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Spectroscopy of EDA Complexes at High Pressures. V. Absorption of Crystalline TCNE Complexes†

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Abstract—Five aromatic hydrocarbon-TCNE complexes are dispersed in sodium chloride pellets and subjected to high pressures (0–25 kbar). The charge transfer absorption is enhanced and displaced toward lower energies at the highest pressure. An exception is the crystalline complex HMB-TCNE which exhibits a blue shift at the highest pressure. The doublet structure in both charge transfer bands of naphthalene-TCNE can be observed at 1 atm and at higher pressures. The importance of the relative sizes of donor and acceptor in environmental interactions are discussed.

Introduction

High-pressure spectroscopic techniques are complementary to conventional methods of molecular electronic spectroscopy as an aid in the understanding of charge transfer (CT) interactions in electron-donor-acceptor (EDA) complexes. This report considers the effect of pressures on crystalline molecular complexes in which aromatic hydrocarbons serve as the donor and tetracyanoethylene (TCNE) is the common acceptor. Crystalline complexes involving the strong acceptor TCNE may still be regarded as weak molecular complexes[1, 2] in which the no bond structure $\Psi(D \cdot A)$ is the most predominant structure in the valence-bond description of the ground state of the complex.[3, 4] Detailed spectroscopic studies of crystalline TCNE complexes are limited to the pyrene-TCNE complex[5] which shows a strong dichroism in accord with theory.[3, 4] The multiple bands which are frequently encountered for TCNE complexes are assigned to CT transitions arising in first order

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approximation from an electron jump between the higher occupied molecular orbitals of the donor and the lowest unoccupied orbital of the acceptor.[6, 7]

Spectroscopic studies of TCNE complexes have been made in several compressed media: liquid solutions,[8] polymer matrices (Part II[9] of this series), and crystals.[10] Bentley and Drickamer[10] subjected crystalline complexes to ultra-high pressures ($P > 100$ kbar) and observed chemical reactions resulting from the extreme pressures. The pressure range in the present work (0–25 kbar) is insufficient to cause irreversible effects. The samples are prepared by mixing crystals of the complex with NaCl powder, and then pressing the mixture into a clear pellet. Since questions have arisen about the usefulness of this technique in electronic spectroscopy, an evaluation of its merits and disadvantages is presented in the next section.

The Pressed Alkali Halide Pellet Technique

It has become customary to use the pressed alkali halide disk technique in electronic spectroscopy in those cases where (1) the material is highly insoluble and cannot be introduced in liquid solutions, (2) the solid material has an exceptionally high molar extinction coefficient, (3) thin single crystals are not easily formed, and (4) a rapid spectral analysis is desired. Since the introduction of this technique into ultraviolet-visible absorption spectroscopy,[11] scattered reports of its applications and limitations have appeared. Possible difficulties with the pressed KBr disk technique in the infrared studies of organic solids have been noted by Baker[12] and Tolk,[13] for example. Experimental techniques, such as mixing, grinding and pressing under vacuum, are not easily reproduced and can frequently lead to physical changes (polymorphism) in the material of interest and to strong physical (and sometimes chemical) interactions at the dispersed microcrystal–alkali halide interfaces. The magnitude of the effects depend upon the lattice energies of the organic and alkali halide phases, relative particle sizes, adsorption of moisture, and stress relaxation in the fused pellet.[12, 13]

These complications, as well as others, are always present in extending this technique to visible-ultraviolet spectroscopy. One additional difficulty is the wavelength-dependent scattering from the alkali halide disk containing organic particles, 0.5–3 μ in diameter. In the region of strong absorption, the light reflected from particle may be commensurate in intensity to that transmitted through the absorbing aggregates dispersed in the alkali halide.[14] The fact that air (i.e. oxygen), which cannot be totally desorbed during pellet pressing, becomes entrapped between salt grain boundaries and that quasihydrostatic pressures produce inhomogeneous fusion during pellet preparation contribute to light scattering which results in flattening of the absorption curve and suppression of fine structure in the absorption bands. These difficulties do not distract from using this technique in electronic spectroscopy, as long as its limitations are clearly recognized. Wyman,[11] Dale[15] and Suzuki[16] have applied this technique to absorption studies of dyes, polyphenyls, and conjugated hydrocarbons, respectively. Van Duuren and Bardi[17] have used KBr pellets for obtaining reflectance fluorescence and excitation spectra of aromatic compounds. The technique has also been applied to the study of solid state absorption of molecular complexes.[2, 14, 18–23] Finally, the spectral study of organic materials at pressures above 12 kbar has been facilitated by mixing the substance with excess alkali halide.[20, 24, 25]

