SPECTROSCOPIC STUDY OF THE PHASE TRANSITION IN DECA(TCNQ)$_2$ SALT

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The DECA(TCNQ)$_2$ salt exhibits a first-order phase transition. Marked changes in the infrared absorption spectrum are observed.

1. Introduction

Hitherto, studies [1–3] of the physical properties of the ion radical salt composed of TCNQ and diethylcyclohexylammonium$^+$ (DECA$^+$) cation have shown it to undergo an irreversible phase transition at 347 K, with a considerable modification of the crystal structure [4] accompanied by drastic changes in specific heat, magnetic susceptibility, and electric conductivity [1–3]. The last decreases by a factor of about 10^4; thus the salt, highly conducting in its low-temperature phase, becomes weakly conducting in the high-temperature phase. In the transition temperature a reorganization takes place in the TCNQ stacks as well as in the system of DECA$^+$ cations.

In the highly conducting phase ($T < T_p$) the TCNQ anion radical stacks form tetrads, with two characteristic face-to-face distances between the planes of the molecules (3.22 and 3.36 Å) and two overlap configurations. In the low-conducting phase ($T > T_p$) the unit cell parameters change considerably; the molecules of TCNQ now form stacks of diads with two face-to-face distances (3.30 and 3.34 Å) and identical overlapping for all the molecules. Moreover, certain changes are observed in the lengths and angles of the interatomic bonds within the TCNQ molecules, as well as differences in the deviations from planarity [4]. The changes in geometry of the ion radicals and TCNQ molecules and the change in their ordering in the phase transition temperature involve variations of the interatomic interactions measurable by IR spectroscopy.

2. Experimental conditions

The complex salt, of stoichiometry 1 : 2, was obtained by Dupuis by an earlier method [2]. Samples for studies of the IR absorption spectra were compressed from carefully dried, mortar ground powders of the salts and KBr at a weight ratio of 1 : 1000. The pellet was

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placed in a thermostat, permitting the measurement of absorption spectra at temperatures above ambient, stabilized with an accuracy of ± 0.2 deg. Spectral studies in the $4000 \div 200$ cm^{-1} range were carried out with a Perkin Elmer 577 spectrophotometer. Our investigation concerned the temperature-variations in shape of the spectrum and changes in the positions and intensities as well as the integral intensities of selected absorption bands.

3. Results

The absorption spectrum of the complex salt DECA(TCNQ)$_2$ (Fig. 1), like those of other conducting salts, differs from the spectra of the donor and the acceptor. In the spectrum of the salt, broad intense absorption bands characteristic for quasi-one-dimen-

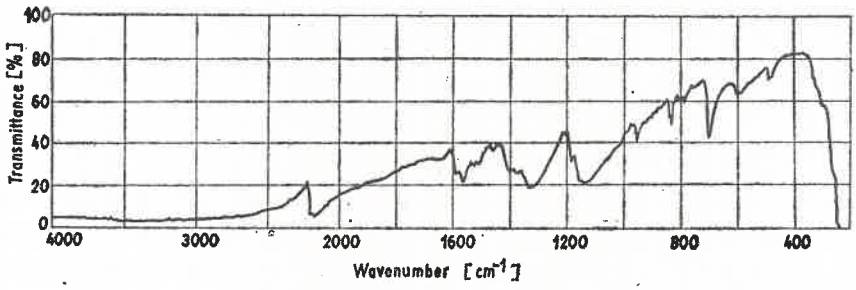

Fig. 1. Absorption spectrum of DECA(TCNQ)$_2$ salt (compressed with KBr at the weight ratio 1:1000) recorded at room temperature

sional highly conducting salts, predominate. The stronger absorption bands recorded for DECA(TCNQ)$_2$, together with their assignment, are given in Table I, as well as the wave numbers and symmetries of the corresponding TCNQ vibrations after Refs [5, 6]. The identification of the individual vibrations was based on the IR polarized reflection spectra of TEA(TCNQ)$_2$ [7], a salt of very similar crystalline and chemical structure.

From Fig. 1 and Table I, absorption bands lying near 2175 cm^{-1}, 1575 cm^{-1} (doublet 1590 and 1562 cm^{-1}), 1330 cm^{-1}, 1130 cm^{-1}, 830 cm^{-1} (triplet 835, 830, 825 cm^{-1}), 695 cm^{-1} and 486 cm^{-1} predominate for DECA(TCNQ)$_2$. Also bands at 952 and 602 cm^{-1} exhibit a high intensity.

