enhanced the recombination in NaX/RT. A similar observation was made by Lednev et al.⁹ previously. However, they failed to observe the conversion between Na_4^{3+} and Na_3^{2+} because their samples seem to contain a considerable amount of water.

Dynamics of Trapped Electrons. Now it is clearly confirmed that Na_4^{3+} is more stable than Na_3^{2+} , the latter is formed from the excited state of Na_4^{3+} , and Na_3^{2+} converts to the primary Na_4^{3+} . The formation process of Na_3^{2+} , not directly observed here in the tens of μ s time range, may involve electron transfer to Na_3^{3+} , Na^+ transfer to Na_2^{2+} , or dissociation of Na^+ from the excited Na_4^{3+} . On the other hand, the back-conversion from Na_3^{2+} to Na_4^{3+} , taking place in about 100 μ s, may consist of back-electron transfer from Na_3^{2+} to Na_4^{4+} , Na^+ transfer from Na_4^{4+} to Na_3^{2+} , or association of Na^+ with to Na_3^{2+} , which of course corresponds to the each of the forward processes. In general, Na^+ transfer or geometrical rearrangements such as dissociation or association of Na^+ is slower and less probable than electron transfer because of the heavier mass of the ion. The idea that geometrical rearrangements of Na^+ would not take place but electrons rather move into surrounding cages upon photoexcitation is also consistent with recent theoretical studies.^{45,46} Hence, we consider that electron transfer between

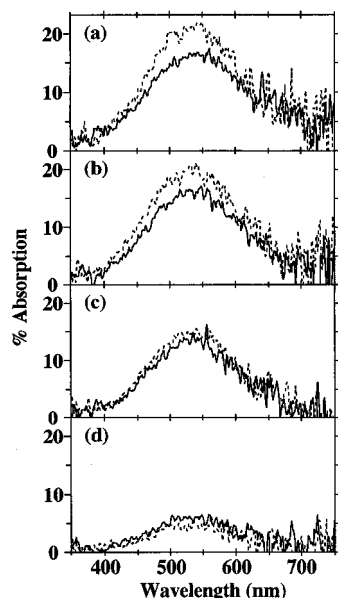


Figure 7. Transient absorption of NaX/RT by double-pulse excitation (solid lines) where the first and second pulses are 248 nm (150 mJ/cm²) and 532 nm (24 mJ/cm²), respectively, and their time interval is 10 μ s. The delay time of the spectra after the first excitation is (a) 20 μ s, (b) 60 μ s, (c) 1 ms, and (d) 1 s. The reference transient absorption spectra without the second 532 nm excitation (dotted lines) are also included.

trapping sites of Na₄⁴⁺, Na₃³⁺, and Na₂²⁺ is stimulated by irradiation. According to the previous studies,^{23,24,47} the stability of the sodium ion clusters formed in zeolites on trapping excess electrons is Na₄³⁺ > Na₃²⁺ > Na₂⁺. Recent ab initio calculations³⁸ also support this ordering. Therefore, electron transfer is only possible from the excited Na₄³⁺ to Na₃³⁺. Furthermore back electron transfer from Na₃²⁺ to Na₄⁴⁺ is feasible from an energetical viewpoint.

Electronic and Geometrical Structure of Electron Trapping Site. Until now we have assigned the observed spectra to three species of Na_n⁽ⁿ⁻¹⁾⁺ on the basis of the similarity to the reference spectra. Here we summarize the relevant results and discuss structures of electron trapping sites. The most direct experimental foundation is electron spin resonance (ESR) data according to which Na₄³⁺ exists in NaX, and Na₃²⁺, and Na₂⁺ are formed in NaA. There is no clear support from ESR experiment that Na₃²⁺ is additionally produced in NaX. If the electron is simply trapped in a rectangular box, quantum mechanical calculation gives 500, 540, 650, and 700 nm as an absorption peak in a box with 0.67, 0.7, 0.77, and 0.8 nm lengths, respectively. This means that an electron in a smaller volume gives a shorter wavelength band.²³ In zeolites, the Na⁺ ion does not form a covalent bond and has a little space to move in the cage. Furthermore, some defects should be performed and/or produced by the heating procedure in zeolite frameworks. This may allow Na⁺ ions to rearrange their geometrical structures to give metastable states like Na₃³⁺ and Na₂²⁺. Thus, absorption spectral changes could be possible without hopping of Na⁺ from site to site, instead electron transfer between these sites is considered to be a plausible mechanism.

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