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Electron-electron and electron-phonon interactions in irradiated N-methyl pyridinium derivatives with TCNQ studied by optical spectroscopy

A. Graja and R. Świetlik

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland

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Résumé. — L'irradiation électronique des semiconducteurs organiques du type NMePy(TCNQ)₂ forme des défauts qui changent leurs spectres électroniques et vibrationnels. Les changements spectraux sont décrits et discutés. Les changements des constantes de couplage électron-phonon en sont déduits; la concentration de défauts ainsi que leur volume sont calculés à partir des mesures spectrales. Le rôle des interactions électron-électron est souligné et il est suggéré que les sels du TCNQ et des dérivés méthylés de la pyridine sont un isolant de Mott.

Abstract. — Electron irradiation of the organic semiconductors of NMePy(TCNQ)₂ type produces defects which change their vibrational and electronic spectra. The spectral changes are described and discussed. The electron-phonon coupling constant changes are deduced; the defect concentration as well as their volume are calculated from spectral measurements. The role of electron-electron interactions are emphasized and we suggest, that the N-methyl pyridinium derivatives with TCNQ are Mott insulators.

1. Introduction.

One of the most important questions in organic semiconductors is to define the role of electron-electron and electron-phonon interactions. Recently Zuppiroli, Przybylski and Pukacki [1] have shown that in a homologous group of N-methyl pyridinium derivatives with TCNQ the electron-phonon interaction is by no means enough for understanding the insulating character of these compounds. In order to explain the properties of the compounds, one needs substantial electron-electron interaction. This conclusion has been drawn from investigations of electron transport properties of irradiated N-methyl derivatives of pyridinium with TCNQ [1] as well as from the analysis of previous studies of the magnetic susceptibility [2], conductivity and thermopower of the nominally pure compounds [3]. The magnetic susceptibilities are typical of Heisenberg systems of localized spins interacting through exchange integrals. The electrical conductivity of nominally pure compounds has been described by a classical, partially compensated one-electron semiconductor model with low temperature behaviour controlled by deep lying electrically active impurities, suitable for transport description. The band model of electrical conductivity is also not entirely consistent with our investigation of the dielectric permittivity and ac conductivity [4]: the dielectric properties of the salts are dependent on hopping charge polarization, in addition to the molecular mechanism.

It seems to us that the best way for understanding the nature of predominant interactions as well as for a common description of the physical properties of N-methyl pyridinium-TCNQ salts is to increase the disorder in a controlled way and to follow the evolution of these properties. This way has been recently proposed jointly by the Poznań and Fontenay-aux-Roses groups [5, 6, 1].

Przybylski, Pukacki and Zuppiroli have shown that the disordering of the N-methyl pyridinium derivatives with TCNQ by electron irradiation changes considerably their transport properties and creates a large variety of new experimental situations. They have considered the origin of the insulating character of the salts, i.e. whether these organic semiconductors are Mott insulators with excitons as the main current carrying excitations or spinless fermion half-filled band Peierls insulators with soliton-antisoliton pairs. We would like to investigate this subject on the basis of the spectral results.

It is well known that the infrared spectra of TCNQ ion-radical salts are mainly determined by the interaction between electrons and intramolecular vibrations [7-9]. This phenomenon was interpreted theoretically by Rice et al. using two different models for conductors with a uniform TCNQ stack [9] and semi-
conductors with isolated TCNQ dimers [8]. In the former case, the absorption bands should arise from the oscillations in phase with the charge density wave state stabilized by intramolecular distortion, i.e. the collective phenomena. In the latter case, they are a consequence of an intradimer electronic excitation, i.e. the local phenomena. In both cases the \( a_n \) modes are activated by coupling with electrons. The coupling between the electrons and the molecular vibrations can be characterized by electron-phonon coupling constants \( g_{e\nu} \). These constants depend on the charge distribution on the TCNQ molecules or ions. Thus, one may expect that the infrared spectrum should be sensitive to a change in the electron distribution induced by irradiation defects, i.e. the spectrum should be sensitive to the localization of the carriers due to random potentials in the environment of the defects. One may expect that IR spectroscopy of irradiated quasi-one-dimensional organic materials can give some information about electron-electron and electron-phonon interactions in these materials.

Earlier experiments performed by a Hungarian group [10-12] as well as ours [12-14] have shown that the IR vibrational spectra of the TCNQ salts change markedly upon irradiation with high energy neutrons or electrons and can give useful information regarding the interactions occurring in organic semiconductors or conductors. A reduction in intensity of some totally symmetric modes and an increase of other modes observed by Kamarás et al. [10, 11] in the neutron irradiated TCNQ salts with \( Q_n^+ \) and \( \text{TEA}^+ \) were discussed in the framework of the electron-vibrational interaction theory. They have also noticed that the relatively high doses required to obtain observable spectral changes point rather to the role of simple electron—vibrational coupling in the salts under investigation. On the other hand, on the basis of the spectral study of the electron irradiated \( \text{MTPP(TCNQ)}_2 \) salt we had proposed [13] that the distortion of the local field in the environment of the defect can reduce the electron-phonon coupling, i.e. can eliminate some of the bands.

