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The Effect of Pressure on the Electronic Absorpion Spectra of TCNQ Ion Radical Salts

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The effect of pressure up to 7 kbar on the electronic absorption spectra of the crystalline TCNQ anion radical salts and Li(TCNQ) in PVA has been studied. For simple TCNQ salts such as Li(TCNQ), a blue shift with an increase in the pressure has been observed in the absorption band associated with the intramolecular transition. The magnitude of the blue shift is between 45 and 86 cm^{-1}/kbar. The observed shift has been discussed in terms of the crystal-field effect of the cations. For *N*-MePhe(TCNQ) and M(TCNQ)$_2$, composed of the formally-neutral TCNQ and its anion radical such as TEA(TCNQ)$_2$, a pressure-induced absorption band has been observed at around 20 kK; it may be assigned to the charge-transfer band between the anion radicals.

The electronic absorption spectra of most organic compounds exhibit a red shift with an increase in the pressure.[1-3] However, the absorption band at 18.5 kK of the quaterrylene ($C_{40}H_{20}$) evaporated film is less affected by the pressure,[4] and in the cases of azulene, ferrocene, and the *trans*-stilbene-2,3-dichloro-5,6-dicyano-*p*-benzoquinone complex, a small blue shift is observed at high pressures.[5] In a previous paper,[6] a large blue shift with the pressure has been reported in several ion radical salts which possess an ionic structure in the ground state.

The electrical conductivity of the anion-radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) depends greatly on the nature of the cation.[7] The salts with metal cations generally show low to intermediate conductivity (10^{-5}—10^{-2} Ω^{-1}cm^{-1}), while the salts with cations of planar aromatic heterocyclic molecules show high conductivity ($\sim 10^2$ Ω^{-1}cm^{-1}). The conductivity of these solids arises from the motion of the odd π electron among the TCNQ sites. Their conduction mechanism has been discussed by several authors.[8-10]

Recently, the crystalline electronic spectra of TCNQ salts have been studied at room temperature.[10-12] The crystalline spectra are quite different from that of the TCNQ anion radical monomer and depend greatly on the nature of the cations. Boyd and Phillips have reported the absorption spectra of the monomer [(TCNQ$^-$)] and the dimer [(TCNQ$^-$)$_2$] in an aqueous solution of Li(TCNQ).[13] The crystalline spectrum of Li(TCNQ) is similar to that of the dimer in an aqueous solution.

We have studied the absorption spectra of several TCNQ salts in the visible region at high pressures and have found spectral blue and red shifts with the pressure in the low-conductive salts and a pressure-induced absorption band in the high-conductive compounds. In this paper these results will be discussed.

Experimental

The samples used in this experiment were all TCNQ salts, including lithium [Li(TCNQ)], potassium [K(TCNQ)], *N*-methylphenazinium [*N*-MePhe(TCNQ)],

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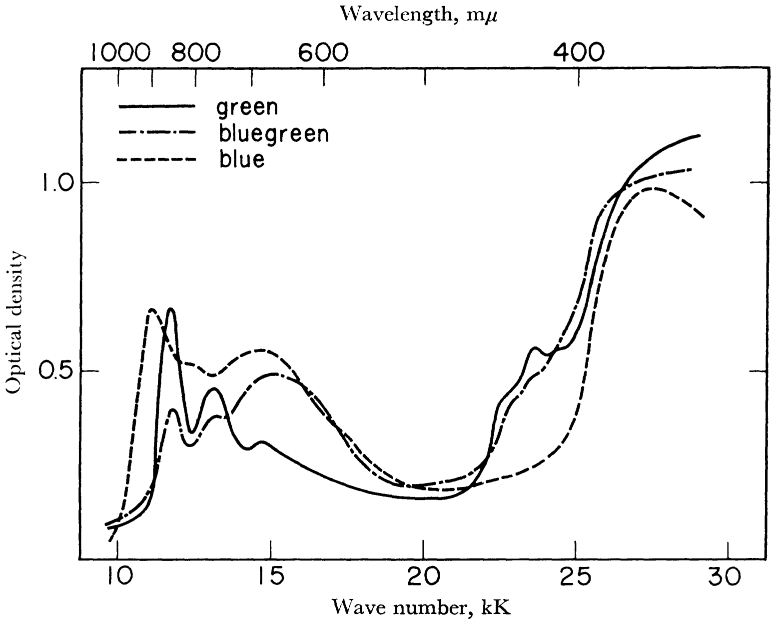

