PHOTOLYSIS OF SOLID $\text{Na}^+\text{C}_{222}\text{Na}^-$ BY AN EXCIMER LASER PULSE AT 308 nm

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Abstract : Illumination of thin dry films of $\text{Na}^+\text{C}_{222}\text{Na}^-$ by short pulses of UV light at 308 nm produces modifications of the optical absorption spectrum similar to those obtained by visible light irradiation. These effects are interpreted in terms of transfer and recombination from the conduction band of the sodide. The quasi reversibility observed in the case of UV irradiation indicates that the process does not involve the 3s3p excited state. Deconvolution of the optical spectrum observed before and after the flash provides informations on the number of absorbing species. Preliminary results obtained with a variety of other sodides are shortly discussed.

INTRODUCTION

Solids containing alkali metal anions are now well known, and the negative valence state of the alkali metals is established beyond any doubt. Among them, the compound $\text{Na}^+\text{C}_{222}\text{Na}^-$, which was the first to be isolated⁽¹⁾, has been the most extensively studied. It has been established that this bright yellow compound is not metallic, even though its conductivity is very low. In fact, the variation of the resistivity with temperature indicates that it behaves like a semiconductor having an apparent band gap of 2.5 eV⁽²⁾. The main peak of the optical absorption spectrum occurs at 650 nm (1.9 eV), which corresponds to a state within the gap. This wavelength is the same in the solid as in solutions of sodium in ethylenediamine. It is therefore attributed to isolated Na^- . The fluorescence of Na^- was observed at low temperatures⁽³⁾, at a position situated at a slightly longer wavelength (682 nm) than that of the major absorption peak. The luminescence was accordingly attributed to the deactivation of a 3s3p excited state. However, this picture is too simple to explain the bi-exponential decay that was observed in these experiments. Two light-emitting states were needed to fit the fluorescence decay curves. These two states have lifetimes of ca. 2 and 5 ns and are not independent ; the long-lived one being populated *via* radiationless decay of the short-lived one. The intensity of the luminescence was found to be strongly temperature dependent, indicating that a variety of non-radiative deactivation pathways were available. The fluorescence yield was also found to depend upon the laser power being used : above a threshold value, the signal decreased with increasing excitation power.

We have recently shown that irradiation of thin layers of $\text{Na}^+\text{C}_{222}\text{Na}^-$ with a pulsed laser light at 605 nm (2.05 eV) led to a partial bleaching of the optical spectrum, followed by a slow incomplete recovery⁽⁴⁾. Analysis of the power dependence of the bleaching indicated that no effects could be observed at relatively low laser power, but that these effects became important at higher levels. An energy threshold was observed. These results were interpreted in terms of population of the conduction band *via* multiphotonic processes.

In this work, we present results obtained with a pulsed laser UV irradiation at 308 nm (4.02 eV). This energy is about twice that used in the visible range, and is much higher than the value of the energy gap determined from the temperature dependence of the conductivity. It is therefore reasonable to assume that monophotonic processes are capable to excite $\text{Na}^+\text{C}_{222}\text{Na}^-$ to the conduction band. The spectral modifications are analyzed, and the kinetics of recombination described. Extension to other sodides will be shortly discussed.

EXPERIMENTAL

$\text{Na}^+\text{C}_{222}\text{Na}^-$ was prepared according to standard procedures (5). Sodium metal (Fluka) was vacuum distilled before use. C_{222} (6) was used as received (Merck). Methylamine was dried over lithium until a stable blue solution could be obtained. All solvent transfers were made by evaporation and condensation in a greaseless vacuum line that could be evacuated to better than 1×10^{-5} torr. Films were formed by rapid evaporation of a relatively concentrated methylamine solution of $\text{Na}^+\text{C}_{222}\text{Na}^-$ on the window of a quartz optical cell. These films were shiny gold by reflection and blue by transmission; Their absorbance was of the order of unity. Films of $\text{Na}^+\text{C}_{222}\text{Na}^-$ are remarkably stable even at room temperature and are not affected by the analysis light. Films of other sodides were obtained in a similar way, but they had to be replaced more often.

The optical measurements were made with the same experimental set-up that was previously described (4). Collinear arrangement of the analyzing and exciting beam was realized and only a spot of ca. 1 mm^2 was studied. Each experiment required to move the sample to get a fresh part of the film. UV laser flashes were obtained from a XeCl^* excimer laser ($\lambda = 308 \text{ nm}$, $\tau = 20 \text{ ns}$) using proper attenuation (collimation). Deconvolution of the spectra were made with the use of the non-linear least squares program KINFIT (7).

RESULTS

Spectral analysis

Optical spectra recorded with the OMA are shown in fig 1. At high energy, the spectrum is strongly bleached just after the laser excitation at 308 nm, but there is an important recovery at longer times. New absorbances at both ends of the spectrum are clearly noticeable, but they disappear at longer times. There was no threshold of the power of the laser on these effects, although at the higher power, it was possible to destroy the layer irreversibly.

Kinetic results

The transients observed at two characteristic wavelengths are reported in fig 2. Variation in absorbance as a function of time are shown. At 750 nm, an immediate growth is observed in a very short time just after the laser pulse. At 450 nm, the same effect is observed. This new absorbance relaxes towards starting values in several hundreds of milliseconds. However, some residual absorbance is created. At wavelengths comprised between 550 and 650 nm, an immediate bleaching followed by a slow recovery to almost the same starting values is observed.