Electron spectroscopy has different possibilities and advantages. Because the electron absorption bands are related to inter- or intramolecular electronic excitations, they can give some information about the electronic energy level, charge distribution, degree of charge transfer and can yield information about the origin of some electronic bands. A possible relationship between the energy of the electronic bands observed in the near infrared region and the activation energy for the electrical conductivity is extremely fascinating for us. Thus one can expect considerable changes of the electron bands in irradiated organic semiconductors.

2. Experimental

We chose to investigate the homologous group of N-methyl pyridinium derivatives with TCNQ. From our previous investigations it is known that in spite of differences in the donor structures (i.e. the number and location of the methyl substituents) the physical [15] and especially the spectral [16] properties of the salts are approximately similar to each other. For this reason we carried out spectral measurements for two salts representative of the group: for an ion-radical salt \( \text{NMe} \_4 \text{MePy(TCNQ)}_2 \) \((\text{N-methyl-4-methylpyridinium-TCNQ})_2\) and \( \text{NMe} 3.5 \text{MePy(TCNQ)}_2 \) \((\text{N-methyl-3,5-dimethylpyridinium-TCNQ})_2\). Because the TCNQ salts of the N-methyl pyridinium cations crystallize either in the triclinic or in the monoclinic system, we chose representatives from both systems: \( \text{NMe} 4 \text{MePy(TCNQ)}_2 \) has a space group \( P1 \) or \( P1 \) whereas \( \text{NMe} 3.5 \text{MePy(TCNQ)}_2 \) belongs to the \( P_{21}/c \) space group [17]. Independent of the space group, the TCNQ's are stacked plane-to-plane, in groups of two, with no direct overlap between adjacent pairs. Within the pairs, there is a favourable exocyclic-double-bond to quinonoid-ring overlap of adjacent molecules, with a short mean perpendicular distance of about 3.2 Å. The TCNQ dimers are lined up in a chain-like fashion approximately in the direction of the b axis. At the same time the dimers form two-dimensional layers \((ab\) plane) between which the donor molecules are arranged in two equivalent positions. The crystals have a well developed long axis and the shape of a rectangular parallelepiped.

Synthesis of the salts, carried out by the method of Melby et al. [18] is described elsewhere [17]. Irradiation of single crystals of the salts was performed by fast (2.5 MeV) electrons from the accelerator of Fontenayaux-Roses; the samples were irradiated at 21 K with selected doses of up to 500 mC/cm².

We have measured the absorption spectra of the pure and electron irradiated salts using a KBr pellet technique in the region from 250 cm⁻¹ to 45 000 cm⁻¹ as well as the single crystal infrared reflection spectra. The main advantage of the latter technique compared to the powder spectra is that polarization directions of the bands can be identified. Thus, one can distinguish in plane intramolecular normal TCNQ modes from the activated by electron-phonon coupling the totally symmetric \( a_n \) vibrations. One can also attribute the frequencies of the bands to the appropriate vibrations. The analysis of reflection spectra enables us to study the electron-phonon coupling constants and their evolution under the influence of irradiation.

For both spectral techniques we have investigated the evolution of spectra as a function of irradiation doses. We have measured and analysed carefully the line positions (wavenumbers \( \omega \)), their shifts \( \Delta \omega \), the integral intensities as well as their changes vs. irradiation dose.

3. Results.

The absorption spectra of pure and irradiated samples are shown in figures 1-3. The IR spectra of nominally pure crystals, shown in figure 1, are dominated by broad and intense absorption bands characteristic of
Fig. 1. — Absorption spectra of pure and irradiated samples with selected doses NMe 3.5 MePy(TCNQ)₂ (a) and NMe 4 MePy(TCNQ)₂ (b) salts.

The spectra of the irradiated samples (Fig. 1) gradually become weaker when the dose is increased: the broad lines change shape and decrease in intensity, some even vanish, and new ones appear; they show weaker absorption for some intramolecular normal IR active vibrations as well as for vibrational features connected with the totally symmetric modes of the TCNQ molecule (aₙ modes) activated by electron coupling. Figure 2 presents more distinctly the evolution of some bands between 1000 and 1400 cm⁻¹.

The spectra of NMe 4 MePy(TCNQ)₂ irradiated with doses exceeding 200-300 mC/cm² (Fig. 1b) are considerably different from the spectrum of the nominally pure sample. Some bands characteristic of the salt have disappeared and new bands have become visible. These new bands characterize a highly defected and surely chemically changed sample.

