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ARTICLES

Photolysis of Na^+(Cryptand[2.2.2])Na^-: Photobleaching of Absorbance and Quenching of Fluorescence

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The optical properties of the alkalide Na^+(cryptand[2.2.2])Na^- are sensitive to the presence of defect electrons and can be dramatically altered by irradiation with light. Fluorescence intensities decrease markedly at excitation power densities above about 1 mW cm^{-2}, even though this power level is some 10^7 times lower than that required to affect the absorbance. Partial recovery occurs in powder samples over a period of several minutes at 30−100 K. The enhanced quenching of fluorescence is attributed to the presence of photoproduced trapped electrons. Pronounced changes occur in the optical absorbance spectra of vapor-deposited thin films of Na^+(cryptand[2.2.2])Na^- following irradiation by high intensity doubled- and tripled-YAG laser pulses. The effects are attributed to the intermediate formation of a "p-band metal" in which half of the electrons in the ground s^2 state of Na^- are promoted to the p-level, resulting in a high concentration of electrons trapped at some distance from the parent anion site.

Introduction

The first salt of an alkali metal anion, Na^+(cryptand[2.2.2])Na^- (abbreviated $Na^+(C222)Na^-$) has been well characterized. The crystal structure,[1] powder and single crystal conductivity,[2] ^{23}Na NMR spectrum,[3,4] thermodynamics of formation,[5] oriented single crystal reflectance spectrum,[6] thin film transmission spectrum,[7−9] fluorescence spectrum,[10,11] and photoelectron emission spectrum[12,13] of the pure compound have been determined. Defect electrons in this sodide have been detected by EPR,[14] and their effect has been studied by photoelectron emission, optical absorption, and fluorescence.[11,13,15,16] The formation of highly mobile exciton-polaritons has been studied by microscopic fluorescence methods,[17,18] and the transient effects of laser photobleaching on the absorption spectrum have been determined at two excitation wavelengths.[14,19] The reader is referred to a number of review articles for the general methodology and background.[20−26]

As a result of these studies, the energy levels available to $Na^+(C222)Na^-$ are rather well established. The ground state of Na^- has a filled 3s band, designated as $3s^2$. The first excited state results from an s to p transition to form the 3s3p state at 1.855 ± 0.005 eV, with relaxation to a state at 1.835 ± 0.005 eV (conversion half-life = 1.7 ns at ≈20 K) which has a fluorescence half-life of 3.5 ns.[10] The conduction band lies at 2.4 ± 0.1 eV[2] and the vacuum level is at 3.1 ± 0.1 eV.[13]

Microscopic fluorescence studies with excitation by a doubled YAG laser (2.34 eV) showed that the initially formed exciton rapidly evolves to a highly mobile exciton-polariton that can migrate as far as 80 μm during its 1−2 ns lifetime.[17,18] Trapping

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of the exciton-polariton at defect sites is thought to be responsible for the fluorescence peak shift of 20−25 meV.[11] The rapid migration of the excitation, coupled with the assumption that defect electrons are efficient fluorescence quenchers, also accounts for the very low fluorescence quantum yield of other alkalides.[16]

Rapid evaporation of methylamine from a solution of $Na^+(C222)Na^-$ produces microcrystals with both defect electrons and empty traps for electrons. The distribution over available energy states is very broad as shown by photoelectron emission studies.[13] There is also a distribution of trapped electron lifetimes after laser irradiation that range from a few seconds to several minutes to hours at 210−240 K, presumably because of the presence of a distribution of trap depths and/or hole−electron distances.[13] The photoelectron emission studies also showed that slowly-grown single crystals of $Na^+(C222)Na^-$ were virtually unaffected by repeated laser pulses at laser powers below the threshold for photobleaching.[13] Apparently, the concentration of both defect electrons and defect traps is dramatically lower in carefully grown crystals than in rapidly precipitated crystallites.

Polycrystalline films of $Na^+(C222)Na^-$, made by rapid evaporation of methylamine from a solution, could be nearly completely bleached by a 605 nm laser pulse during a 15 ns period, when about 2×10^{15} photons impinge on a 1.0 mm^2 area of the film.[14] The process was partially reversible with recovery of 50−80% of the initial absorbance in about 100 ms at room temperature. Below a threshold of about 3×10^{14} photons per pulse, no effects were observed, even with multiple pulses. Later studies[19] with an excimer laser at 308 nm (4.03 eV) showed similar results. At both laser energies, new permanent absorbances at both lower and higher energies than the main peak of Na^- were observed.

The present study was undertaken to answer a number of questions about the nature of the defects in $Na^+(C222)Na^-$ and their effect on spectra. In particular, we wished to explore the role of defect electrons as quenchers of fluorescence and the nature of the new absorbers that are produced by laser photobleaching.