Fig. 1. The absorption spectra of Li(TCNQ) PVA films of three different concentrations; ——— the green, —·—·— the blue green, and -------- the blue PVA film.

quinolinium [Q(TCNQ)$_2$], bipyridinium [BiP(TCNQ)$_2$], 4-amino-2,3,5,6-tetramethylanilinium [DAD(TCNQ)$_2$], triethylammonium [TEA(TCNQ)$_2$] and cobalticinium [CoC(TCNQ)$_2$]. These compounds were provided by Kondow, who has previously reported their preparations in detail.[10] Li(TCNQ)-polyvinylalcohol (PAV) film was prepared by drying a 10 wt% warm aqueous slurry of PVA in which Li(TCNQ) was dissolved. A uniformly-colored plastic film was formed after the evaporation of the solvent. The absorption spectra were measured on powdered samples rubbed on a quartz glass plate and on PVA film at room temperature by using a Shimazu SV-50A spectrophotometer. The high-pressure optical cell has been described elsewhere.[4] A hydrostatic pressure up to 7 kbar was applied by means of a pressure-transmitting medium (kerosene or white gasoline) through a pressure-intensifier. The pressure was determined by a Harwood manganine resistance gauge and a Heise Bourdon tube gauge.

Results and Discussion

Figure 1 shows the absorption spectra of Li-(TCNQ) PVA film of three different concentrations at 1 bar. In the green PVA film, the absorption peaks almost agree with that in acetonitril. Therefore, Li(TCNQ) seems to be in a monomer state in the green film. The absorption spectrum of the blue PVA film is similar to that of the dimer of the TCNQ anion radical in an aqueous solution, and it has a new absorption peak at 11.0 kK which does not exist in the monomer state. In the blue green PVA film, the dimer and the monomer may be supposed to coexist. The absorption peak at 11.0 kK in the dimer state revealed a small red shift (-18 cm^{-1}/kbar) with an increase in the pressure, while the other absorption peaks of these PVA film were insensitive to the pressure up to 7 kbar.

Figure 2 shows the effect of the pressure on the absorption spectra of the crystalline K(TCNQ). The crystalline spectra of K(TCNQ) exhibited absorption bands located at 8.3, 16.1, and 27.5 kK. The two peaks in the visible region showed a large blue shift with an increase in the pressure (+45 and +58 cm^{-1}/kbar for the 16.1 and 27.5 kK peaks respectively). Similar results on Li(TCNQ) have been reported in a previous paper.[6] The rates

TABLE 1. SPECTRAL DATA FOR TCNQ ANION RADICAL SALTS, NEUTRAL TCNQ, AND THREE ORGANIC COMPOUNDS

Compound	Absorption peak (kK)	Pressure shift (cm^{-1}/kbar)
Li (TCNQ)	26.5	+86
	16.0	+51
	7.7	—
in PVA film	11.0	−18
K (TCNQ)	27.5	+58
	16.1	+45
	8.3	—
TCNQ	22.3	−84
Azulene	14.4	+ 6[a]
Ferrocene	23.3	+20[a]
trans-Stilbene-DDQ	16.0	+ 5[a]

a) Ref. 5.