The electronic absorption spectra of the NMe 4 MePy(TCNQ)₂ salt are shown in figure 3. Unfortunately the interpretation of the electronic spectrum of the nominally pure TCNQ salts has not been too clear up to now. Torrance et al. [19] described bands close to 3000-5000 cm⁻¹ and 9000-11000 cm⁻¹ as intermolecular charge-transfer transitions whereas the bands near 16000 cm⁻¹ and 27000 cm⁻¹ were attributed to intramolecular electronic excitations. A somewhat different interpretation, based on the electronic structure of the crystal, was given by Tanaka et al. [20]. They pointed out e.g. that the band close to 10000 cm⁻¹ depends on the donor properties and is, in general, a mixture of inter- and intramolecular CT excitations. Yakushi et al. [21] considered the band close to 11000 cm⁻¹ as mainly due to the lowest π-π* transition of the TCNQ⁻ ion and not to charge transfer between the TCNQ⁻ ions. The band close to 16000 cm⁻¹ was assigned to a doublet — doublet transition which has the character of the local excitation.
Table I. — Assignment of the strongest absorption bands in IR region of NMe 4 MePy(TCNQ)₂ salt.

<table>
<thead>
<tr>
<th>Frequency [cm⁻¹]</th>
<th>Intensity</th>
<th>Symmetry</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 060</td>
<td>w</td>
<td>a₈</td>
<td>CH stretching</td>
</tr>
<tr>
<td>2 670</td>
<td>w</td>
<td>a₈</td>
<td>CH stretching</td>
</tr>
<tr>
<td>2 200</td>
<td>s</td>
<td>a₈</td>
<td>CN stretching</td>
</tr>
<tr>
<td>2 170</td>
<td>vs</td>
<td>a₈</td>
<td>CC stretching (pyridine)</td>
</tr>
<tr>
<td>1 578</td>
<td>vw</td>
<td>a₈</td>
<td>CC ring stretching</td>
</tr>
<tr>
<td>1 550</td>
<td>s</td>
<td>a₈</td>
<td>CH bending</td>
</tr>
<tr>
<td>1 515</td>
<td>w</td>
<td>b₁u</td>
<td>CH bending</td>
</tr>
<tr>
<td>1 312</td>
<td>vs</td>
<td>a₈</td>
<td>CC ring stretching</td>
</tr>
<tr>
<td>1 126</td>
<td>vs</td>
<td>a₈</td>
<td>CC ring stretching</td>
</tr>
<tr>
<td>948</td>
<td>m</td>
<td>a₈</td>
<td>C(N₂)₂ deformation</td>
</tr>
<tr>
<td>840</td>
<td>w</td>
<td>b₃u</td>
<td>CH bending out of the plane</td>
</tr>
<tr>
<td>830</td>
<td>m</td>
<td>b₂g</td>
<td>CH deformation out of plane (pyridine)</td>
</tr>
<tr>
<td>750</td>
<td>w</td>
<td>b₂g</td>
<td>CH bending out of plane</td>
</tr>
<tr>
<td>690</td>
<td>s</td>
<td></td>
<td>CC stretching</td>
</tr>
<tr>
<td>600</td>
<td>w</td>
<td>b₂g</td>
<td>CH bending (pyridine)</td>
</tr>
<tr>
<td>588</td>
<td>w</td>
<td>a₈</td>
<td>out of the plane</td>
</tr>
<tr>
<td>580</td>
<td>vw</td>
<td>b₁u</td>
<td>CC stretching</td>
</tr>
<tr>
<td>480</td>
<td>m</td>
<td>b₃u</td>
<td>CC bending</td>
</tr>
<tr>
<td>299</td>
<td>w</td>
<td>a₈</td>
<td>CCN bending</td>
</tr>
</tbody>
</table>

vs — very strong, s — strong, m — medium, w — weak, vw — very weak.

It is most important to obtain more detailed and qualitatively new spectroscopic data to establish the interpretation of the visible and near-infrared spectra of the TCNQ salts. We hope that the technique of irradiated samples will also be useful for this purpose.

Figure 3 shows that the samples irradiated with weak doses distinctly display weaker absorption due to the electronic charge transfer mode close to 3 600 cm⁻¹. The same was observed for the high-frequency component of the doublet close to 11 500 cm⁻¹, contrary to which the low-frequency component seems to increase initially with electron dose. The intramolecular electronic band close to 16 000 cm⁻¹ changes considerably: for lower doses its intensity increases whereas for higher (D > 20 mC/cm²) it decreases. The band close to 27 000 cm⁻¹ is also very susceptible to irradiation.