Experimental Section

The synthesis of single crystal and polycrystalline samples of $Na^+(C222)Na^-$ and other sodides has been described elsewhere[23,27,28] as has the instrumentation for time-resolved luminescence studies with excitation by a doubled YAG laser.[10] The vapor deposition apparatus used to prepare stoichiometric thin films of $Na^+(C222)Na^-$ (500−2000 Å thick) has been described in detail.[9,29]

The photobleaching light source was a Spectra Physics Nd:YAG pulsed laser (Quanta-Ray Model No. DCR-11) capable of producing 7 ns pulses of the fundamental, doubled, and tripled frequencies. The maximum energy densities at the substrate of the 532 and 355 nm pulses were 7.5 mJ mm^{-2} (10^{18} photons per pulse) and 0.90 mJ mm^{-2} (10^{17} photons per pulse), respectively. The laser beam entered the deposition system through the glass bell jar wall. An interior front-surface mirror then directed the beam through the substrate and film. The film was then physically rotated to the optical system. The minimum amount of time between a laser pulse and an absorbance scan was approximately 5 s. The duration of an optical absorbance scan was approximately 1 min.

Results

Fluorescence Quenching. Previous time-resolved fluorescence spectra used 560−618 nm pulses with 6 ps duration, a repetition rate of 1 MHz, and energies of the order of 1 nJ per pulse.[10,11,16−18] This is 5 orders of magnitude smaller than the energy required to photobleach the absorbance of thin films. Thus, no appreciable change in the *ground-state* population of Na^- occurred as a result of the laser pulses. Even the most intense pulses used, directly from the doubled YAG laser, were over 2 orders of magnitude below the photobleaching threshold. In spite of these limitations, the effect of repeated excitation pulses on the intensity of the fluorescence was pronounced at the higher average power levels.

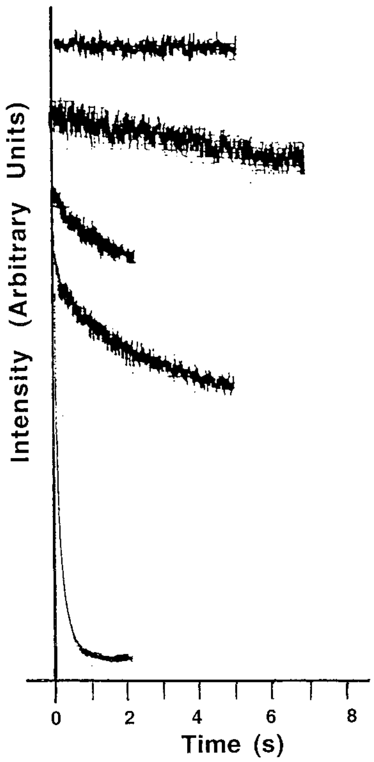
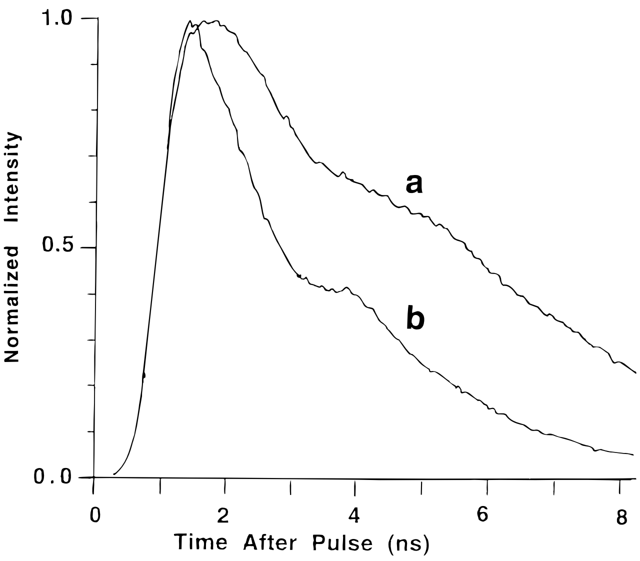


Figure 1. Fluorescence bleaching as a function of time at various power levels. Excitation was produced by a doubled Nd:YAG laser at 532 nm (2.33 eV), and the fluorescence response was monitored at 1.85 eV. The polycrystalline sample was kept at 26 K. Power densities from top to bottom in W cm^{-2} were 10^{-7}, 10^{-6}, 10^{-3}, 5.0×10^{-2}, and 1.0. The curves are displaced vertically for clarity.

When a collection of single crystals was irradiated for ~0.1 s at various power levels from 60 μW cm^{-2} to 20 W cm^{-2}, the fluorescence intensity was proportional to the excitation power up to about 0.6 W cm^{-2} (see Figure 2 of ref 16) after which the slope decreased. Figure 1 shows that steady illumination of a polycrystalline sample at various power levels for a few seconds results in a dramatic decrease in fluorescence intensities for excitation power densities above about 1 mW cm^{-2}. We believe that this results from fluorescence quenching by photoproduced trapped electrons in the sample. More direct evidence for fluorescence quenching by trapped electrons is illustrated in Figure 2. We had previously shown that large shiny crystals of $Na^+(C222)Na^-$ had longer fluorescence lifetimes than powdered samples.[17,18] As shown in Figure 2, there is a correlation between the EPR signal intensity (due to trapped defect electrons in the sample) and the fluorescence decay time. Increased defect electron content (sample b) leads to faster decay. The same conclusion was reached from the fact that the fluorescence quantum yields of a number of other sodides[17] are several orders of magnitude lower than for $Na^+(C222)Na^-$. EPR and magnetic susceptibility studies show that these systems have much higher defect electron concentrations, suggesting that it is the presence of defect electrons that reduces the quantum yields.