The most serious disadvantage of the pressed alkali halide pellet technique stems from the uncertainty of the state of aggregation of the organic material in the fused pellet. Suzuki[16] mentioned the possibilities ranging from heterogeneous mixtures to solid solutions (molecularly dispersed), but favored the view that randomly oriented microcrystals are trapped in the salts. This latter view has been tacitly assumed in nearly all of the work mentioned previously and is supported by the expected spectral shift relative to liquid solution spectra and by the correspondence of the spectral band positions to those measured for single crystals or solid films.[20,24,26] The nature of the dispersive state of organic materials in salt pellets has recently been questioned again by Pitts *et al.*[27–29] who observed photoinduced bimolecular reactions which can be interpreted by assuming molecular dispersion and the presence of diffusion analogous to liquid solution processes. This view is dismissed by Bernas, Leonardi and Renaud[26] who conclude from X-ray studies that an appreciable portion of the organic solid is associated in crystalline aggregates. The latter authors attribute the interesting results of solid state photochemistry to reactions at the microcrystalline surface in contact with the alkali halide ions of the pellet. The above assertion[29] that heterogeneity and not pressure are responsible for solid state reactions is consistent with spectral studies at high pressures. An external pressure of 10 kbar produces a reversible ~ 10 mμ red shift in the anthracene absorption.[20, 24] These observations as well as the conclusion[26] that the anthracene dimerization process is independent of the pressure (3–12 kbar) applied in pellet preparation disprove Wan *et al.*[29] who regard the pellet as retaining an internal pressure proportional to the applied pressure during pellet preparation.

It is concluded that the pressed alkali halide pellet technique produces microcrystalline aggregates within the fused pellet. This is certainly the case for TNB[20] and TCNE complexes in pellets because they yield in favorable cases vibrational structure superimposed on the CT bands, in agreement with single crystal data.

CT Crystal Spectra

Five crystalline complexes between TCNE and aromatic hydrocarbon donors were dispersed in NaCl pellets. The 1 : 1 complexes crystallized from ethyl acetate or methylene chloride solvents containing equimolar amounts of the two components. Single crystals of NaCl were crushed in an agate mortar to a fine powder. A mixture of 2–5 mg crystalline complex and 200 mg NaCl powder was transferred to a steel capsule and shaken at high speeds. The pellet was then formed in a 13 mm die under a ten ton load exerted in a Carver press. The moisture affinity of the resulting transparent pellet demands immediate fusion of a rectangularly cut (0·070 in. × 0.100 in.) portion into the sample chamber of the high pressure optical cell. The high pressure spectroscopic techniques are described elsewhere.[9, 20, 25]

The CT band maxima of the complexes in pellets at 1 atm are compared with those observed in other media in Table 1. The spectra of the molecular complexes in NaCl pellets are in reasonable agreement with those observed in KBr pellets and in thin films. The differences in $\nu_{\max}$ are small for pyrene and durene which show well-separated CT bands. However, the spectra of phenanthrene and naphthalene complexes may vary by as much as 700 cm^{-1} for different crystalline environments. The first charge transfer (CT-1) band of pyrene-TCNE near 15 kK was not accessible to our high-pressure apparatus and is not listed in Table 1. Single-crystal spectra are difficult to measure, but Kuroda and coworkers[2, 5, 6, 31] succeeded in obtaining polarized absorption spectra of pyrene-TCNE microcrystals. A solution-crystal red shift is observed, as expected. Phenanthrene-TCNE and durene-TCNE show an apparent blue shift which is more likely due to an intensity redistribution than a genuine spectral shift.

The CT bands of the pellets are illustrated in Figs. 1 and 2. They are similar in gross shape to solution spectra except for the durene-TCNE complex,[9, 32] where the short wavelength shoulder has become the predominant peak (~ 425 mμ) in the crystal spectrum. In other words, the CT-2 band has the larger transition moment in the crystalline environment. The unique feature of crystal spectra is the appearance of vibrational structure, superimposed on the CT-bands. This structure has been observed previously in single crystal and pellet spectra.[2, 6, 10, 32] Figure 1 shows a clear doublet for the naphthalene-TCNE complex. Such structural detail is absent in liquid, frozen, and plastic solutions. The vibrational peaks are separated by 1260–1350 cm^{-1} in the pellet spectrum, which may be compared with the 1300 cm^{-1} doublet in the single crystal pyrene-TCNE spectrum.[6] In the case of the anthracene-TNB crystal spectrum[33] the vibrational structure of intramolecular origin is difficult to identify. The existence of a 1070 cm^{-1} fundamental is fairly certain and can be identified with the degenerate TNB ring stretching frequency in the anthracene-TNB complex.