The normalized integral intensities of the IR activated a₃ modes and of some other modes of TCNQ for NMe 3,5 MePy(TCNQ)₂ are shown in figure 4; the identical results we obtained for NMe 4 MePy(TCNQ)₂ salt. We would like to call attention to the strong and monotonic dependence of intensity versus dose, up to about 100 mC/cm² (for a₃ modes) and very small values and weak dose-dependence of the intensities above 100 mC/cm² (Fig. 4a). It is also very significant that dose-dependence of different modes is practically the same. The dose-dependence of the out-of-plane normal modes of TCNQ (Fig. 4b) is weaker than the dependence of the a₈ modes, but as before it is practically the same for different normal modes.

Figure 5 shows the integral intensity of the electronic
Fig. 4. Normalized integral intensities of the IR activated $a_g$ modes (a) and of some TCNQ normal vibrations (b) for NMe$_{3.5}$MePy(TCNQ)$_2$ as a function of irradiation dose.

Fig. 5. Relative integral intensity of the electronic absorption band dose to 16 000 cm$^{-1}$ as a function of irradiation dose: the points representing the electrical conductivity are marked also [1, 6] (□ — NMe$_4$MePy(TCNQ)$_2$, ○ — NMe$_{3.5}$MePy(TCNQ)$_2$). The line is only guide for the eye.

Apart from the powder absorption spectra we have carried out investigations of reflection spectra of irradiated single crystals. As has been said before, these spectra show the activated $a_g$ modes if the light polarization is parallel to the TCNQ quasi-chain direction. IR reflection spectra of the nominally pure and irradiated samples of NMe$_4$MePy(TCNQ)$_2$ single crystals with doses of 30 and 100 mC/cm$^2$ are shown in figure 6. For higher doses, the reflection coefficient is constant for the whole spectral region.

It is symptomatical that the IR reflectivity is more susceptible to irradiation than the absorption: the reflection spectrum of the 100 mC/cm$^2$ irradiated crystal almost disappears whereas the absorption spectra of the 100 mC/cm$^2$ and higher irradiated samples still show the bands. The higher sensitivity of the reflection spectra emphasizes the obvious fact that the crystal surface is more susceptible to the influence of atmosphere; i.e. partial decomposition of the crystal is easier on the surface.

4. Discussion.

The aim of our discussion is to point out the influence of irradiation disorder on the spectral properties of the salts, on the electron-electron and electron-phonon interactions and in addition we will try to discuss the nature of the insulator state of the salts under investigation.

4.1 Radiation Induced Resistance Changes. According to Zuppiroli [25] there are two factors which determine the defect production rates. The first one is a physical factor: the average lifetime of an excitation in the crystal, mainly related to electron interactions. The second one could be called chemical; it is the stability of the molecule or the group of molecules in the excited state. It is also well known that radiolysis is the main formation process of stable defects in organic solids, when irradiated with electrons or X- or $\gamma$-rays. The incident radiation provides the creation of strongly excited states inside the crystal, and one should expect that damage is nearly the same in the bulk and in the surface. However comparison of the IR absorption spectra with the reflection spectra of the salts shows that the changes at the surface are considerably higher than in the bulk: the absorption bands of the heavily irradiated crystal are easily measurable whereas the reflection spectrum of a similarly damaged crystal is absolutely inaccessible to measurement. In our opinion the excited TCNQ molecules or ions may be easily oxidized by atmospheric oxygen. This chemical reaction is most
efficient at the surface of the crystal. Anion radicals are expected to act as strong electron donors, since their ionization potentials are very low. One can expect therefore that they interact easily with O₂, a weak electron acceptor, or else with water vapour. The expected features of these interactions are the appearance of new bands or a broadening and energy shift of the bands.

The analysis of the spectra of the salts (Fig. 3) shows the appearance of a new band close to 20 500 cm⁻¹. Similar spectral changes were observed by Pukacki [27] in an acetonitrile solution.

The change in the absorption spectra of similar organic salts after the introduction of oxygen was measured by Nomori et al. [28] and by Nakatani et al. [29]. They observed e.g. the appearance of a new absorption band at 21 050 cm⁻¹; this absorption was attributed to the product of oxidation i.e. to α, α’-dicyano-p-toluoylcyanide. A similar attribution of the band at 20 830 cm⁻¹, observed by Cehak et al., was given [30]; the last authors interpreted this band as a characteristic one for the final product of hydrolysis of TCNQ. In principle both attributions could be acceptable. In our opinion the former is better confirmed by our measurements. The TCNQ⁻ anion radicals are cent of interaction with oxygen and therefore the band about 20 500 cm⁻¹ increases distinctly in heavily irradiated crystals.

The salts irradiated with doses much exceeding 100 mC/cm² are strongly decomposed; this is a conclusion from IR measurements as well as from electron spectroscopy.