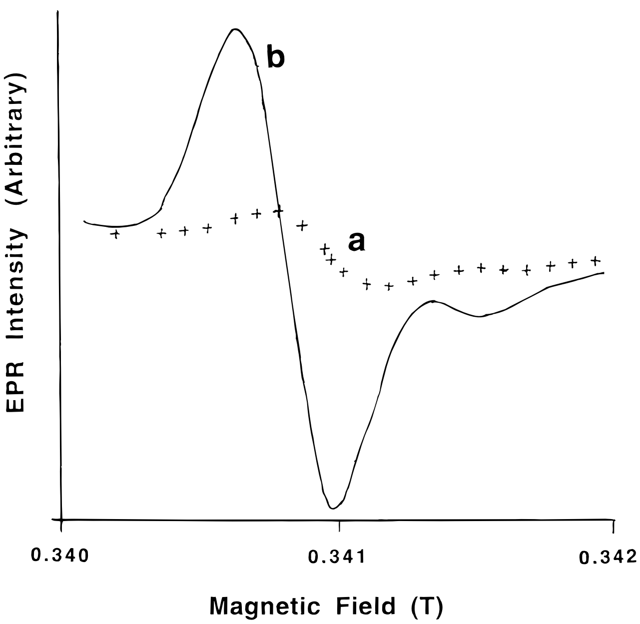


Figure 2. (Top) Time profiles of the fluorescence intensities of two polycrystalline samples of Na$^+$(C222)Na$^-$ that show the effect of the initial trapped electron concentration on fluorescence lifetimes. (Bottom) EPR signal intensities of the two samples, showing that the trapped electron concentration in sample b is about 7 times that in a. Note the more rapid decay of the fluorescence of the sample with a higher defect electron concentration.

Previous studies of photoelectron emission from various samples of Na$^+$(C222)Na$^-$ before and after irradiation with laser pulses at 532 nm showed the presence of both defect electrons and empty traps that could accept electrons.[13] Although "high quality" crystals showed very small concentrations of both defect electrons and traps, rapidly precipitated samples showed a broad distribution of the energies of both defect electrons and traps from near the ground state energy of Na$^-$ to at least 1.5 eV above this level. The time evolution of photoelectron emission after single laser pulses at 170−240 K showed a distribution of recovery times, ranging from seconds to minutes to hours (or longer).[13] Thus, this sodide has a variety of trap depths and energies. Both initially present defect electrons and traps that can be populated by photoexcited electrons are commonly present, at least in surface states, in Na$^+$(C222)Na$^-$ and in other alkalides.

As shown in Figure 1, the fluorescence intensity decreases with time of irradiation at 532 nm. The effect is, however, at least partially reversible. Figure 3 shows the effect of repeated irradiation at 36 K for a polycrystalline sample (b) with various delay times between irradiation. The EPR spectrum of this sample (Figure 2, bottom) showed the presence of a relatively high concentration of defect electrons. Nearly complete recovery of the fluorescence intensity occurred after a waiting period of 3 min. By contrast, polycrystalline sample a with a low defect electron content showed *no* recovery upon standing, even at 110 K.

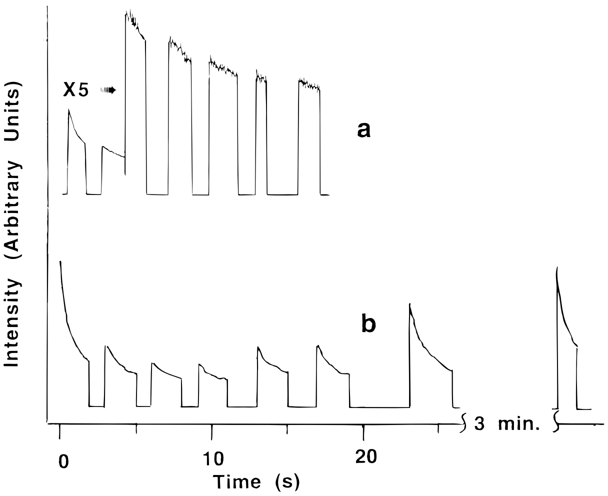


Figure 3. Effect of trapped electron concentration on recovery of fluorescence following laser irradiation at 532 nm of the samples considered in Figure 2. Sample b, with higher defect electron concentration, showed recovery of fluorescence intensity at 36 K upon standing for various times after cessation of irradiation. Recovery was nearly complete after 3 min without irradiation. Sample a, by contrast, showed no recovery even at 110 K.

