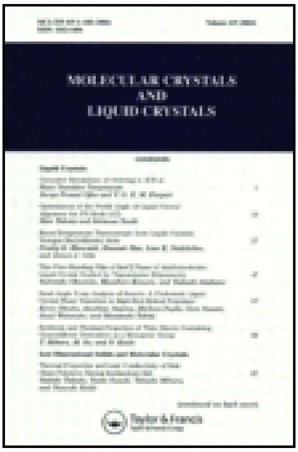

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Unpaired Spin Generation Under Near IR Radiation in Electrooptic m-Nitroaniline Crystal. NIR Absorption, Dilatometric and EPR Studies

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UNPAIRED SPIN GENERATION UNDER NEAR IR RADIATION IN ELECTROOPTIC m-NITROANILINE CRYSTAL. NIR ABSORPTION, DILATOMETRIC AND EPR STUDIES.

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Abstract Near IR spectra in the 5700 - 7000 cm^{-1} region and thermal expansion coefficients of the meta-nitroaniline (m-NA) crystals in the (010) cleavage plane have been measured within the 290 - 380 K temperature range. From the temperature dependence of the NIR absorption results that at 320 K the conformations of the $-NH_2$ group and phenyl ring start to change. The change of slope on the thermal expansion curves indicates 330 K as possible phase transition temperature.

The irradiation of the sample in the NIR spectrophotometer at 6800 cm^{-1} by 72 houres causes the weak EPR signal which gains strongly the intensity after heating at 323 K.

The results are discussed in terms of an infrared photochemical reaction and intra- and inter-molecular interactions and motions.

INTRODUCTION

In search for a relationship between infrared spectra and nonlinear optical properties of m-NA crystal some vibronic couplings with the intramolecular charge transfer (CT) have been detected in the vibrational m-NA spectra.[1] Further studies of the vibronic couplings by means of resonance Raman spectra have also suggested an intermolecular CT and radical-ions formation in the crystal.[2] The occurence of the unpaired spins in the m-NA crystals was already found by the EPR method by Urbański *et al.* and it was explained by crystal imperfections connected with crystallization from the ethanol solution.[3] The number of unpaired spins, evaluated as 10^{15} per gramm, corresponded well to the weak electrical conductivity ($1.3 \times 10^{-15}\ \Omega^{-1}cm^{-1}$) of the crystal which increased with the temperature raising.[3]

On the other hand, Asaji and Weiss observed an abnormal current above 350 K during the study of the pyroelectric effect of the m-NA crystals.[4]

The new bands in the resonance Raman spectra,[2] which appeared only at 18838 cm^{-1} exciting laser line, correspond to the aniline radical-ions. Thus it seemed interesting to measure the NIR absorption spectrum in the overtone $-NH_2$ stretching region.[5] The 18838 cm^{-1} is the almost exactly doubled frequency of the Nd^{+3}YAG laser (9400 cm^{-1} = 1.06 μm) usually used in second harmonic generation (SHG) experiments.

At about 9400 cm^{-1} the second overtones of the $-NH_2$ stretching vibrations occur[5] and it is possible, as it was already suggested in[6], that the NIR absorption is an important stage of SHG.

Therefore the second goal of this work was to study whether an EPR signal does occur in the m-NA crystals growing from melt and whether the weak NIR radiation could influence the signal or to create unpaired spins.

Since the temperature increase may cause a phase transition also the dilatometric studies above room temperature have been undertaken. At room temperature m-NA crystallizes in the orthorhombic $Pbc2_1$ space group.[7]

EXPERIMENTAL

The commercial m-NA (Reachim) was purified by the zone refinement and single crystals were obtained by the Bridgeman method from melt. The platelet of 0.75 mm thickness was cut from a large crystal parallely to the (010) cleavage plane and used to measure the NIR spectra and the sample ≈ 8x3x1.5 mm^3 was used in the dilatometric studies.

The NIR spectra were measured on the spectrometric assembly set up from a SPM-2 Carl Zeiss monochromator, a wolfram lampe with a chopper and PbS detector. The temperature of samples was controlled by a home made regulator with 1 K accuracy. The spectra measured in the 5700 - 7000 cm^{-1} region are shown in Fig. 1.

The measurements of the thermal expansion were carried out by means of device described previously[8] along the a and c axes. The re-

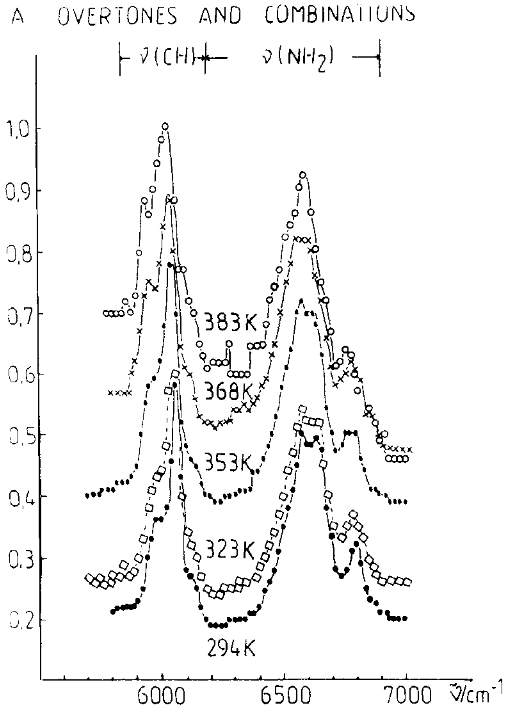

FIGURE 1 Near IR spectra of m-NA single crystal in the ac plane.