4.2 ELECTRON-PHONON COUPLING. — As has been already stated the TCNQ molecules of the salts are arranged in weakly interacting dimers. The spectrum of TCNQ salts with isolated radical-ion TCNQ dimers has been described by Rice et al. [22]. It consists of a primary electronic charge-transfer mode and a series of oscillations in the radical-electron-electric dipole moment driven by the antisymmetric modes of the internal molecular vibration of the dimer. The latter is a consequence of the intramonomer electron-molecular-vibration coupling and, for short, we shall refer to them as « activated ag modes ». According to Rice et al. [8, 9] the intradimer π molecular orbital hopping (or resonance) integral t, the TCNQ monomer ag molecular vibration frequencies ωₐ and the electron-phonon coupling constants gₐ describe the IR spectrum of the salts.

The spectra of the salts with interacting dimers are mainly determined by the Rice mechanism mentioned above. Considering the interdimer interactions the certain role of oscillations in phase with the charge density wave state stabilized by intramolecular distortion one can notice. This additional mechanism of activation of the ag modes shifts the bands of the activated modes in comparison with the bands activated by intradimer electronic excitation.

Recently, Garrigou-Lagrange et al. [23] starting from the model of Rice et al. [22] and taking into account a general expression for the complex electronic susceptibility \[ \chi(\omega) = \chi_1(\omega) + i\chi_2(\omega) \] have evaluated the renormalized frequencies \[ \bar{\omega}_a \] of the vibronic lines and the integrated intensities \[ I_a \] of these lines for the dimerized phase of the organic semiconductors. They have obtained two expressions:

\[
\begin{align*}
\omega_a - \bar{\omega}_a & \approx g^2_a \chi_1 \\
I_a & \approx g^2_a \frac{\omega_a}{\bar{\omega}_a} (\chi_1^2 - \chi_2^2)
\end{align*}
\]

with four relevant parameters: \( \omega_a \) — the bare frequency of ag mode, \( g_a \) — the linear electron-phonon coupling constant, \( \chi_1 \) and \( \chi_2 \) — the real and imaginary parts of the bare electronic susceptibility. Thus these expressions will be useful for the analysis of the electron-phonon coupling in irradiated TCNQ salts of N-methyl pyridinium derivatives. Assuming that equations (1) and (2) are valid for irradiated salts also, and supposing that the electronic susceptibility of the irradiated salt is nearly the same as that of the pure salt, we directly obtain the electron-phonon coupling constant of the irradiated crystal \( g^*_a \) as:

\[
g^*_a \approx g_a \frac{\omega_a - \bar{\omega}_a}{\sqrt{\omega_a - \bar{\omega}_a}}
\]

from equation (1), and

\[
g^*_a \approx g_a \frac{I_a \bar{\omega}_a}{\bar{\omega}_a}
\]

from equation (2).

The experimental frequencies of some activated ag modes for nominally pure \( \bar{\omega}_a \) and irradiated with selected doses \( \omega_a \) samples are collected in table II.

The frequencies \( \omega_a^* \) are slightly higher than \( \omega_a \) (blue shift); these shifts are larger for higher doses of radiation. The similar, but considerably higher shifts were observed by Kamarás et al. [10] for TEA(TCNQ)₂ and Nn(TCNQ)₂. Figure 7 shows the comparison of the \( \Delta \omega = \bar{\omega}_a^* - \bar{\omega}_a \) mode shifts of Qn(TCNQ)₂, TEA(TCNQ)₂ on the ground of the investigations of Kamarás et al. and of one of our salts : NMe 4 MePy(TCNQ)₂. We noticed identical shifts for some left modes, especially for modes \( \bar{\omega}_a^* \) and \( \bar{\omega}_a^*_g \).

Considerably higher frequency shifts of the modes of the salts studied by Kamarás et al.[10] are connected with different mechanisms responsible for the spectra. In Qn(TCNQ)₂, where the molecules are arranged uniformly along the chains, the CDW phase oscillation mechanism [9] occurs. It is of opinion that in the pure material, electrons may have a collective behaviour with coherence lengths as long as 100 lattice constants. Defects induced by irradiation reduce strongly this coherence length. On the other hand,
Table II. — Activated \(a_g\) modes of NMe 4 MePy(TCNQ)\(_2\) salt for selected concentration of defected TCNQ dimers.