One needs to be reminded at this point that the initial photoexcitation produces a highly mobile exciton-polariton[17,18] and that the fate of such a species is to either emit light or be trapped at a defect site, probably at a defect electron, which provides a radiationless return to the ground state. Another point that should be made is that the maximum relative recovery occurs at photon energies of 1.85 eV, the energy of maximum short-time (exciton-polariton) emission. Excitation of the "wings" at both 1.87 and 1.68 eV showed substantially less recovery.

Samples subject to the laser pulse intensities described above retained their shiny gold color with no indication of damage. Indeed, experiments with thin films of Na$^+$(C222)Na$^-$ showed no change in the absorption spectrum at power levels much higher than those used in the fluorescence studies. Thus, the decrease in fluorescence intensity does not result from depletion of Na$^-$, but rather from fluorescence quenching by radiation-induced defects, which are probably defect electrons.

Laser Photobleaching. Earlier studies of partially reversible laser photobleaching of polycrystalline films of Na$^+$(C222)Na$^-$ at ambient temperatures[14,30] prompted us to study the effect on well-defined films produced by codeposition of sodium and cryptand[2.2.2] onto a sapphire substrate. The earlier studies were made with polycrystalline films prepared by solvent evaporation from a solution of Na$^+$(C222)Na$^-$ in methylamine. Our ability to prepare uniform stoichiometric films by vacuum codeposition permitted quantitative studies of the absorbance. Uniform laser irradiation of the entire region of the film subject to absorbance measurements also eliminated spot-to-spot variations.

Initial experience with a continuous He−Ne laser at 632 nm and repeated flashes from a xenon flash lamp (10^4 higher power

TABLE 1: Effect of Initial Bleaching Pulses on the Peak Absorbance and Integrated Intensity of $Na^+(C222)Na^-$ Films

		peak absorbance		percent decrease	
run no.	temp (K)	initial	after one pulse	peak	integrated absorbance
1	213	1.61	1.05	35	8.2
2	103	1.69	1.16	31	7.2
3	148	1.51	1.10	27	6.9
4	213	1.38	1.14	17	9.4
5	213	2.56	2.17	15	0.0
6[a]	213	1.69	0.80	53	6.3

[a] At 355 nm irradiation.

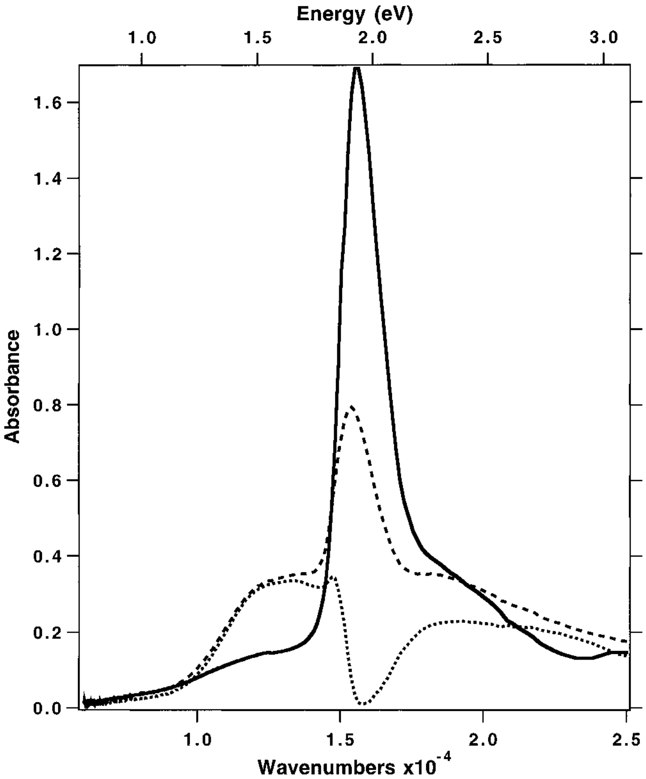


Figure 4. Change in absorbance of a vapor-codeposited film of $Na^+(C222)Na^-$ after a single 355 nm (3.50 eV) laser pulse. Solid line, initial spectrum; dashed line, spectrum after the pulse; dotted line, result of subtracting the contribution to the spectrum of the residual Na^- absorption. Although the Na^- peak absorbance decreased by 53%, the total integrated absorbance after the pulse decreased by only 6%, indicating that only slight decomposition had occurred.

level) showed no effect on the absorbance of stoichiometric $Na^+(C222)Na^-$ films, even though the total number of photons absorbed was many times that used to yield photobleaching in previous studies with single laser pulses.[14,30] The films were subject to illumination temperatures of 210, 230, 250, 270, and 290 K, but no photobleaching occurred. Thus, photobleaching is a nonlinear phenomenon, requiring the input of at least a threshold number of photons during the excited state lifetime (5−10 ns) as observed earlier.

