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Raman Effect and Infrared Reflectivity in MNEB $(TCNQ)_2$ and TEA $(TCNQ)_2$

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RAMAN EFFECT AND INFRARED REFLECTIVITY IN MNEB(TCNQ)$_2$ AND TEA(TCNQ)$_2$

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Abstract Raman and IR spectra of MNEB(TCNQ)$_2$ and TEA(TCNQ)$_2$ are reported for 300K, 80K, and 4K. An interpretation of the electron-molecular vibration interaction in terms of the dimer theory of Rice is presented.

The organic linear chain semiconductors MNEB(TCNQ)$_2$ (methyl-N-ethyl-benzimidazolium tetracyanoquinodimethane) and TEA(TCNQ)$_2$ (triethyl-amine-tetracyanoquinodimethane) are materials in which the electron-molecular vibration interaction can be studied[1, 2]. We have measured Raman spectra on needle crystals of 1x0.1x2 mm^3 in the E||c configuration. For the infrared reflectivity measurements we used single crystals[3] of about 8x6x15 mm^3.

Fig. 1 shows the Raman spectrum of MNEB(TCNQ)$_2$ at 80K. All lines are quite weak, probably due to missing resonance enhancement. Observed are the TCNQ intramolecular modes at 2212 cm^{-1}, 1602 cm^{-1}, 1432 cm^{-1} and 1187 cm^{-1}, in value close to the TCNQ^o intramolecular modes[2, 4].

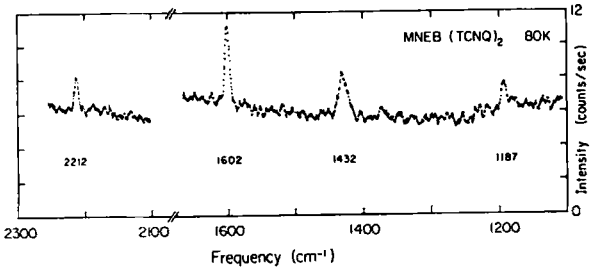


Figure 1

Raman spectrum of MNEB(TCNQ)$_2$ at 80 K. 4579 Å, 1 mWatt on a 40 μm spot.

The IR reflectivity data measured in the frequency range from 50 to 26000 cm^{-1} were subjected to a Kramers-Kronig analysis. The resulting frequency dependent conductivities are shown in Figs. 2 and 3. A fine structure[5] is resolved particularly well in the 80 K and 4 K spectra of $TEA(TCNQ)_2$ (Fig. 3), but it can also be identified in $MNEB(TCNQ)_2$ (Fig. 2). Several lines appear as multiplets rather than doublets. Furthermore some of the additional peaks are found

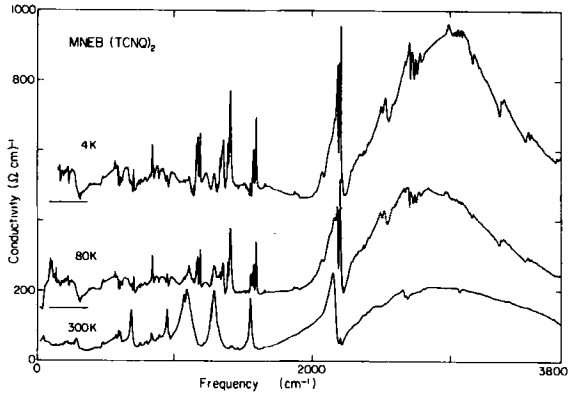


FIGURE 2

Conductivity versus frequency for $MNEB(TCNQ)_2$ at 4K, 80K, and 300K.