Table 1 CT-Band Maxima (kK) of TCNE Complexes in Various Media at 298°K and One Atmosphere

	Solid			Solution		Plastic
Donor	Film	NaCl pellet	KBr pellet[a]	n-Heptane	Ethyl acetate[b]	Cellulose acetate[c]
HMB		18.2	18.4	19.0	19.5	18.9
Durene	19.5, 23.5	19.8, 23.5		20.4, 22.1	21.5	20.8
Naphthalene[d]	18.6, 23.3	18.3, 24.6	17.9, 23.2	18.8, 24.0	20.0, 24.7	19.2, 23.8
Phenanthrene	21.0	20.0	18.5, 18.9 26.3	19.8	20.2	19.2
Pyrene	20.0[e]	20.1	20.0	20.9	21.7	21.1

[a] Reference 2.

[b] Reference 30.

[c] Section 9.

[d] The apparent large differences result from the presence or absence of the doublet structure in the CT spectrum.

[e] Single crystal data, c-spectrum (Ref. 6, 31).

According to charge-transfer theory[1a] the intramolecular vibrations should be characteristic of the acceptor molecule because the CT transition is naively viewed as an electron jump to the lowest unoccupied orbital of the acceptor. The infrared and Raman spectra of solid TCNE[34] show the in-plane C—C stretching motion to have strong absorption in this energy region, although this does not prove the identity of the complex vibration. The crystal environment is unique in providing sufficient order, apart from temperature, to reveal the vibrational progression superimposed on the electronic CT-absorption. But long range order is not necessary to observe this structure because the structure is clearly developed in pellets. Kuroda *et al.*[31] find the CT-bandwidths ($\Delta\nu_{1/2}$) to be similar for solution and crystal spectra. Qualitative comparisons of the CT-spectra from TCNE-complexes in pellets

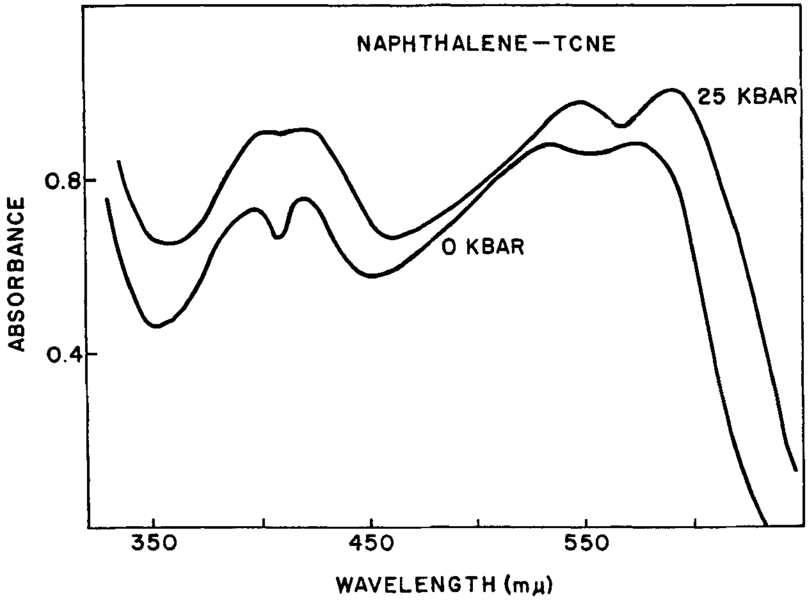

Figure 1. The absorption spectrum of crystalline naphthalene-TCNE complex at 1 atm and 25 kbar.