The Nd:YAG pulsed laser was capable of illuminating the ~1 cm^2 film area with up to 10^{18} photons in 7 ns. During the course of this work, 14 different vapor-deposited films of $Na^+(C222)Na^-$ were studied, 10 with irradiation at 532 nm and 4 at 355 nm. At a typical film thickness of 1000 Å, a 1 cm^2 film area contains $\sim 2 \times 10^{16}$ Na^- ions. The absorbance of such a film at 532 nm is ≈0.4, and at 355 nm it is ≈0.06. With excited state lifetimes of at least 2−5 ns, therefore, it was possible to convert essentially all of the ground state ($3s^2$) Na^- ions to the excited state (3s3p), at least with 532 nm radiation. Of course, the laser intensity could be decreased to values below the photobleaching threshold as well.

At either irradiation wavelength, when the number of photons was 10−20 times smaller than the number of Na^- ions, *no* change in absorbance occurred even with many repeated pulses. Any changes in absorbance at short times (less than about 1 min) could not have been observed, since the film had to be moved from the radiation position to the analysis position after a laser pulse. Films exposed to the highest laser intensity at 532 nm were completely bleached (or vaporized?) by one pulse.

Single 7 ns pulses at intensities above the threshold caused three kinds of alteration of the absorbance: (1) a change in shape with decrease of the Na^- peak at 1.6×10^4 cm^{-1} and growth at both lower and higher energies; (2) a decrease in the integrated absorbance because of partial decomposition; (3) a time- and temperature-dependent regrowth of the Na^- band, accompanied by a decrease in integrated absorbance due to film decomposition. Enough experiments were done to permit effective separation of these phenomena.

To assess the extent of irreversible decomposition, the integrated absorbance *vs* wavenumber was determined. This is proportional to the oscillator strength and is therefore a measure of the loss of absorbers. The scan range was generally limited to $(0.5-2.8) \times 10^4$ cm^{-1} so that changes outside of this range could not be evaluated. This was not a serious limitation since the absorbances at these extremes were generally small and changed little as a result of laser irradiation.

Generally, the first pulse of sufficient intensity to alter the spectrum resulted in a much smaller amount of decomposition than would be indicated by the decrease in Na^- absorbance. Table 1 gives the data for seven films studied with two different optical systems. Figure 4 shows the change in shape that occurred following a single 355 nm laser pulse with the film at 213 K. The spectrum after the pulse has been corrected for the 6% overall decomposition that occurred. Note the drastic decrease in the Na^- absorbance and the growth at both lower and higher energies. The residual Na^- peak has also shifted to lower energies by 135 cm^{-1}. Subtracting the shifted spectrum of Na^-, attenuated by an amount that removes the Na^- peak but does not "dig a hole" in the spectrum, reveals two very broad peaks produced by the irradiation. Their maxima occur at 1.3×10^4 and 1.9×10^4 cm^{-1}. The difference spectrum given in Figure 4 clearly shows the presence of the two peaks produced by the laser pulses. Four additional pulses further reduced the peak absorbance by 42%, but with only 10% change in the integrated absorbance. The overall effect was a 74% reduction of the peak absorbance accompanied by 16% decomposition.

While repeated pulses at 355 nm continue to bleach the Na^- absorption, the effect "saturates" with 532 nm pulses. Figure 5 shows the change in peak absorbance with pulse number for a film kept at 263 K. After an initial sharp decrease, the peak absorbance levels off, with subsequent changes largely caused by decomposition. Although the species produced by photolysis contribute to the peak absorbance, the contribution of the Na^- peak is at least 20% and remains constant.

At temperatures below about 230 K the absorption spectrum after a pulse is independent of time. At higher temperatures, however, there is both partial recovery of the Na^- spectrum and irreversible decay of the radiation-produced peaks. This is illustrated in Figure 6. The initial spectrum at 213 K is that obtained after three 532 nm laser pulses. During the 2 h period as the temperature was increased to 258 K, the integrated absorbance showed an overall decomposition of 12% but an *increase* at the wavelength of the Na^- peak of 37%. Even when the absorbance of the radiation-produced species decayed to