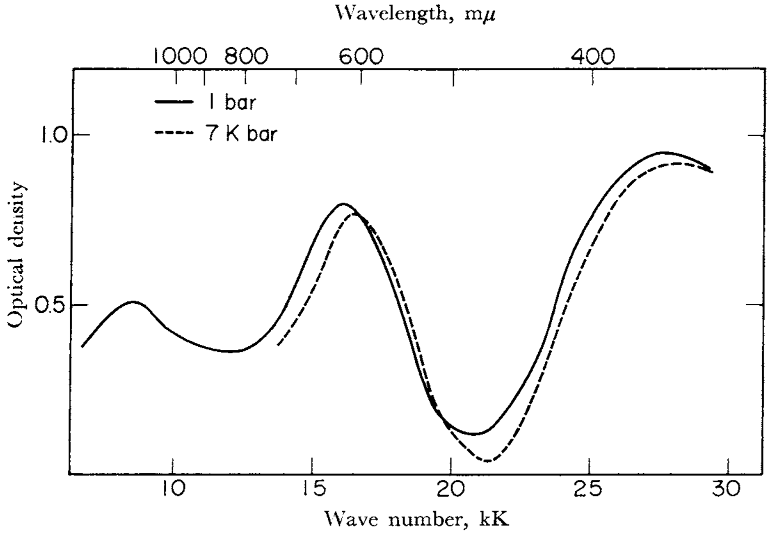

Fig. 2. The pressure dependence of the absorption spectra of the crystalline K(TCNQ).

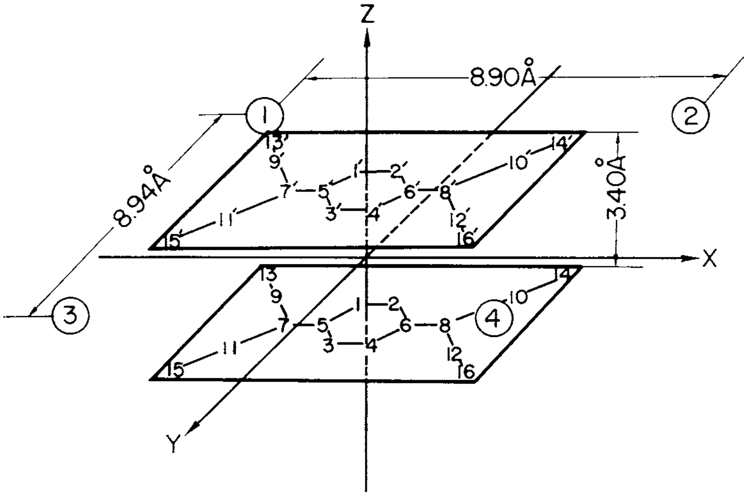

Fig. 3. The assumed crystal field for K(TCNQ).

of the pressure shift of several TCNQ salts are given in Table 1. The energy shifts are approximately proportional to the applied pressure.

The absorption spectra of crystalline Li(TCNQ) and K(TCNQ) are similar to that of the dimer in an aqueous solution. The spectroscopic evidence supports a bimolecular association of the TCNQ ion radicals in the solid. As has been stated earier, the absorption bands of the dimer observed in the PVA film were insensitive to the pressure. Therefore, it seems that the major contribution to the blue shift arises from the crystal field*1 of metal-positive ions.

In accordance with Menefee and Pao,8) the pressure dependence on the splitting of energy levels brought about by a model crystal field of the cations was tentatively calculated to explain the large blue shift. The crystal field was assumed on the basis of the crystal structure of K(TCNQ)14) which is shown in Fig. 3; two molecules of TCNQ$^-$ are stacked face to face with a spacing of 3.4 Å, and four positive nuclei with a point charge of $+e/4$ are put on the corners of the rectangle (8.94×8.90 Å) formed in the middle between two molecules and the parallel to the TCNQ$^-$ molecular plane. Since this cluster belongs to the D_{2h} symmetry group, the new molecular orbitals are given by:

$$\Phi_{n-} = A_{n-}(\phi_n - \phi_n'), \quad \Phi_{n+} = A_{n+}(\phi_n + \phi_n'),$$

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*1 "Crystal field" means the electrostatic field by ions in the crystal.