According to the assignment of Table I, totally symmetric vibrations A_g of the TCNQ molecules correspond to the bands of the first group. Similar bands occur for TEA(TCNQ)$_2$ also, with polarization perpendicular to the plane of the TCNQ molecules. Such polarization, as well as the high extinction of the bands and their considerable half-width, show them to originate in electron-phonon coupling. In accordance with the theory of Rice [8, 9], as a result of such coupling they become infrared active with, simultaneously, a large oscillator strength and polarization perpendicular to the plane of the TCNQ molecules. It is significant that the bands of DECA(TCNQ)$_2$ originating in coupling between A_g vibrations and electrons are shifted by about 30 cm^{-1} towards higher frequencies compared with the bands of TEA(TCNQ)$_2$, pointing to weaker electron-phonon coupling in DECA

TABLE I

Description and definition of the symmetry vibrations of the strongest absorption bands in IR region in $DECA(TCNQ)_2$ salt

$DECA(TCNQ)_2$			$TCNQ^0$		
ν [cm^{-1}]	Intensity	Assignment	ν [cm^{-1}]	ν [cm^{-1}] [5, 6]	Symmetry [5, 6]
2190	v s	CN stretch	2230	2228	B_{1u}, B_{2u}
2162	v s	CN stretch	—	2229	A_g
1590, 1562	s	CC ring stretch, CC wing stretch, CH bend	—	1602	A_g
1528	m	CH bend, CC wing stretch, CC ring stretch	1547	1545	B_{1u}
1500	m	CH bend, CC ring stretch	1544	1540	B_{2u}
1456	w	CC ring stretch, CH bend		1451	B_{3g}
1398	w	CH bend	1405	1405	B_{1u}
1365	m	CC ring stretch, CH bend	1354	1354	B_{2u}
1330	v s	CC ring stretch, CC wing stretch	—	1454	A_g
1204	w	combination vibration		1137	
1180, 1132	v s	CH bend	—	1207	A_g
952	s	CC ring stretch	961	962	B_{1u}
860	w	CH bend out of the plane	864	859	B_{3u}
835, 830, 825	s	CC ring stretch	—	948	A_g
782	w		772		
748	v w	CH bend out of the plane	750	752	B_{2g}
695	s	CC ring stretch, CC wing stretch	—	711	A_g
602	w	out of the plane	600	593	B_{2g}
585	v w				
570	v w				
542	v w	CC wing stretch, CC wing bend, CCN bend	550	549	B_{1u}
486	m	CC wing stretch, CCC wing bend, CCN bend	—	602	A_g
310	m	CCC ring bend, CCC wing bend, CCN bend	—	334	A_g

v — very strong, s — strong, m — medium, w — weak, v w — very weak.

$(TCNQ)_2$. The broad absorption bands at about 1330 cm^{-1} and 1130 cm^{-1} specific for conducting TCNQ salts exhibit, in the case of $DECA(TCNQ)_2$, half-widths of 115 cm^{-1} and 135 cm^{-1}, respectively, as well a structure. It is moreover worth stressing that, in the spectral region studied, the low-frequency wing of a very strong, broad band lying at about 3950 cm^{-1} is apparent. The band is related with intermolecular charge transfer:

$$TCNQ_a^- + TCNQ_b^0 \rightarrow TCNQ_a^0 + TCNQ_b^-$$

Figs 2–6 show characteristic results of our temperature-dependent studies. The spectrum of the high-temperature phase of DECA $(TCNQ)_2$ differs strongly from that of the salt in temperatures below the transition point (Fig. 2). The high-temperature phase