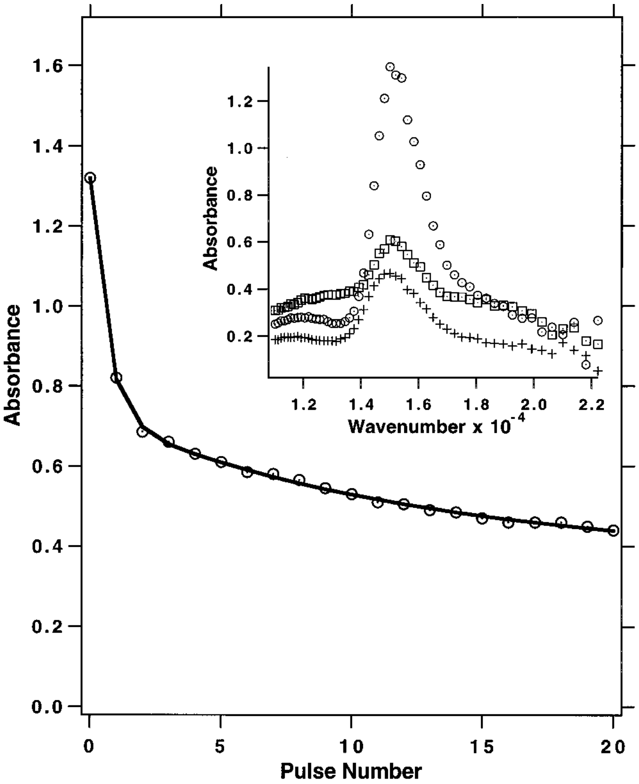


Figure 5. Change in the peak absorbance of Na$^-$ following repeated 532 nm laser pulses. The inset shows the initial absorption spectrum at 210 K (circles) and spectra after 10 pulses at 213 K (squares) and 10 more pulses at 210 K (plus signs).

essentially zero at 283 K 5 h after the first spectrum, the absorbance at the Na$^-$ position had increased by 17%. The postirradiation behavior of a film subject to five 355 nm pulses was similar. These results show that the photobleaching process is at least partially reversible and also that the species produced by laser irradiation are much more susceptible to irreversible decomposition than is the parent sodide.

Discussion

It is clear that trapped defect electrons in Na$^+$(C222)Na$^-$ are ubiquitous. They range from weakly trapped electrons produced by light absorption that can recombine with the Na° center in seconds to minutes at 30 K to deeply trapped electrons that do not disappear in hours at 240 K. A sensitive probe for defect electrons is fluorescence, which appears to be effectively quenched by trapped electrons. The sequence of events following excitation is (1) the formation of mobile exciton-polaritons after rapid energy loss of the initially produced excitons,[17,18] (2) movement of the highly mobile exciton-polaritons at group velocities as high as 10^7 cm s^{-1}, (3) localization of the excitons at defects and/or by production of phonons of energy ≈25 meV, and (4) fluorescence from the localized state or enhanced radiationless decay. We propose that the latter process is especially favorable and responsible for the drastically reduced fluorescence intensity of other sodides. It is noteworthy that, although the quantum yields for other alkalides are reduced by several orders of magnitude compared with that for Na$^+$(C222)Na$^-$, the lifetimes are comparable.[17] This is consistent with prior formation of excitons and/or exciton-polaritons with quenching of the fluorescence after localization. The reader is referred to a paper by Cooper and Newman[31] for a description of the nature of exciton-polaritons in CdTe, which have group velocities up to 2.5 × 10^5 cm s^{-1}, and for references to prior studies of exciton-polaritons.

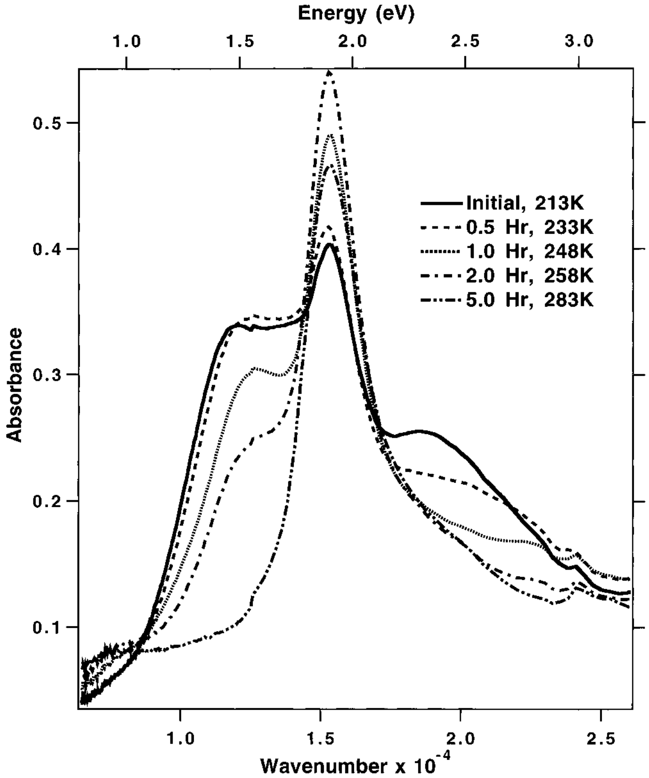


Figure 6. Time and temperature dependence of the spectrum of a photolyzed Na$^+$(C222)Na$^-$ film. The initial spectrum was taken 3 h after preparation, during which time it was kept at 213 K and subjected to three 532 nm laser pulses. Note that decay of the radiation-produced peaks at both lower and higher energies than that of the Na$^-$ peak was accompanied by growth of the Na$^-$ absorbance. Also, decay of the higher energy peak was faster than that of the lower energy peak.