14) G. R. Anderson and C. J. Fritchie, Jr., Paper for Second National Meeting of the Society for Applied Spectroscopy, San Diego (1963), p. 111.

where ψ_n and $\psi_{n'}$ are the nth molecular orbitals centered on the first and second TCNQ$^-$ radical ions respectively, and where A is the normalization coefficient. For $\psi_{n'}$, the results of the open-shell SCF-LCAO-MO calculations by Lowitz[15] were used here;

$$\begin{aligned}\psi_8(b_{1u}) = &-0.22901(\phi_1+\phi_2+\phi_3+\phi_4)\\ &+0.18931(\phi_5+\phi_6)+0.50263(\phi_7+\phi_8)\\ &+0.01933(\phi_9+\phi_{10}+\phi_{11}+\phi_{12})\\ &-0.23007(\phi_{13}+\phi_{14}+\phi_{15}+\phi_{16}),\\ &(E=1.92061\ \text{eV}),\ (n=8)\end{aligned}$$

$$\begin{aligned}\psi_9(b_{2g}) = &-0.25063(\phi_1-\phi_2+\phi_3-\phi_4)\\ &-0.26414(\phi_5-\phi_6)+0.45618(\phi_7-\phi_8)\\ &+0.08375(\phi_9-\phi_{10}+\phi_{11}-\phi_{12})\\ &-0.20304(\phi_{13}-\phi_{14}+\phi_{15}-\phi_{16})\\ &(E=4.4249\ \text{eV}),\ (n=9,\ \text{highest occupied level})\end{aligned}$$

$$\begin{aligned}\psi_{10}(b_{1u}) = &-0.19752(\phi_1+\phi_2+\phi_3+\phi_4)\\ &+0.51425(\phi_5+\phi_6)-0.19426(\phi_7+\phi_8)\\ &-0.16327(\phi_9+\phi_{10}+\phi_{11}+\phi_{12})\\ &+0.18226(\phi_{13}+\phi_{14}+\phi_{15}+\phi_{16}),\\ &(E=8.89412\ \text{eV}),\ (n=10,\ \text{lowestvacant level})\end{aligned}$$

where ϕ_i is the atomic orbital for the ith atom and where E is the eigenvalue. The stabilization energy by the crystal field is given by;

$$\begin{aligned}\Delta E &= \int \Phi_n V \Phi_n \mathrm{d}\tau\\ &= (-\mathrm{e}^2/4)\int \Phi_n(1/r_1+1/r_2+1/r_3+1/r_4)\Phi_n \mathrm{d}\tau,\end{aligned}$$

TABLE 2. BOND LENGTHS IN K(TCNQ)[a)]

C(1)-C(2)	1.37 Å
C(2)-C(6)	1.42
C(6)-C(8)	1.40
C(8)-C(10)	1.41
C(10)-N(14)	1.13

a) Ref. 14.

TABLE 3. THE STABILIZATION ENERGY AND THE SPLITTING ENERGY BY THE CRYSTAL FIELD AT THE ATMOSPHERIC PRESSURE AND AT 10 kbar (a), AND THE PRESSURE SHIFT OF SEVERAL TRANSITIONS (b)

(a)

Molecular orbital	ΔE (eV)			
	1 bar		10 kbar	
$\Phi_{8-}(a_g)$ $=N_{8-}(\psi_8-\psi_8')$	−2.732	>0.568	−2.935	>0.759
$\Phi_{8+}(b_{1u})$ $=N_{8+}(\psi_8+\psi_8')$	−2.164		−2.176	
$\Phi_{9-}(b_{3u})$ $=N_{9-}(\psi_9-\psi_9')$	−2.532	>0.508	−2.698	>0.656
$\Phi_{9+}(b_{2g})$ $=N_{9+}(\psi_9+\psi_9')$	−2.024		−2.042	
$\Phi_{10-}(a_g)$ $=N_{10-}(\psi_{10}-\psi_{10}')$	−2.024	>0.399	−2.159	>0.515
$\Phi_{10+}(b_{1u})$ $=N_{10+}(\psi_{10}+\psi_{10}')$	−1.625		−1.644	

(b)