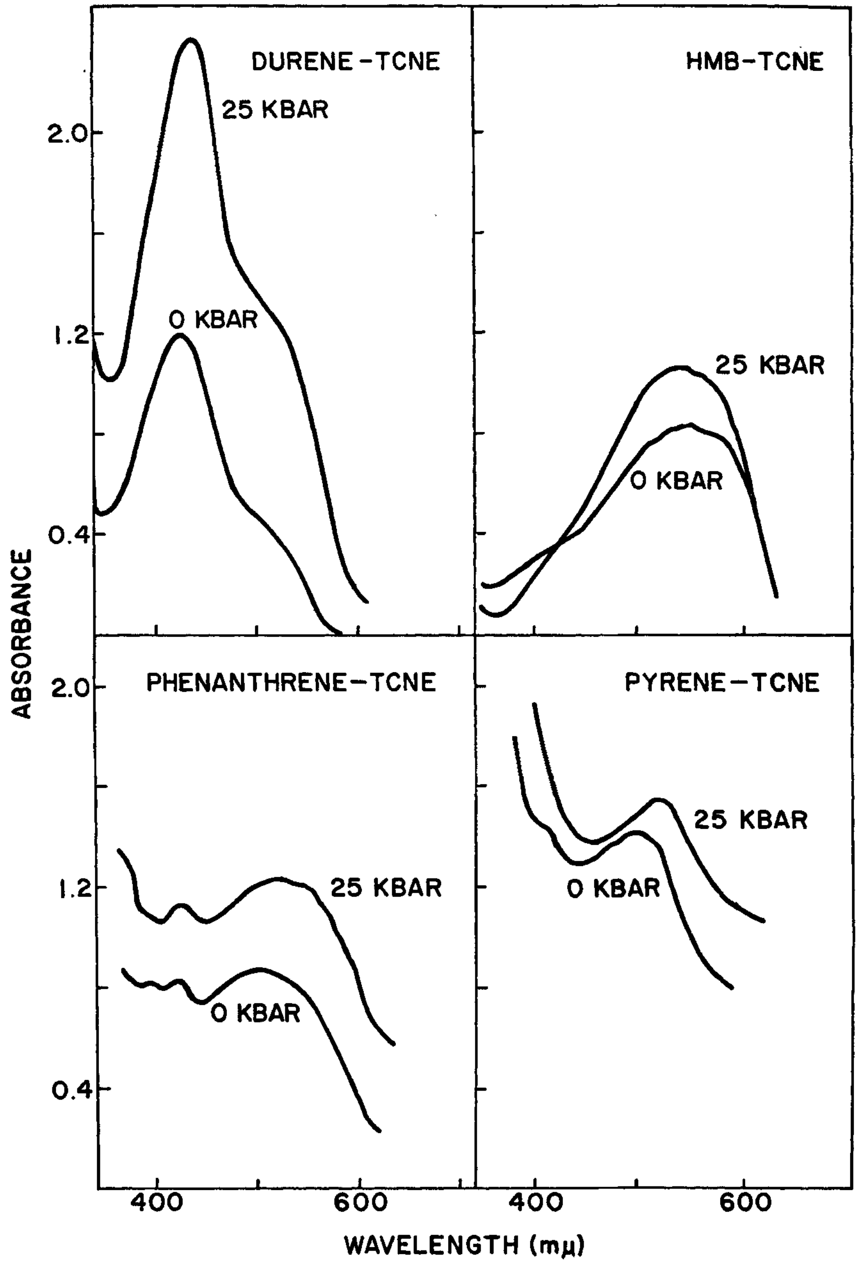

Figure 2. The absorption spectra of four crystalline aromatic hydrocarbon-TCNE complexes at 1 atm and 25 kbar.

and in polymer matrices[9] reveal that the bandwidths are larger in the pellet spectra. This may be a manifestation of the limitation of the pressed-pellet technique.

High-Pressure Spectra

The effects of high pressures on the CT-spectra are shown in Figs. 1 and 2 and summarized in Table 2. The numerical values of the spectral shift $\Delta\nu$ and the observed absorbance ratios $A(P)/A(0)$ are subject to large errors added to the uncertainties already evident for pellet spectra at one atmosphere. The significant trends show that the spectral shift at 25 kbar can be less than, equal to, or larger than the corresponding shift in polymer matrices.[9] TCNE complexes exhibit a smaller pressure shift than other complexes in pellets.[35–37] It is interesting to compare the HMB-TCNE blue shift with the 1500 cm^{-1} red shift of the HMB-chloranil CT-band at 25 kbar, observed by Stephens and Drickamer.[35] The naphthalene-TCNE complex shows a significantly smaller red shift in the crystal than in the polymer.[9] Further, the relative magnitudes for the CT-1 and CT-2 bands are apparently reversed in the two environments. When the vibrational structure is not clearly developed, then the measured pressure shift of the band maximum

TABLE 2 Spectral Parameters of TCNE Complexes at 25 Kbar[a]

Donor	Pellet		Plastic[b]	
	$\Delta\nu$(cm^{-1})	$A(25)/A(0)$	$\Delta\nu$(cm^{-1})	$A(25)/A(0)$
HMB	+170	1.3	+540	1.8
Durene	−750	2.0	−460	1.9
Naphthalene	−480, −200	1.15, 1.25	−850, −1300	2.9, 2.1
Phenanthrene	−1060	1.5	−820	1.8
Pyrene	−760	1.1	−820	2.6

[a] Estimated uncertainties at 25 kbar are ±200 cm^{-1} in the shift and ±0.2 in the absorbance ratio.