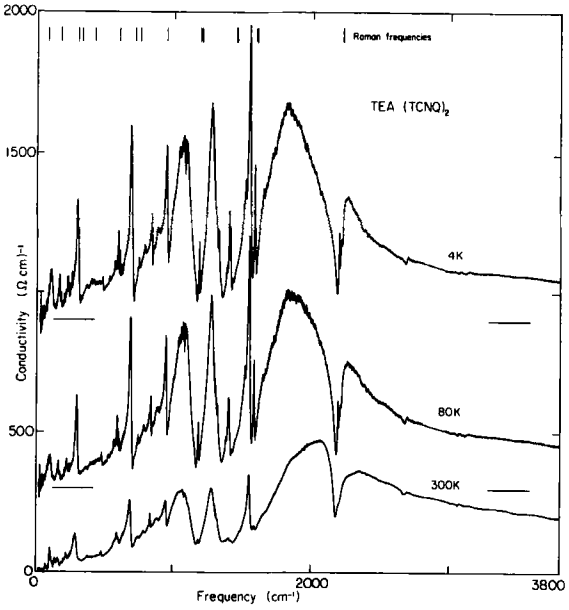
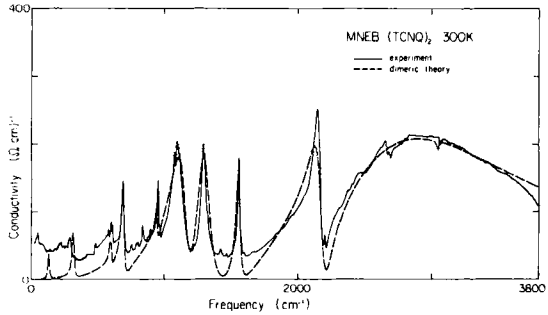


FIGURE 3

Conductivity versus frequency for $TEA(TCNQ)_2$ at 4K, 80K and 300K.

near the Raman frequencies suggesting that even modes appear in the IR spectrum at low temperatures due to a loss of inversion symmetry. The splittings may be associated with structural phase transitions in a similar way as in TTF TCNQ [6]. Indeed, a Peierls transition has been proposed to occur in TEA(TCNQ)$_2$ around 220K[7,2] and a marked drop in electrical conductivity has been reported for MNEB(TCNQ)$_2$ at 250K [8].

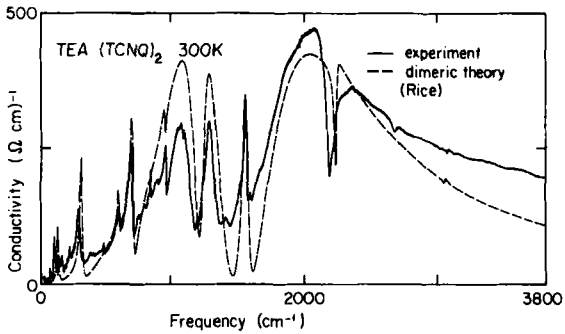
We have attempted to interpret the data in terms of the two theoretical models derived by Rice and coworkers[1, 9]. It turned out that the Peierls model[1] gives a rather poor fit while the dimer theory[9] describes the 300K data surprisingly well, as shown in Figs. 4 and 5. The agreement between dimer theory and experiment



ω_α	λ_α	γ_α
3048	.0003	10
2212	.0450	10
1602	.0900	10
1432	.1350	10
1187	.0390	30
948	.0030	10
711	.0360	10
602	.0070	10
334	.0700	10
144	.1000	10

FIGURE 4 Theoretical dimer fit to 300K conductivity data of MNEB(TCNQ)$_2$ using the parameters ω_{CT} = 2700 cm^{-1}, γ_e = 2700 cm^{-1} and t = 1330 cm^{-1} for the energy, damping constant and resonance integral, respectively, of the electronic charge transfer band. The ("bare") phonon frequencies ω_α and the damping constants γ_α are given in cm^{-1}, and the parameters λ_α are the dimensionless electron-phonon coupling constants.

is particularly striking in the case of MNEB(TCNQ)$_2$ (Fig. 4) whereas it is less spectacular - although still considerably better than using the Peierls model[1] - in the case of TEA(TCNQ)$_2$ (Fig. 5). The dimer theory also provides a good general fit to the 4K MNEB(TCNQ)$_2$ data if one uses ten times smaller vibrational damping constants γ_α and an electronic damping constant γ_e = 1100 cm^{-1}. It is worth noticing that the resulting coupling parameters λ_α are very similar in the two compounds (except for the 2200 cm^{-1} mode) and compare also favourably with the corresponding values obtained for MEM(TCNQ)$_2$ [9], which yields additional support to the dimer theory. On the other hand the observed fine structure in the low temperature IR spectra cannot be explained using this model, which indicates that the dimer theory is not the whole story.



ω_α	λ_α	γ_α
3048	.0003	10
2229	.0050	10
1602	.0850	10
1454	.1400	10
1207	.0400	20
948	.0010	10
711	.0250	10
602	.0050	10
334	.0900	10
144	.1000	10

FIGURE 5 Theoretical dimer fit to 300K conductivity data of TEA(TCNQ)$_2$ using ω_{CT} = 1800 cm^{-1}, γ_e = 1700 cm^{-1} and t = 1310 cm^{-1}.

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