<table>
<thead>
<tr>
<th>Mode of TCNQ(^0)</th>
<th>(\omega_a) of pure sample</th>
<th>(\bar{\omega}_a)* of samples irradiated, with defect concentrations (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3 %</td>
<td>5.8 %</td>
<td>8.7 %</td>
</tr>
<tr>
<td>3</td>
<td>1 602</td>
<td>1 550</td>
</tr>
<tr>
<td>4</td>
<td>1 454</td>
<td>1 312</td>
</tr>
<tr>
<td>5</td>
<td>1 207</td>
<td>1 126</td>
</tr>
<tr>
<td>6</td>
<td>948</td>
<td>948</td>
</tr>
<tr>
<td>7</td>
<td>711</td>
<td>690</td>
</tr>
<tr>
<td>8</td>
<td>602</td>
<td>588</td>
</tr>
<tr>
<td>9</td>
<td>334</td>
<td>299</td>
</tr>
</tbody>
</table>

(*) Found from spectral data.

they are the main source of pinning of CDW's and thus may strongly change the infrared spectrum. In Qn(TCNQ)\(_2\) defects may separate the chains into smaller segments [25] which behave similarly to the tetrads in TEA(TCNQ)\(_2\) and then, for higher doses, to the diads in the N-methylpyridinium derivatives with TCNQ. The coherence length of the latter is reduced to the dimension of a single dimer in a practical manner, and therefore the mechanism of activation of the above-mentioned totally symmetric modes is inadequate. Since in the TCNQ salts with pyridinium derivatives, each unpaired electron is localized on a dimeric TCNQ unit, the spectrum of the low-lying excitations should be that of a radical-ion TCNQ dimer [8, 22]. In this way the very weak change of the activated \(a_g\) modes as a function of defect concentration of the NMe 4 MePy(TCNQ)\(_2\) spectrum may be understood.

On the other hand, the high sensitivity of the spectra of Qn(TCNQ)\(_2\) and similar salts with TCNQ uniformly arranged along the chains is a consequence of introducing barriers which shorten the range of delocalization. Thus, the spectrum of an irradiated uniformly stacked TCNQ salt approaches that of the dimerized TCNQ salts, as the defect concentration increases. One may expect that the frequencies of the \(a_g\) modes of the irradiated TCNQ salts with fully isolated TCNQ dimers will be completely insensitive to the concentration of irradiation induced defects. As has been previously said, in the N-methylpyridinium derivatives with TCNQ the acceptor molecules are grouped into weakly interacting dimers, and that is why we observe a certain dependence of frequency shifts with defect concentration (Fig. 7 and table II).

The relative changes of the electron-phonon coupling constants as a function of defect concentration are independent of the mode. The mean values of these changes, calculated from equation (3), are shown in figure 8. It is necessary to say that equation (4)
is less useful for calculating $g^*_a/g_a$ because the determination of the intensities of the shifted bands is rather difficult.

The evolution $g^*_a/g_a$ as a function of defect concentration was determined on the basis of the assumption that the electric susceptibility of the crystal does not change as a result of irradiation. This assumption can be supported to some extent by dielectric investigations; microwave dielectric constant of irradiated crystals is nearly independent of irradiation dose [31]. However, this is a rather weak argument. Therefore we have recalculated $g^*_a/g_a$ for different doses taking into account the formula derived by Wong [32]. He has found that dimeric absorption corresponding to $a_g$ modes of monomers occurs at:

$$\overline{\omega}_a \simeq \omega_a \left(1 - \frac{g^2_a}{\hbar^2 \omega_a^2} \varepsilon_0\right)^{1/2} \tag{5}$$

where $\varepsilon_0$ is the electronic coupling strength and $\hbar$ the Planck constant; the other parameters are the same as in equations (1) and (2). The relative changes of the electron-phonon coupling constants $g^*_a/g_a$ found from equation (5) are the same as those found from equation (3) and shown in figure 8; this supports our earlier conclusions.

A slow decreasing of the constants $g^*_a$ and a tendency to saturation for defect concentrations surpassing about 30% indicate that a contribution of the collective phenomena is inconsiderable in the case of our salts. From a comparative analysis of the spectral data of our salts and $Qn(TCNQ)_2$, we estimate this contribution to be smaller than about 10%.

4.3 Concentration and Volume of Irradiation Induced Defects. — The radiation induced damage of the TCNQ molecule changes its vibrational properties and thereby excludes it from the measured band. Statement of this fact enables us to draw conclusions about the concentration of irradiation-induced defects and their volume from the analysis of integral intensities of the main, acceptable to measurement, IR absorption bands.

Assuming that a transition moment $\mu_{01} = \langle \psi_0 | \mu | \psi_1 \rangle$ of the TCNQ molecule normal IR active vibrations is insensitive to changes of the local potential in the environment of the irradiation defect and that the integral intensity of a band is simply proportional to a number of unperturbed oscillators $I \sim \mu_{01}(N - n)$ one can calculate the concentration of defected TCNQ molecules from the formula:

$$C_m = \frac{n}{N} = 1 - \frac{I^*_a}{I_a} \tag{6}$$

where $N$ and $n$ are the total (in nominally pure sample) and defected numbers of TCNQ molecules, respectively, $I_a$ and $I^*_a$ are integral intensities of the bands of nominally pure and irradiated samples, respectively.