[b] Reference 9, except for pyrene-TCNE.

may in part be the result of intensity redistribution among the vibrations comprising the CT band. This factor does not appear very significant judging by other CT spectra, although its contribution may not be negligible.

The absorbance of the CT-band at high pressure increases generally less than for compressed plastics[9] or compressed CH_2Cl_2 solutions[8] except for durene-TCNE. It has already been mentioned that this complex shows a significant intensity redistribution in the crystal-pellet environment relative to the cellulose acetate (CA) matrix. A similar cause may be responsible for both effects. It is noted in Figs. 1 and 2 that the vibrational structure is retained and $\Delta\nu_{1/2}$ is not appreciably affected at high pressure. The salt powder surrounding the microcrystals of the complexes must transmit nearly hydrostatic pressures to the molecular solids, since structural detail is not destroyed by non-uniform shear forces creating defects and inhomogeneous intermolecular interactions. The spacing between vibrational bands, as expected, remains nearly constant under compression. The spectral changes at high pressures can be repeatedly achieved without irreversible effects in this pressure range.

Discussion

The percent electron transfer in the ground state is estimated from visible and infrared data to be 5–10%.[38, 39] The absence of ion pairs is confirmed by resistivity and e.s.r. measurements.[2, 31] The percent ionic character in crystalline TCNE complexes is expected to be higher than in nonpolar solution or in complexes formed with weaker acceptors, although the pressure perturbations can yet be discussed in terms of molecular forces rather than crystalline fields. The pressure shift of the CT spectra (band maxima) can be discussed in terms of the various interactions contributing to the relative displacement of the normal and excited CT state. In Part IV[41] the pressure shift is discussed in terms of the pressure dependence of the solvation of the normal state Ψ_N, the excited state Ψ_E, the no-bond structure $\Psi_0(D,A)$ and the dative bond structure $\Psi_1(D^+\text{–}A^-)$. The solvation effects at high pressure result in red shifts when the dipole moment increases upon excitation. The other factor which affects the net shift results from CT forces between the components of the pair. It is shown[41] that CT interactions in compressed complexes become more important and separate the two states, i.e. opposing the solvation effects. The magnitude of the pressure shift is determined by the balance between the dielectric and CT forces. The blue shift from CT forces is expected to be larger for stronger complexes. Hence a smaller red shift is expected and observed for TCNE complexes compared to TNB,[36] TCPA[40] and haloquinone complexes.[35, 41] The CT forces are not only dependent upon the average intermolecular separation of the two planar π-components but also the size and orientation of the acceptor relative to the donor molecule. This feature is perhaps best illustrated for the HMB-TCNE complex, in which the CT forces predominate at the higher pressures. It is the size of TCNE relative to chloranil[35] which must be responsible for the large difference in pressure response of the two HMB complexes. Repulsive interactions[42] of the methyl groups (in HMB) with the TCNE π-system is also expected to contribute to the blue shift by increasing the energy of the CT state. This contention is supported by the fact that the absorption of HMB-TCNE (Table 2) is not unusually strengthened compared to other complexes. It is concluded from the pressure shift studies that EDA complexes with a large contribution of the dative-bond structure to the ground state will reveal a blue shift at higher pressures.

External pressures on the compressible complex[43] increase orbital overlap. Since the average separation of donor-acceptor pairs is expected to be smaller in the crystal than in solutions at 1 atm, a smaller increase in absorbance with pressure is observed.[9, 43] The durene-TCNE complex shows the largest enhancement in the transition moment which suggests that pressure contributes to a better packing of TCNE among the methyl groups of durene. The crystal structure analysis of pyrene-TCNE[44, 45] shows that the components are nearly coplanar but their centers of symmetry are not superimposed. The calculations of Kuroda *et al.*[2] also reveal that the relative intensity of the CT-1 and CT-2 bands are very sensitive to the rotation of the respective molecular symmetry axes. The difference in the relative pressure behavior of the two CT bands in durene and naphthalene complexes emphasizes the importance of size and relative orientation of the donor-acceptor pair, although the accuracy of the data does not permit a detailed analysis.

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