DISCUSSION

The optical spectrum of thin films of $\text{Na}^+\text{C}_{222}\text{Na}^-$ as well as that of other alkalides was previously extensively studied (8). It was found that, contrary to many alkalides, the optical spectrum of films of $\text{Na}^+\text{C}_{222}\text{Na}^-$ shows several peaks located at 15400 (650), 18900 (529), and 24500 (408) cm^{-1} (nm). The major peak at 650 nm is slightly temperature dependant, the position of the maximum shifts towards the red by $-1.6 \text{ cm}^{-1}/\text{deg}$, while the peak broadens by $1.1 \text{ cm}^{-1}/\text{deg}$. The origin of the major peak is attributed to a ground state to bound excited state transition ($3s^2 \rightarrow 3s3p$), while that of the additional shoulders is not known.

Figure 1 : Absorbance spectra of a layer of $\text{Na}^+\text{C}_{222}\text{Na}^-$ upon irradiation by a laser pulse at 308 nm (a) before ; (b) immediately after ; (c) after a few seconds

Figure 2 : Transient absorbances of a layer of $\text{Na}^+\text{C}_{222}\text{Na}^-$ as a function of time measured at 2 different wavelengths

Optical spectra of $\text{Na}^+\text{C}_{222}\text{Na}^-$ recorded on the OMA system show the same general overall features as those published or recorded on conventional spectrophotometers. However, it was found that the spectrum varies from point to point of the layer, since the area of measurement is of the order of 1 mm^2 . The relative magnitudes of the three peaks depended upon the spot being studied. The reason why this was not observed with conventional recording systems is that our system samples an area at least 100 times smaller and therefore the heterogeneities of the layer are not averaged over a large area. In order to ascertain that the same species were still in presence, the spectra were deconvoluted in a sum of individual peaks. It was found that they could all be represented, in the range from 400 to 800 nm, by a sum of three independent lorentzian curves (on an energy scale). Other analytical functions were tried but did not converge. The positions of the maxima were 15150 (660), 18500 (540) and 25000 cm^{-1} (400 nm) and the typical bandwidths were 4000 , 5600 and 3200 cm^{-1} , respectively. As can be seen in fig 3, there is a considerable overlap of the individual component curves. (The asymmetry of the curves is due to the fact that the spectra are drawn on a wavelength scale). Although reasonable fits could be observed in a variety of situations : before, just after or at long times after the laser pulse, complete and unambiguous analysis of the optical spectrum is made difficult by the impossibility to measure a good baseline : variations of absorbance are reliable, but there are more uncertainties on the individual spectra. This problem is quite general for all the work on solid state sample, since it is impossible to take into account the light losses caused by scattering from the sample. Another problem encountered was the need to change the position of the layer after each laser shot.

Figure 3 : Decomposition of spectra of $\text{Na}^+\text{C}_{222}\text{Na}^-$ (left) before and (right) after the laser pulse

Upon UV irradiation, the new spectrum obtained just after the flash can still be fitted with three lorentzian curves centered at about the same position as before irradiation but there is a very large effect upon the bandwidth, each line becoming broader.

The observed optical spectrum consists of several contributions, that of the original Na^- , plus that of all absorbing species, namely those present in the conduction band.

In a case involving low laser power ($\Delta A = 0.11$ at 660 nm), the variation of the peak position is of the order of 100 cm^{-1} while the width at half height varies by more than 650 cm^{-1} . Clearly according to the literature values, such an effect cannot be attributed only to a temperature increase due to the laser beam. In cases involving larger irradiation powers, the broadening of the line may become much larger, of the order of 3000 cm^{-1} , implying temperature variations of about 3000 K . This is unrealistic, since in every case a recovery of the major part of the initial spectrum was observed.

It is therefore assumed that the general broadening of all three components of the spectrum is due to a very broad absorbance, whose origin lays in the conduction band.

It was observed that for similar bleaching of the 660 nm peak, UV light irradiation caused much less destruction of the layer than similar irradiation in the 600 nm region ⁽⁴⁾ as indicated by spectra recorded at longer times.

CONCLUSION

Irradiation at 605 nm can only populate the 3s3p excited state. For low power density, the deactivation of this state occurs in times of the order of 5 ns. When laser power becomes sufficiently high, the concentration of Na^{-*} on the 3s3p level becomes large and other deactivation pathways become available through reactions such as :

This scheme does not explain however the long time dependance of the recovery of the initial absorbance. This phenomenon can easily be explained by a partial transfer from the 3s3p state to the conduction band via a multiphotonic process, followed by a slow, non radiative return to the ground state.

Results presented here with UV irradiation support the previous hypothesis. Under illumination at 308 nm, the conduction band may become directly populated without involving the 3s3p state. However, it must be noted that the 3s3p excited state may become populated via the conduction band. This is clearly shown by the shape of the fluorescence spectrum obtained with irradiation at 413 nm.

The kinetics of recovery of the signal are very similar to those obtained with illumination at 605 nm, thus indicating that the same state was involved in the process.

Most of the excited states involved are fairly delocalized in the conduction band, and the probability of reactions leading to decomposition is decreased. The nature of the state in the conduction band is still unknown.

The situation with other sodides (K⁺C222.Na⁻, Cs⁺(18C6)₂.Na⁻, Rb⁺18C6.Na⁻, Rb⁺HMCy.Na⁻) has not yet been elucidated. These compounds display a very low fluorescence ⁽⁹⁾, and in nearly every case studied, the effect of the laser light is to destroy irreversibly the layer, whatever the power being used (a possible exception being Cs⁺(18C6)₂.Na⁻). A possible explanation of the reaction of Na^{-*}(3s3p) with defect electrons situated in shallow traps.

Further work involving low temperature and other excitation energies will be needed.

The support of NATO, grant No.0106/88, of CNRS and of HEI is gratefully acknowledged

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