The situation is more complex for the activated $a_g$ modes. As it has been said above, these modes appear as a result of the coupling between the radical electron and the antisymmetric modes of the internal molecular vibration of the dimer. Thus, the damaging of one of the TCNQ molecules of the dimer eliminates the whole dimer from the activated $a_g$ band. Moreover the irradiation influences the spectral properties of unperturbed dimers; it has been shown formally as the change of electron-phonon coupling constants $g^*_a/g_a$ (Fig. 8). For relatively small doses, for which the assumption about single molecular damage within the dimer is fulfilled, one can calculate the concentration of defected dimers $C_d$ by the same formula as for TCNQ normal IR active vibrations, equation (6), but taking into account the change of spectral properties of dimer described by formulae (1) and (2). It results that:

$$C_d = 1 - \frac{I^*_a(\omega_a - \overline{\omega}_a) \omega_a^*}{I_a(\omega_a - \overline{\omega}_a) \omega_a} \tag{7}$$

where $I^*_a$ and $I_a$ are the integral intensities of activated $a_g$ modes of irradiated and nominally pure samples, respectively. It should be emphasized that the change of spectral properties of the dimer has small influence on the final defect concentration. For heavily irradiated samples the number of undefected dimers approaches zero while the number of repeatedly defected ones becomes noticeable.

One can calculate a concentration of perturbed but not damaged dimers $C^*_d$ and one can define the volume of irradiation induced defect as:

$$\xi = C^*_d/C_d = \frac{I^*_a/I_a}{1 - I^*_a/I_a} \tag{8}$$

Using this formula for the dose $D = 100$ mC/cm², i.e. the dose for which there is no more unperturbed dimers, we find $\xi = 0.15$, in other words, the volume of the defect or the value of the perturbed area surpasses the volume of the dimer by about 15%. This estimation seems to be reasonable in comparison with the total volume change per molecular defect equal to $1.50 \pm 0.25$ times the molecular volume deduced by Trouilloud et al. [26] from volume change measurements of the irradiated TTF-TCNQ crystals.

Figure 9 shows a comparison of the concentration of defected molecules $C_m$ and defected dimers $C_d$ with defect concentration as a function of the dose, calculated from the magnetic susceptibility, $C_d$ [1]. The number of localized spins is about 30 times larger than the number of dopants calculated from the transport properties [1]. A completely different defect concentration found from the electrical transport properties testifies that the electrical active impurities and defects are the complex and extended disturbances. The comparison of the defect concentrations
also shows that, the TCNQ salts with N-methyl pyridinium derivatives are systems in which the electron irradiation creates more easily the intradimer charge disorder than the spin disorder and above all more easily than electrically active defects.

4.4 INTER- AND INTRAMOLECULAR ELECTRONIC EXCITATIONS. — Electronic absorption spectra of the TCNQ salts reflect the intermolecular charge transfer and intramolecular excitations. These two channels could lead to electron excitation to the conducting band.

Przybylski et al. [5, 1] have demonstrated that the single crystal needle axis conductivity of N-methyl pyridinium derivatives with TCNQ increases as a function of the dose (at low doses) to a value about ten times larger. At a dose of about 20 mC/cm², it saturates and reaches a maximum, then the conductivity starts decreasing.

Figure 5 shows that the electronic band close to 16 000 cm⁻¹, reveals a similar dependence as the electrical conductivity, but a considerably weaker dependence on irradiation dose. Our preliminary results show that there are two typical courses of normalized intensities of the electronic bands as a function of the irradiation dose (Fig. 10). The maxima of intensity at a dose of $D_o$ were observed for the bands close to 10 000 cm⁻¹, 16 000 cm⁻¹, and 27 500 cm⁻¹ (Fig. 10a). For bands close to 3 600 cm⁻¹ and 11 500 cm⁻¹, at low doses the intensity decreases as a function of the dose, at about $D_o$ it reaches a minimum and then increases up to a dose of about 2.5 $D_o$, reaches a maximum and then decreases again (Fig. 10b). In spite of rather large errors, the character of these curves was similar for all studied salts and for all indicated bands; therefore we can draw our conclusions.

In a system of weakly interacting TCNQ dimers with one radical electron two types of optical transitions have to be taken into account: intramolecular transitions in which an electron is excited to a higher level on the same unit which may be TCNQ⁺, TCNQ⁻ or dimer (TCNQ)₂, and charge-transfer transitions in which an electron is excited to a neighbouring molecule. It results from solution studies [33] that: TCNQ⁺ has the absorption band at about 25 x 10³ cm⁻¹; TCNQ⁻ at about 23 x 10³ and 13 x 10³ cm⁻¹; and the dimer (TCNQ)₂ has three absorption bands 10 x 10³, 16 x 10³ and 27 x 10³ cm⁻¹.