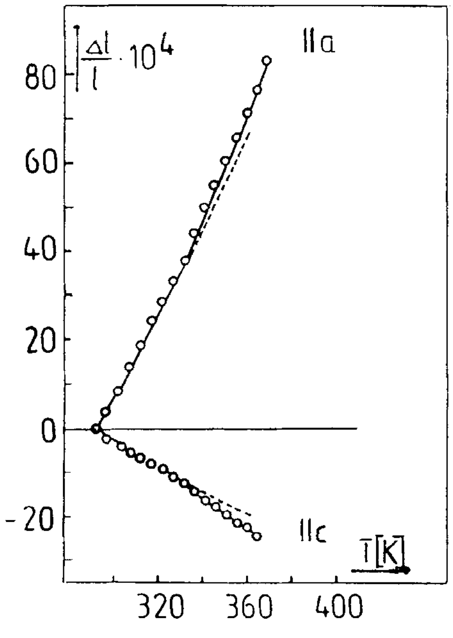

FIGURE 2 Relative elongations in the m-NA cleavage plane.

sults are presented in Fig.2.

The EPR spectra were measured on a SE/X-28 spectrometer with a MX-201R microwave unit and frequency calculator, produced by Technical University of Wrocław, in the X band fequency. The spectra were recorded for powdered and single crystal samples at room temperature, without irradiation and after the 72 hours exposition at 6800 cm^{-1} in the NIR spectrophotometer. Then the irradiated samples were heated in a dryer at 323 K during 1 hour and the measurement of EPR spectrum was repeated.

RESULTS AND DISCUSION

1. The changes in the NIR spectra of the m-NA crystals with growing temperature are greater than expected for internal vibrations. Besides the usual line width increase of the bands in both the $-NH_2$ (6200-7000 cm^{-1}) and the -CH (5700-6200 cm^{-1}) overtone and combination regions the better resolution of the bands is observed at higher temperatures. Moreover the $2\nu^{as}_{NH2}$ to the lower frequency and the background of the spectrum increases with the the temperature increase.

The background increase at about 4000 cm^{-1} was observed during the electrochemical synthesis of polyaniline and was explained by the electronic absorption connected with a benzenoid-semiquinoid transition.[9] Also in the NIR region between 5000 and 7000 cm^{-1} the electronic transition were observed in the polyaniline films and in the theories of the electronic energy levels of polyanilines the polaron structure, e.i. the structure with free spin and positive charge on the nitrogen atom, was considered.[10]

2. The change of slope of the linear relative elongation dependences on temperature are clearly seen at 330 K. The linear thermal expansion coefficients corresponding to the four different slopes of curves are given in Table 1.

3. The non-irradiated m-NA samples have not revealed any EPR signal. After the 72 hours exposure to NIR a very weak signal has been observed which has strongly been enhanced by heating of both powdered and single crystal samples.

The powdered samples have given only one signal with the g value

TABLE I Thermal expansion coefficients in the cleavage (010) plans of the m-NA crystal.

T [K]		α [10^6deg^{-1}]
295 - 330	∥ a	97.4
330 - 370	∥ a	119.3
295 - 330	∥ c	-29.5
330 - 370	∥ c	-32.4

equal 2.0563 ∓ 0.0005 and the spectral width 15.34 mT, whereas the single crystals have revealed a more complicated spectrum. It consists from the broad band with g = 2.1770 ∓ 0.0005, the line width 15.50 mT and from the structured band, shown in Fig.3, with the average value g = 2.1177 ∓ 0.0008 and the line width 11.14 mT.

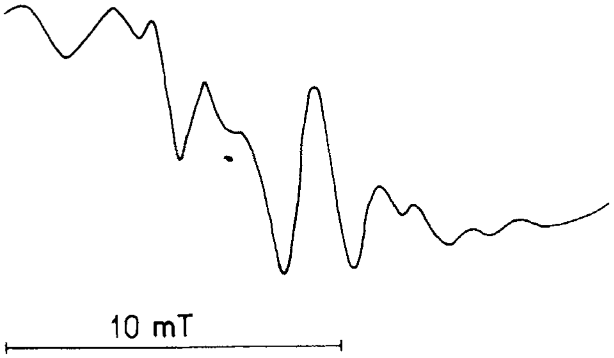

FIGURE 3 EPR spectrum of m-NA single crystal after 72 h irradiation by NIR and 1 h.heating at 323 K.

The possibility that the signal originates from O_2 impurities was rather excluded according to earlier results by Harbour and Loutfy.[10]

4. From the thermal expansion study it results that during heating the crystal unit cell is deformed. This deformation, i.e. the dilatation along the a axis and the contraction along the c axis , involves a re-

orientation of the whole molecule what could explain the changes observed in Fig. 1 in the -CH vibration region. The rotation of the $-NH_2$ group, detected by ^{1}H NMR,[11] probably causes the enlargement of the bands in the 6200-7000 cm^{-1} region with temperature increase. On the other hand, the appearance of the EPR signal generated by NIR and direct heating might be a result of a photochemical reaction in infrared. Such kind of reaction was described by Goodall *et al.*[12] in the case of nitrometane where the excitation of the C-H stretching overtone caused the proton transfer. It seems that in the m-NA crystal, the NIR radiation initiates a photochemical reaction within the $-NH_2$ group, connected with a proton transfer and the unpaired spin formation. These spins are stabilized by the subsequent heating which unables the motions mentioned earlier and which changes the character of intra- and intermolecular interactions.

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