Vibrational Spectra of Tetracyanoethylene

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Since tetracyanoethylene (TCNE) was synthesized for the first time by Cairns et al.,[1] much attention has been directed to the π-complexes formed by TCNE with aromatic compounds. However, previous work on the vibrational spectra and assignments of this molecule has been very limited. The infrared spectrum of TCNE was first reported by Looney and Downing,[2] who also gave the C≡N and C=C stretching frequencies in the infrared and Raman spectra. When we were almost finished with the present work, Long and George[3] published a paper in which the infrared and Raman spectra of the powdered solid were treated, together with the infrared spectrum of solution, and tentative assignments were given on the basis of spectra correlations.

On the other hand, in the normal coordinate treatments of molecules with π-electron systems, it was found necessary to supplement the basic Urey-Bradley force field (UBFF)[4,5] with additional cross terms, for example, "resonance-interaction terms" between the C—C stretching coordinates in benzene,[6-8] and

1) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. Mckusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

2) C. E. Looney and J. R. Downing, ibid., **80**, 2840 (1958).

3) D. A. Long and W. O. George, *Spectrochim. Acta*, **19**, 1717 (1963).

4) H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).

5) T. Simanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

6) S. Califano and B. Crawford, Jr., *Spectrochim. Acta*, **16**, 889 (1960).

7) J. R. Scherer and J. Overend, ibid., **17**, 719 (1961).

8) W. D. Jones, *J. Mol. Spectrosc.*, **10**, 131 (1963).

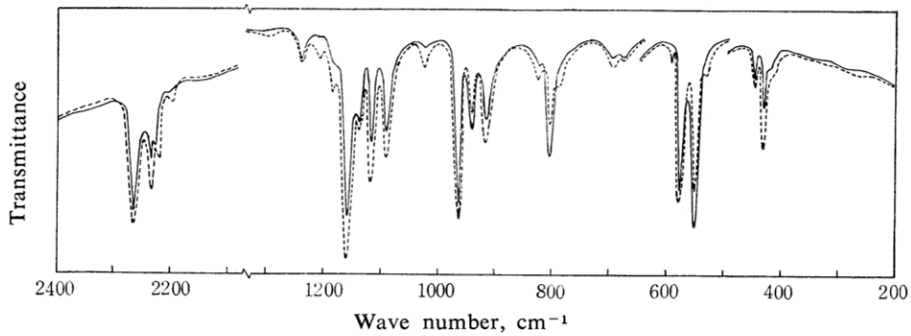

Fig. 1. Infrared spectrum of highly-oriented crystal of tetracyanoethylene.
—— Electric vector perpendicular to direction of crystal growth
---- Electric vector parallel to direction of crystal growth

" trans-interaction terms " between trans-hydrogen bending coordinates[9] or " bond-flexibility terms "[9,10] in ethylene and its derivatives. Thus, one might not expect the basic UBFF to be a satisfactory description of the potential function for TCNE, for in this case it is well recognized that resonance plays an important structural role.

In the present work, we have studied the polarized infrared spectrum of a highly-oriented crystal of TCNE and the Raman spectrum of a sample consisting of several lumps of the crystals. The infrared spectra of the powdered solid, solution, and vapor were also measured for comparison. In order to make vibrational assignments and to determine the force constants for this molecule, the normal coordinate treatments for the in-plane vibrations were carried out by using the basic UBFF and also a slight modification of it.

Experimental and Observed Spectra

A sample of TCNE kindly supplied by Dr. Kenichi Kudo was twice sublimed at 130~140°C/1~2 mmHg. The colorless, crystalline solid thus obtained melts at 199~200°C in a sealed capillary tube, the melting point being in good agreement with the literature values.[1,11]

Infrared Spectra. — The infrared absorption spectra in the region 4000~480 cm^{-1} were obtained by using a Perkin-Elmer model 21 spectrophotometer equipped with a lithium fluoride or sodium chloride prism, and by a Nippon Bunko model DS-301 (double monochromator) spectrophotometer equipped with two potassium bromide prisms. For measurements in the far-infrared region, 500~200 cm^{-1}, a Parkin-Elmer model 221 spectrophotometer equipped with a cesium bromide prism and a Nippon Bunko model DS-402G grating spectrophotometer were used.