The recovery of fluorescence after photolysis at 36 K shown in Figure 3 for a sample with a substantial concentration of defect electrons, and the absence of such an effect for a less doped sample, is difficult to understand. Apparently, the latter type of sample has a larger concentration of empty sites near the surface in which the photoelectrons can be trapped, while the "doped" sample has such traps already filled, leaving only very shallow traps for additional electrons.

Laser photolysis of thin (500–2000 Å) films of Na$^+$(C222)Na$^-$ shows a pronounced threshold effect. This clearly demonstrates the absence of changes in the absorption spectrum following a laser pulse until the intensity becomes high enough to produce appreciable concentrations of excitons that can interact with one another. A likely result is the formation of a "p-band metal" in which overlap of the excited p states of Na$^-$ produces a transient metallic state. This might be accompanied by a change in orientation of the complexed cation, Na$^+$(C222), similar to that which occurs at the order–disorder transition of Cs$^+$(18-crown-6)$_2$e$^-$.[32] If this change is "locked in" at the temperature of the experiment, electron trapping at new sites might occur.

The low-energy absorption band formed by photolysis is very similar to that formed by vapor codeposition of Na and C222 when there is a slight excess of C222 compared with that in Na$^+$(C222)Na$^-$.[6] Both the shape of the extra absorbance and its tendency to decay at room temperature are similar to the behavior of the low energy band produced by photolysis. Figure 7 shows the spectrum obtained with a 10% excess of C222, both initially and after standing 20 h at room temperature. Also shown is the difference spectrum. On this basis, we assign the low energy band to electrons trapped at anion vacancies produced by photolysis.

Spectra very similar to those obtained by laser photolysis were

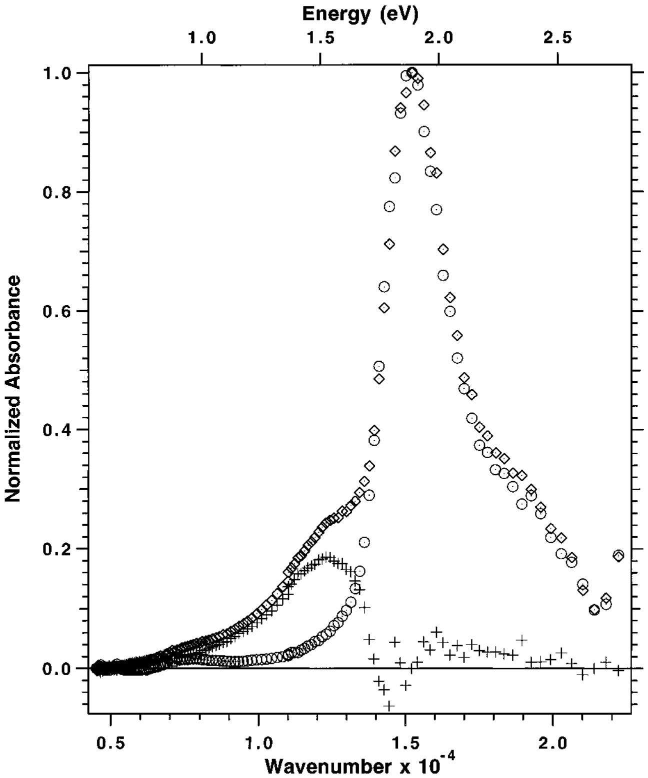


Figure 7. Spectra obtained by vapor codeposition of Na and C222 at a mole ratio of 2.0:1.1 (deficient in sodium). The extra absorption at ~12 000 cm^{-1} in the initial spectrum (diamonds) is presumably due to electrons trapped at Na^- vacancies. Trapped electrons react more rapidly with the cryptand than do Na^- ions, so the spectrum upon standing 20 h at room temperature (circles) shows no absorbance from trapped electrons. The difference spectrum is shown by plus signs.