Transition energy at 1 bar (eV)	Transition	Pressure-induced shift (cm^{-1}/kbar)
0.508	$B_{1u} \leftarrow A_g$	+120
2.644	$B_{2u} \leftarrow A_g$	− 4
3.721	$B_{3u} \leftarrow A_g$	+269
4.978	$B_{3u} \leftarrow A_g$	+ 24
5.857	$B_{1u} \leftarrow A_g$	+144

where r_a is the distance from each atom of TCNQ$^-$ to the nucleus, a, which was obtained from the bond lengths shown in Table 2 and from the bond angles (assumed to be 120 or 180°). The calculated values of ΔE (for $n=8, 9, 10$) and the splitting energy by the assumed crystal field at the atmospheric pressure and at 10 kbar are shown in Table 3.[*2] It was assumed that, at 10 kbar, TCNQ salts were isotropically compressed in volume to 90.5%[*3] without a change in the TCNQ$^-$ molcular structure. The stabilization energy and the splitting energy by the crystal field were larger on the low-energy level than on the high energy level, and both increased with an increase in the pressure. Table 3(b) gives the pressure-induced shift of some of the transitions considered; this shift was calculated according to the results shown in Table 3(a). A considerable blue shift was obtained. On the basis of the calculated results, it seems reasonable to conclude that the large blue shift of the electronic

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15) D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).

[*2] In the calculation of ΔE, as usual, terms coming from nonadjacent atoms were ignored, and for the integrals in terms of atomic orbitals, the following approximations were made;

$$\int \phi_i^2/r_a \mathrm{d}\tau \simeq 1/r_{a'},\quad \int \phi_i\phi_j/r_a \mathrm{d}\tau \simeq \tfrac{1}{2}(1/r_{ai}+1/r_{aj})S_{ij},$$

$$\int \phi_i\phi_{i'}r_a \mathrm{d}\tau \simeq 1/r_a\delta_{ii'}$$

where r_{ai} is the separation of the positive nucleus, a, and the i atom, where S_{ij} is the overlap integral, and where $\delta_{ii'}$ is the overlap integral which refers to the same kind of atoms located on two TCNQ$^-$ molecules. For $S_{\mathrm{CC'}}$, S_{CN} and $\delta_{\mathrm{CC'}}$ (or $\delta_{\mathrm{NN'}}$), the approximate expressions which Roothaan [*J. Chem. Phys.*, **19**, 1445 (1951)] has given for three two-center integrals, ($2p\pi_{\mathrm{C}}$–$2p\pi_{\mathrm{C}}$), ($2p\pi_{\mathrm{C}}$–$2p\pi_{\mathrm{N}}$), and ($2p\sigma_{\mathrm{C}}$–$2p\sigma_{\mathrm{C}}$) respectively, were used.

[*3] This value is the volume change with the pressure for general crystals of aromatic molecules, as extrapolated from Bridgman's data [Samara and Drickamer, *J. Chem. Phys.*, **37**, 474 (1962)]. The compressibility of ion radical salts has not been measured, but it is probably less than that of ordinary hydrocarbon solids.

transition observed in Li(TCNQ) and K(TCNQ) arises from the crystal field of metal cations.

Li(TCNQ) and K(TCNQ) have the absorption band in the near-infrared region. The effect of the pressure on these peaks has not yet been studied becasue of interference by the absorption of water contained in the pressure-transmitting medium. This band can be assigned to the charge-transfer band between the anion radicals.[12] It is well-known that the charge-transfer band of molecular complexes shows a red shift at high pressures.[2] A similar effect may be expected for $TCNQ^-$ ion radical salts.*[4] The electrical resistance of Li(TCNQ) drops rapidly in the low-pressure region and levels off at high pressures. The values of the activation energy decreases from 0.32 eV at 1 bar to 0.07 eV at 169 kbar.[16] Since the near-infrared band is located in the energy region of twice the activation energy for electrical conductivity, the study of the pressure effect on this band is important. The new absorption band at 11.0 kK in the blue PVA film of Li(TCNQ) can be assigned to the charge-tranfer band between TCNQ-anion radicals which corresponds to the crystalline absorption band in the near-infrared region, for this band does not exist in the monomer state and the spectral red shift was observed at high pressures.