Let us consider that the electronic spectrum is a superposition of these absorption features in different proportions [34], and moreover let us consider that the electronic bands 10 x 10³, 16 x 10³ and 27.5 x 10³ CM⁻¹ (Fig. 3) are mainly due to dimer excitation; and the bands 3 600 cm⁻¹ and 11 500 cm⁻¹ are due to charge transfer phenomena.

Irradiation is responsible for the following effects in our crystals:

(i) increase of the density of charge carriers connected with doping effect,
(ii) localization of carriers,
(iii) destruction of the crystal.

The strong increase of electrical conductivity for small doses (Fig. 5) shows that the effect (i) is the most important. The increase of electron density induces an increase of intensity of dimer bands but the decrease of charge-transfer bands (the increase of Coulomb interactions). At about $D = 20$ mC/cm² effect (ii) starts to prevail over (i) and one observes the decrease of electron density in the conducting chains. It is observed as a decrease of electrical conductivity, decrease of the intensity of dimer bands and increase of charge-transfer bands (the decrease of Coulomb interactions). Finally at higher doses the effect (iii) begins to be the most important and it is seen as a decrease of electrical conductivity and the intensity of dimer bands. This process becomes to be important at a dose of about 50 mC/cm² — as is seen from the dependence of charge-transfer bands.

This simple model explains qualitatively the shape of the curves shown in figure 10 and interesting
analogy between electrical conductivity and dimer bands (Fig. 5). The essence of this model is strictly connected with a new view on the origin of the electronic bands in the TCNQ salts where TCNQ molecules are grouped into weakly interacting dimers. However it should be supported by broader experimental evidence and more precise quantitative considerations. The work is in progress.

4.5 CAN THE SALTS BE MOTT INSULATORS? — The N-methyl derivatives of pyridinium with TCNQ are the materials which, according to the electron's picture, should be a metal. In order to explain the insulating character with a gap of about 0.6 eV we need either substantial Coulomb interactions or a chain distortion e.g. a tetramerization. Taking into account the structural peculiarities of the salts we are in agreement with Zuppiroli et al. [1] that substantial Coulomb interactions are needed to explain the insulating character of the salts. It is well known that electron-electron interactions can lead to a Mott insulator state whereas electron-phonon interactions produce polarons. The electron-phonon coupling constants describe the latter. In fact, these coupling constants of the salts do not exceed 80 meV [35] whereas the on-site Coulomb interactions are about 1.2 eV. As shown above, (e.g. Fig. 8) the coupling constants decrease with increasing defect concentration.

We have shown above (e.g. Fig. 8) the constants' decrease with increasing defect concentration. Thus the role of the polaronic contribution is decreasing in heavily irradiated salts. We also stressed that the contribution of the collective phenomena is rather small in our salts; the activation of $a_g$ modes is mainly a consequence of an intradimer electronic excitation. These are the spectral observations which are indicative of the electron localization on the TCNQ dimers. Thus our investigation suggests that the salts are Mott insulators with correlated electrons sitting on the dimer pairs. This model is consistent with the magnetic properties typical of a Heisenberg system of localized spins with low exchange between sites [2]. A Mott insulator model is not contradictory to the electric transport properties of the nominally pure [3] and electron irradiated salts [1, 5, 6].

5. Conclusions.

In this paper we have shown experimentally that the electron irradiation of TCNQ salts with N-methyl pyridinium derivatives leads to extensive spectral changes. The IR spectra gradually become more and more detailed, some of the bands vanish, and new ones appear. The vibrational features connected with the totally symmetric modes of the TCNQ molecule ($a_g$ modes) activated by coupling with electrons are particularly sensitive to electron irradiation. Irradiated salts also show changes in the region of the electronic absorption (NIR-VIS-UV). Such changes of band intensity imitate the electrical conductivity as a function of the dose. The position of the electronic absorption bands is insensitive to irradiation in a practical manner whereas the $a_g$ modes are shifted towards the higher frequencies (a blue shift). One possible explanation is that electron-phonon couplings are weakened for irradiated crystals. The analysis of the IR spectra of the salts enables us to draw the conclusion that a contribution of collective phenomena in the activation of $a_g$ modes is inconsiderable in the case of our salts.

We have proposed a new way of determining the defect concentration in the irradiated solid. The total volume per defect has been found to be about 1.15 times the dimer volume. Finally we wish to point out that, as we have revealed in this study, it is important to take strong electron donor properties of TCNQ-anion radicals into account. The analysis of the IR spectra of the salts enables us to draw the conclusion that a contribution of collective phenomena in the activation of $a_g$ modes is inconsiderable in the case of our salts.

In concluding this paper the importance of the electron-electron interactions of these salts must be emphasized. Although our investigations are concentrated on a spectral or molecular approach, the conclusions found in this study will be useful for understanding the band properties of the salts. Thus we suggest that N-methyl pyridinium derivatives with TCNQ are Mott insulators.

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