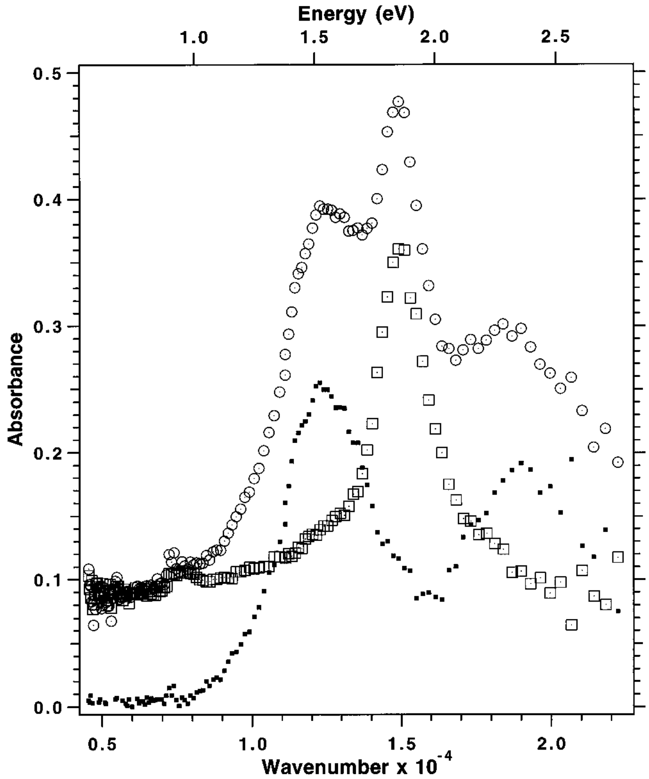


Figure 8. Spectra of a $Na^+(C222)Na^-$ film obtained by sequential deposition of six layers, 300 Å of C222 and 40 Å of Na, repeated three times. The initial spectrum at 233 K is given by circles. After 30 min at 233 K the spectrum shown by squares was obtained. The difference spectrum is given by the dots.

sometimes observed *initially* when $Na^+(C222)Na^-$ films were prepared by *sequential* deposition of rather thick layers of C222 and Na. Figure 8 shows the initial spectrum and that produced 30 min after deposition at 233 K for a six-layer film consisting of three sets of layers, each with 300 Å of C222 and 40 Å of Na. In most experiments of this type, however, by the time the first spectrum was obtained the higher energy peak shown in Figure 8 was gone although a lower energy peak or shoulder was common. When more layers, each about a tenth of these in thickness, were deposited in separate experiments, the spectra more closely resembled that of stoichiometric $Na^+(C222)Na^-$ films produced by codeposition.

The strong similarity between the spectra shown in Figure 8 and that following photolysis (Figure 4) suggests the presence of common species. In sequential depositions, as the sodium film diffuses into a cryptand layer, we presume initial formation of $Na^+(C222)e^-$ with its characteristic low energy peak, in addition to $Na^+(C222)Na^-$. The remaining sodium metal film, if well dispersed over the sample, could be responsible for the higher energy peak at ~18 000 cm^{-1} (2.23 eV). Payan has shown[33,34] that a film of sodium metal 40 Å thick has an absorption peak at 18 000 cm^{-1}, although its absorbance is less than 0.06 AU. We have noted[35] that pure alkali metal films deposited on sapphire or fused silica substrates tend to form "islands" that do not coalesce until several hundred angstrom average thickness is reached. If a similar phenomenon had occurred in the experiments of Payan, perhaps uniform films would have a higher absorbance.

The origin of the higher energy peak is thus difficult to determine. For every electron ejected by photolysis, there is initially left behind a sodium atom, Na°. Normally, we would expect rapid recombination of Na° with e^-_t to form Na^-. If, however, a structural reorganization occurs that is unfavorable for the trapping of Na^- but permits trapping of electrons, the effect of photolysis may be to separate e^- and the species produced from Na° into nonequilibrium traps that prevent easy recombination. A possible candidate for the species responsible for the higher energy peak is the sodium atom itself. The absorption spectrum of Na° trapped in rare gas matrices[36] is somewhat matrix-dependent, but bears a strong resemblance to the high energy peak seen in this work. This assignment would be expected to produce atomic sodium that should be readily detectable by EPR methods. Samples in EPR tubes subject to high intensity laser pulses showed no evidence of sodium atoms or other species with a large contact density at the sodium nucleus.[37]

A more likely candidate for the higher energy absorber is a sodium metal film or sodium clusters produced by agglomeration of the initially produced Na°. If thin uniform films were formed, they might have high enough extinction coefficients to be responsible for this absorption. Reversal of the postulated structural reorganization that formed the electron traps might then limit the rate of recombination of Na(s) with e^-_t, and competition between recombination and decomposition of the cryptand by the highly reactive trapped electrons would result in a lower oscillator strength. Without more information about the species produced when $Na^+(C222)Na^-$ films are subject to high intensity laser irradiation, these assignments remain questionable. Unfortunately, we do not at this time have the capability of removing these reactive films from the vapor deposition apparatus for analysis by other techniques such as EPR, electron microscopy, XPS, etc.

Conclusions

This work and previous studies clearly show that $Na^+(C222)Na^-$ can be "doped" with defect electrons in various energy states and with a range of trap depths. When the population of excited state species is low enough to consist of isolated excitons and exciton-polaritons, the concentration of such defect electrons is too low to be observed in the absorption spectrum. The major indications of their presence and time evolution are EPR, photoelectron emission, and fluorescence spectra. When, however, the intensity of photolysis pulses is high enough to convert the 3s^2 ground state to the 3s3p excited state, probably accompanied by reorientation of the cryptated cation, a "p-band metal" is formed that leads to semipermanent trapping of electrons and sodium atoms or sodium metal. Upon warming, some recombination occurs, but this competes with cryptand decomposition by reaction with the "chemically hot" species, e^-_t and Na°. When the concentration of Na$^-$ in the film becomes small enough, the "p-band metal" can no longer form and repeated pulses do not bleach the remaining absorbance of Na$^-$ but, rather, just lead to partial photodecomposition.

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