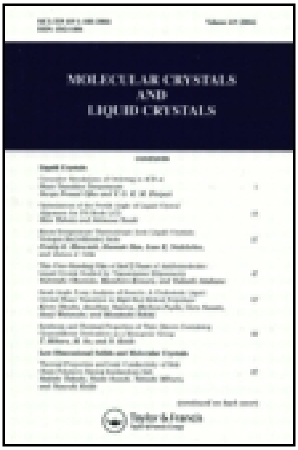

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Roman Swietlik & Andrzej Graja (1985): Influence of Radiation Damage on the Optical Properties of NHe 4 MePy(TCNQ)^2 , Molecular Crystals and Liquid Crystals, 120:1, 129-132

To link to this article: http://dx.doi.org/10.1080/00268948508075774

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 129-132
0026-8941/85/1204-0129/$10.00/0

INFLUENCE OF RADIATION DAMAGE ON THE OPTICAL PROPERTIES OF NMe 4 MePy$(TCNQ)_2$

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Abstract Influence of radiation damage on the IR properties of TCNQ salts with pyridinium derivatives were discussed. The suggestion is given that the salts are Motte insulators.

INTRODUCTION

Infrared spectra of TCNQ ion-radical salts are mainly determined by the interaction between electrons and intramolecular vibrations. Thus, one may expect that the IR spectrum should be sensitive to a change in charge distribution induced by irradiation defects; the same can be said about electronic excitations.

We chose for investigation an ion-radical salt NMe 4 MePy$(TCNQ)_2$. Some measurements were also carried out for NMe 3,5 MePy$(TCNQ)_2$; in both salts the TCNQ molecules are grouped into weakly interacting dimers.[1]

EXPERIMENTAL AND RESULTS

Irradiations of single crystals were performed by fast (2.5MeV) electrons at 21 K with selected doses. We have measured the absorption spectra of the salts using a KBr pellet technique as well as IR reflection spectra of single crystals.

The absorption spectra of the salts show pronounced change due to the electron irradiation. IR spectra gradually becomes more and more detailed, the broad lines sharpen, some of them even vanish, and new ones appear; they show also weaker absorption for some intramolecular normal IR active vibrations as well as for vibrational features connected with the completely symmetric modes of TCNQ (a_g modes) activated by coupling with electrons. Irradiated samples show distinctly weaker absorption due to the electronic CT mode near 3600 cm^{-1}, the same we observed for low-frequency component of the doublet near 11000 cm^{-1}. The band which can be attributed to intramolecular electronic excitation of TCNQ at 16000 cm^{-1} decreases with increasing dose, and a new absorption band appears at about 20200 cm^{-1}.

IR reflection spectra of nominally pure and irradiated NMe 4 MePy$(TCNQ)_2$ single crystals are shown in Fig.1. Infrared reflectivity is more susceptible to irradiation; e.g. the reflection spectrum of 100 mC/cm^2 irradiated crystal almost disappears.

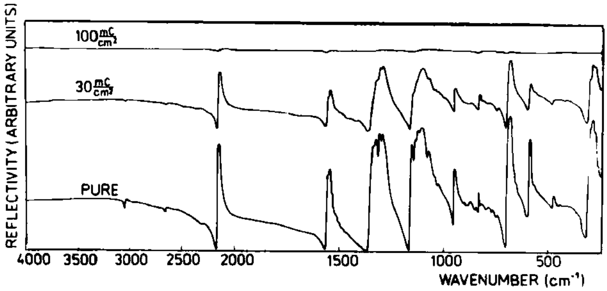

FIGURE 1 IR reflection spectra of nominally pure and irradiated single crystal NMe 4 MePy$(TCNQ)_2$.

DISCUSSION

The frequencies of the activated a_g modes of irradiated samples are slightly higher than these of pure sample. The similar, but considerably higher shifts were observed by Kamarás et al.[2] for Qn$(TCNQ)_2$ and TEA$(TCNQ)_2$.

Assuming that the integral intensities of activated a_g modes are proportional to the number of dimers, we estimated the value of perturbated area; it surpasses the dimer by about 15%. This value and a small decreasing of the electron-phonon coupling constants for irradiated crystals (by about 10% at defect concentration 29%) indicate that a contribution of collective phenomena is inconsiderable.[6] Thus, the activation of a_g modes of NMe 4 MePy$(TCNQ)_2$ occurs mainly by the ion-radical dimer CT oscillations.

The normalized integral intensities of the IR active normal /b/ and activated a_g modes /a/ are plotted as a function of dose in Fig.2.

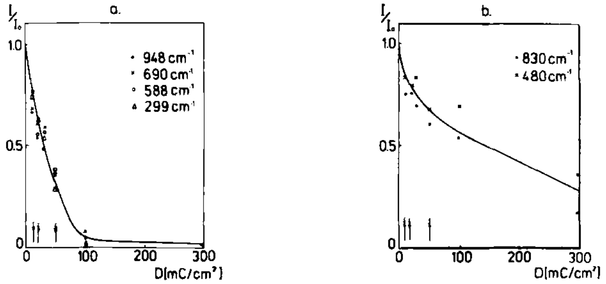

FIGURE 2 The normalized integral intensities of the activated a_g modes /a/ and of some normal modes of TCNQ /b/ as a function of irradiation dose. The points for NMe 3,5 MePy$(TCNQ)_2$ are marked by arrows.

The radiation induced damage of TCNQ molecule changes its vibrational properties and thereby excludes it from measured band. The loss of the intensities of the normal modes of TCNQ enables one to calculate the defect concentration. The damaging one of the TCNQ molecule from the dimer eliminates the whole dimer from the activated a_g modes. Moreover, the neighbouring TCNQ dimers are perturbated and their a_g modes are shifted. The last effect manifests itself as a deviation of the defect concentration calculated for a_g modes from duplicated concentration calculated for IR active normal modes. The comparison of the defect concentrations as a function of doses, calculated from different properties shows that the NMe 4 MePy$(TCNQ)_2$ is a system in which CT dimer excitations are easier than spin excitations and above all more easier than charge excitations.[6] This is a behaviour of localized electrons on TCNQ dimer.

Our spectral investigation suggests that the salt is a Mott insulator with correlated electrons sitting on dimer pairs. This model is consistent with magnetic properties of the salts[4] and is not contradictory to electrical transport properties.[3,5]

We are grateful to Dr. L. Zuppiroli for the irradiation of the samples.

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