Figure 4 shows several isobars of the absorption spectra for *N*-MePhe(TCNQ). The pressure effect on the bands at 11.5 and 17.0 kK is not clear, for these bands are appreciably weak and diffused. The pressure shift of the band at 26.0 kK was not observed, at least up to 7 kbar. However, a remarkable pressure effect was observed; that is, the pressure-induced absorption band was found at around 20 kK at high pressures. The absorption intensity of this band increased with an increase in the pressure. This bahaviour was reversible with a decrease in the pressure. *N*-MePhe(TCNQ) shows an unusually high conductivity $(1.4\times 10^2\Omega^{-1}\cdot\mathrm{cm}^{-1})$ in spite of a simple salt of the M(TCNQ) type.[7] According to the crystal structure analysis by Fritchie,[17] $TCNQ^-$ molecules pack face to face to form a regular linear chain column with an interplanar spacing of 3.26 Å. This interplanar spacing is much shorter than the van der Waals distance. Therefore, the strong charge-transfer interaction may be expected to have been induced by compression. The absorption intensity increased remarkably with the pressure. As has been expected from Mulliken's charge-transfer theory,[18] the absorption intensity of the charge-transfer band increases with the pressure[2]. Thus, the pressure-induced absorption band at 20 kK may be ascribed to a new charge-transfer absorption band.

Figures 5 and 6 show several isobars of the absorption spectra for $TEA(TCNQ)_2$ and $Q(TCNQ)_2$. The pressure-induced absorption band was found at around 20 kK at high pressures. The absorption intensity of this band increased with an increase in the pressure. On the other hand, the absorption intensity of the weak peak at 17 kK, the nature of

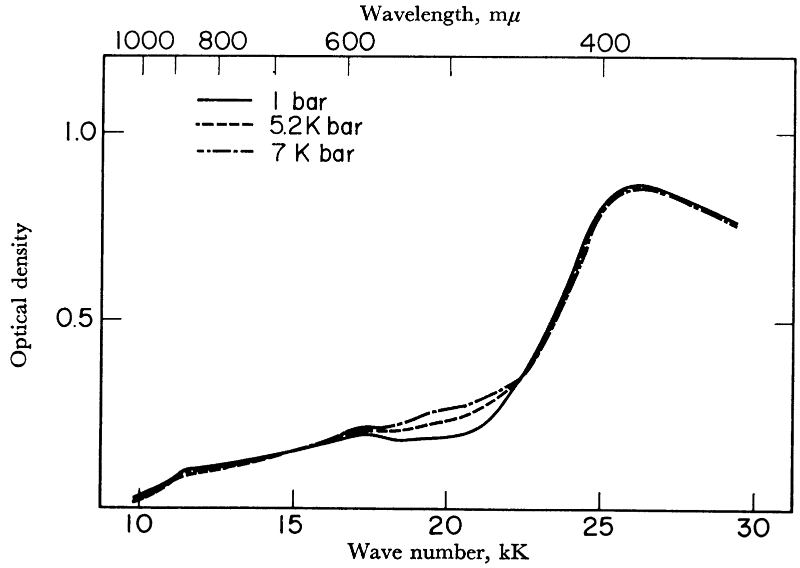

Fig. 4. The pressure dependence of the absorption spectra of the crystalline *N*-MePhe(TCNQ).

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*[4] In the case of Na(chloranil) salt, the inter-radical charge-transfer band has shown a red shift with an increase in the pressure.[6]

16) I. Shirotani, T. Kajiwara, H. Inokuchi and S. Akimoto, This Bulletin, **42**, 366 (1969).

17) C. J. Fritche, Jr., *Acta Cryst.*, **20**, 892 (1966).

18) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952), *J. Phys. Chem.*, **56**, 801 (1952).