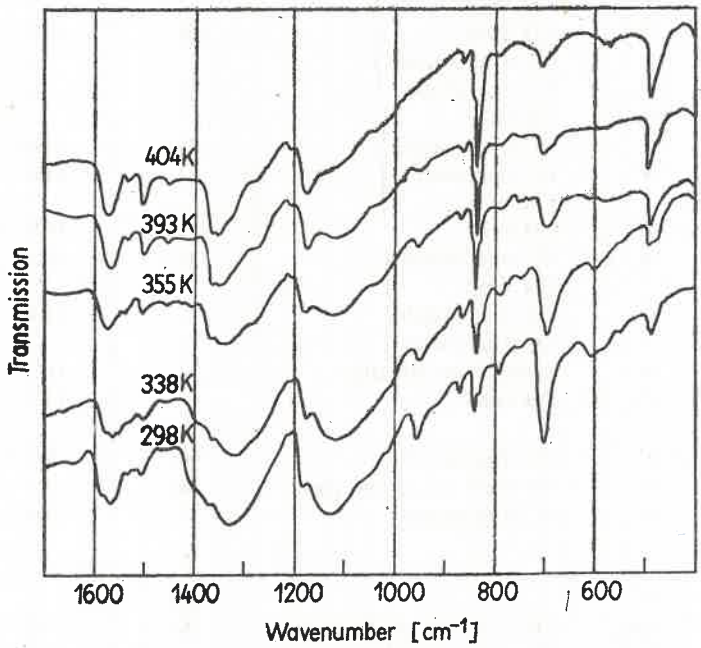

Fig. 2. Thermal evolution of the absorption spectrum of $DECA(TCNQ)_2$ salt

exhibits a narrowing and a change in shape of some of the absorption bands e.g. the composite band with maximum near 1565 cm^{-1} is markedly resolved into bands at 1500 and 1570 cm^{-1}, corresponding to stretching vibrations of C–C bonds of the ring and the "wings", and one notes the presence of a weak band at 1530 cm^{-1} presumably corresponding to CH bending vibrations. The centres of the 1330 cm^{-1} and 1130 cm^{-1} bands shift towards higher frequencies. The side maxima forming the structure of these broad absorption bands are also perturbated; as is obvious from Fig. 3, showing their thermal evolution.

The changes in shape are the strongest for the composite bands at 830 and 486 cm^{-1} (Fig. 4). In the high-temperature phase they become well apparent triplets, with one of the components predominating in either. In the transition point these predominant components

exhibit a steep increase in intensity due to weakening of the selection rules. As a result of distortion of the TCNQ molecules and especially of deviations from planarity, the symmetry falls to less than D_{2h} and the transition probabilities for the frequencies corresponding to the components 830 cm^{-1} and 486 cm^{-1} increase by a jump in the high-tempera-

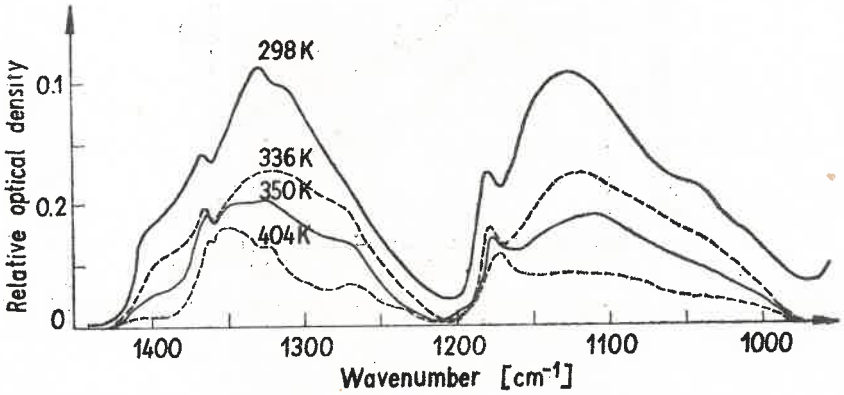

Fig. 3. Thermal evolution of the absorption bands at 1330 cm^{-1} and 1130 cm^{-1}. The spectra were taken at heating

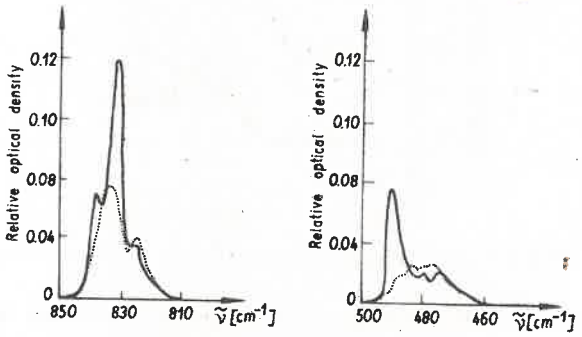

Fig. 4. Absorption bands near 830 cm^{-1} and 486 cm^{-1} for the highly (·····) and weakly (———) conducting phases

ture phase. The predominance of these bands upwards of the transition point can serve as a criterion of the structural phase transition.

It is noteworthy that almost all the bands maintain their positions unchanged with varying temperature. The fact is extremely important since it proves that temperature variations in the spectra cannot be interpreted as being due to changes in electron–phonon coupling.

