The Spectral Blue Shift of Li(TCNQ) at High Pressures

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The energies of the electronic transitions of most organic crystals are shifted toward the lower side with an increase in the pressure.1–3) However, the absorption band at 540 mμ of quaterrylene ($C_{40}H_{20}$) evaporated film is less affected by the pressure,4) and in the cases of azulene and ferrocene a small blue shift is observed at high pressures.5)

The activation energy of Li(TCNQ) decreases from 0.32 eV at 1 bar to 0.07 eV at 169 kbar.6) However, a large blue shift was observed with a change in the pressure on the absorption spectra of Li(TCNQ).

A hydrostatic pressure was applied to the optical cell by means of a pressure-transmitting medium, kerosene, up to 7 kbar at room temperature.

Figure 1 shows the absorption spectra of crystalline Li(TCNQ) at 1 bar and 5.4 kbar. Two bands situated in the visible region showed a large blue shift with an increase in the pressure. The rates of pressure shift are listed in Table 1. Since the crystalline absorption spectrum is similar to that of the dimer $(\mathrm{TCNQ}^-)_2$ in an aqueous Li(TCNQ) solution,7) the large blue shift may be explained by assuming a bimolecular association of (TCNQ^-) ion radicals in the solid.

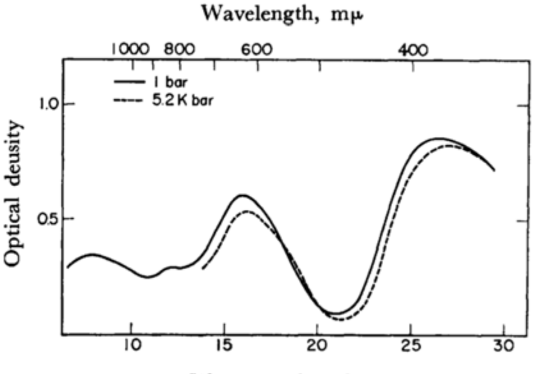

Fig. 1. The pressure dependece of the absorption spectra of Li(TCNQ).

TABLE 1. PRESSURE SHIFT OF THE OPTICAL ABSORPTION PEAK FOR SEVERAL ANION RADICAL SALTS

Compound	Absorption peak (kK)	Pressure shift ($\mathrm{cm^{-1}/kbar}$)
Li(TCNQ)	26.5	+86
	16.0	+51
	7.7	—
K(TCNQ)	27.5	+58
	16.1	+45
	8.3	—
DAD(TCNQ)	25.8	+52
	11.6	—
Na(chloranil)	26.2	+62
	11.8	−58
Azulene	14.4	+ 6a)
Ferrocene	23.3	+20a)

a) Ref. 5

However, the absorption band of the salt in a PVA solid solution was insensitive to the applied pressure. Therefore, it is assumed that the major contribution to the blue shift does not arise from the bimolecular association in the crystalline state, but from the crystal field of metal-positive ions.

The near-infrared band at 7.7 kK observed in the solid Li(TCNQ) can be assigned to an inter-radical charge-transfer band.8) The pressure effect on this peak could not be observed because of interference by the transmitting fluid. Generally, the charge-transfer bands of molecular complexes show a red shift at high pressures.2) The low-energy band at 7.7 kK may be expected to be shifted to the red with a change in the pressure.

Similar results for K(TCNQ), diaminodurene (DAD) (TCNQ), and Na(chloranil) are listed in Table 1. The 11.8 kK band of Na(chloranil), which did not appear in solution spectra, showed a red shift at high pressures. This may be ascribed to the inter-radical charge-transfer band in the solid.

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