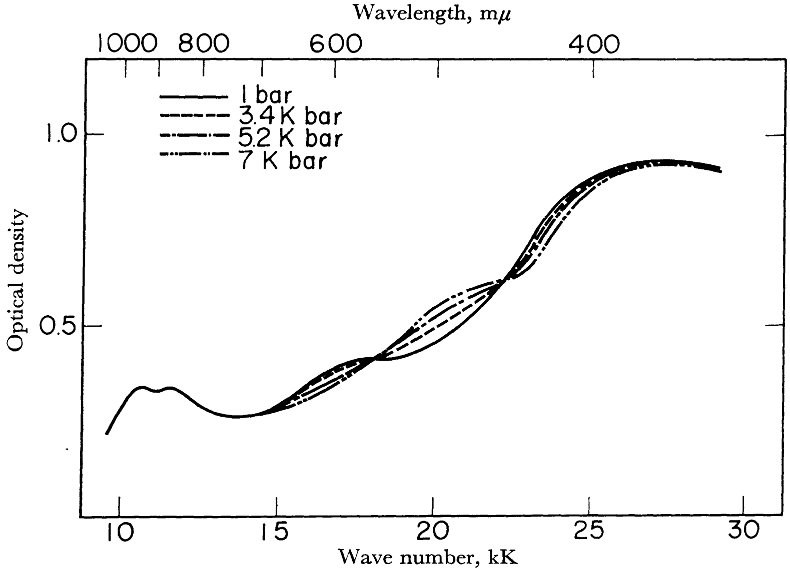

Fig. 5. The pressure dependence of the absorption spectra of the crystalline TEA(TCNQ)$_2$.

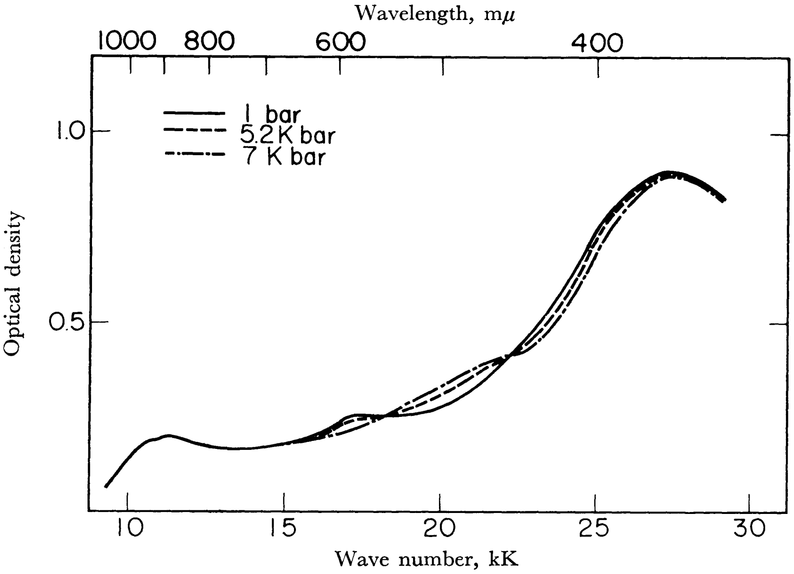

Fig. 6. The pressure dependence of the absorption spectra of the crystalline Q(TCNQ)$_2$.

which was not clear, decreased with an increase in the pressure. These pressure effects were reversible with a decrease in the pressure. Similar results were also obtained for BiP(TCNQ)$_2$, CoC(TCNQ)$_2$, and DAD(TCNQ)$_2$.

The TCNQ salts of the M(TCNQ)$_2$ type show a high conductivity and a small activation energy.[7] The crystalline structure has been analysed for TEA(TCNQ)$_2$ and Q(TCNQ)$_2$.[19] TCNQ$^-$ molecules pack face to face with an interplanar spacing of 3.21—3.32Å. The strong charge-transfer interaction may be expected to be induced by compression in these TCNQ anion radical salts, also. Thus, the pressure-induced absorption band may be ascribed to a new charge-transfer absorption band.

The pressure shift of the bands at 11 and 27 kK associated with the intramolecular transition was not obaserved, at least up to 7 kbar. The energy shift with the pressure may arise from the characteristic crystalline structure of TCNQ salts. Further, in the case of the M(TCNQ)$_2$ type, the crystal-field effect is considered to be weakened by the

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19) H. Kobayashi, private communication.

presence of the neutral TCNQ molecules.

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