The phase transition near 347 K is well apparent as an inflection in the $I(T)$ graphs (Figs 5, 6). For most bands, the thermal activation energy in the high-temperature phase is 2 to 3 times less than in the low-temperature phase. This is the case for the 1330, 1130, 952, 860, 782 and 695 cm^{-1} bands (e.g. Fig. 5). However, the activation energy of the bands

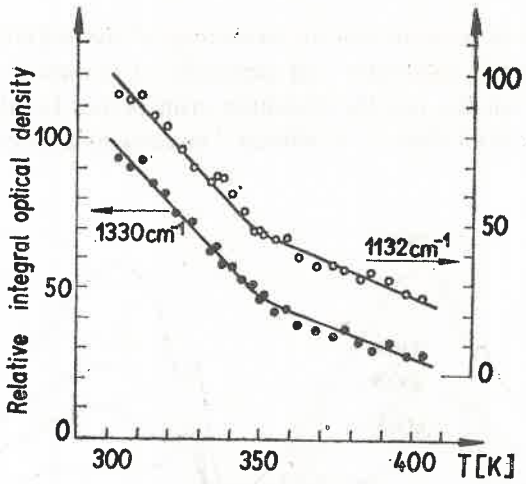

Fig. 5. Thermal variation in integral intensity of the absorption bands near 1330 cm^{-1} and 1130 cm^{-1}

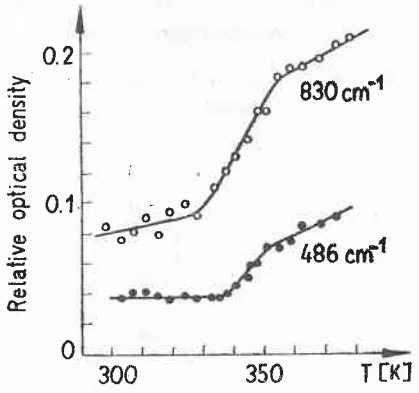

Fig. 6. Thermal intensity variation of the bands at 830 cm^{-1} and 486 cm^{-1}

considerably exceeds that calculated on the assumption of constant intermolecular interaction, for which case the band intensities are determined by the difference in Boltzmann population of the levels only. Fig. 6 shows a different example of thermal intensity variations as observed for the 830 and 486 cm^{-1} bands which undergo a considerable enhancement in the transition temperature.

We draw attention to the fact that the thermal changes exhibited by the absorption bands are reversible only above the transition point. When cooled, a sample previously at $T > T_p$ exhibits but an increase in band intensity in accordance with Boltzmann's law.

4. Conclusions

Our study of the infrared absorption spectra of $DECA(TCNQ)_2$ salt show the intensities of the bands at 830 cm^{-1} and 486 cm^{-1} to increase drastically in the phase transition temperature due to the decrease in symmetry of the TCNQ molecules. The predominance

of these bands is characteristic for the high-temperature phase. Moreover, the shape of the intensity vs temperature dependence also changes for the majority of the bands in the transition, pointing to variations in the respective transition moments as the result of changes in the charge distribution on the individual atoms of the TCNQ molecule. The last conclusion confirms earlier studies by Flandrois and Chasseau [10].

In addition, the present work proves that vibrational spectra can serve for detecting the phase transition, at least for the TCNQ salt studied.

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REFERENCES

[1] S. Flandrois, G. Sauthoff, *J. Phys. Chem. Solids* **34**, 1779 (1973).
[2] S. Flandrois, P. Delhaes, J. C. Giuntini, P. Dupuis, *Phys. Lett.* **45A**, 339 (1973).
[3] S. Flandrois, M. L. Choukroun, P. Delhaes, D. Chasseau, J. Gaultier, C. Hauw, M.-T. Hiraboure, P. Dupuis, *Proc. Conf. Organic Conductors and Semiconductors*, Siófok, Hungary 1976, p. 499.
[4] M.-T. Hiraboure, *Thèse*, Université de Bordeaux I, 1976.
[5] B. Lunelli, C. Pecile, *J. Chem. Phys.* **52**, 2375 (1970).
[6] T. Takenaka, *Spectrochim. Acta* **27A**, 1735 (1971).
[7] A. Brau, P. Brüesch, J. P. Farges, W. Hinz, D. Kuse, *Phys. Status Solidi* (b) **62**, 615 (1974).
[8] M. J. Rice, C. B. Duke, N. O. Lipari, *Solid State Commun.* **17**, 1089 (1975).
[9] M. J. Rice, L. Pietronero, P. Brüesch, *Solid State Commun.* **21**, 757 (1977).
[10] S. Flandrois, D. Chasseau, *Acta Cryst.* **B33**, 2744 (1977).