Solid. — The highly-oriented, tabular crystals of TCNE were carefully prepared by the gradual heating of the purified solid up to about 140°C with a slight temperature gradient and at a pressure of 1~2 mmHg. The maximum size of these crystals was ca. 6×3 mm.; polarization microscopic examination was used to choose the best oriented crystal to be placed in the spectrophotometer beam. By X-ray diffraction studies, it was found that the solid TCNE prepared in the present work has the same crystal form as that (monoclinic crystals of the space group $P2_1/n$—C_{2h}^5) obtained by Bokoe and Trueblood[12] by recrystallization from a mixture of carbon tetrachloride and ethyl acetate, and that the crystals grew elongated along the b axis with the tabular ($\bar{1}01$) face.

Infrared polarization measurements for the crystal were made with silver chloride transmission polarizers, except in the far-infrared region, where transmission polarizers made of polyethylene sheets were used. The observed absorption spectra are shown in Fig. 1. The solid and broken lines represent the absorption curves obtained with polarized radiation, with the electric vector perpendicular to and parallel to the direction of crystal growth respectively. From Fig. 1, it may be seen that the absorption bands can be classified by their dichroic properties into three groups: (1) a group of bands which exhibit a high parallel dichroism ($\parallel$ band), (2) a group of bands which show nearly the same absorption intensities for both the parallel and perpendicular polarized radiations with a slight predominance of absorption intensity for the former ($\parallel \perp$ band), and (3) a group of bands which exhibit perpendicular dichroism ($\perp$ band). The observed bands, their relative intensities, and their dichroic properties are listed in Table I. The infrared spectrum of the powdered solid was also recorded by the use of the potassium bromide disk and Nujol mull; this procedure showed the same frequencies and relative intensities as those in the spectrum of the crystal.

Solution. — The infrared spectra of TCNE were

9) J. R. Scherer and J. Overend, *J. Chem. Phys.*, **33**, 1681 (1960).
10) T. Shimanouchi, ibid., **26**, 594 (1957).
11) "Organic Syntheses," Vol. 39, 64 (1959).
12) D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr.*, **113**, 1 (1960).

also measured for the saturated solution in dichloromethane or dibromomethane by using various fixed-thickness cells (0.2~1.0 mm.). The solution spectrum over the region 4000~200 cm^{-1} could be obtained by using either of these solvents, thus avoiding the strong interference due to solvent absorptions. Because of the limited solubilities of TCNE in these solvents, however, only the absorption bands which correspond to the relatively intense bands in the solid spectrum were observed. The observed bands and their relative intensities are given in Table I.

TABLE I. OBSERVED FREQUENCIES (cm^{-1}) OF TETRACYANOETHYLENE*1

Infrared				Raman
Crystal		Solution*2	Vapor*3	Crystal
				2313 vw
2262 m	∥ ⊥	2255 m	2248 s	
		2249 vw		
				2250 s
				2237 s
2230 m	∥	2222 m	2217 m	
2221 vw	⊥			
2216 vw	∥			
				2195 vw
2194 vw	∥			
				1573 s
				1537 w
				1284 m
1233 w	∥ ⊥			
1206 vw	∥			
1181 vw	∥			
1155 s	∥	1153 s	1153 s	
1138 vw	∥ ⊥			
1115 m	∥	1109 m	1111 m	
1086 m	∥	1079 m	1070 m	
1021 w	∥			
959 s	∥ ⊥	956 s	953 m	
935 m	⊥	927*w		
916 m	∥	905*m	902 m	
825 w	∥		822 w	
804 m	⊥		785 m	
797 sh	∥			
696 w	∥			
675 w	∥ ⊥			
				679 m
				592 vw
586 vw	∥			
579 s	∥ ⊥	575 m		
555 s	⊥	553 s		
537 vw	∥			
				536 vw
				508 vw
444 w	∥ ⊥			
429 m	∥			
ca. 420 sh				
				370 vw
				360 vw
				251 w

*1 s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

*2 Measured with a saturated solution in CH_2Cl_2 except for bands marked with * which are measured with a saturated solution in CH_2Br_2.

*3 Measured only in the LiF and NaCl prism regions.

Vapor.—The vapor spectrum in the region 4000~650 cm^{-1} was obtained by using a 10 cm. cell kept at ca. 200°C[13] by electric heaters. From Looney and Downing's data[2] the vapor pressure of TCNE was estimated to be more than 150 mmHg at this temperature. The spectrum obtained gave broad bands instead of fine structures due to the rotation of the molecule. The observed bands and their relative intensities are given in Table I, together with similar data for the corresponding bands of solid and solution. The correspondence of the bands among vapor, solution, and solid is fairly good as far as the comparison can be made indicating intermolecular forces in the solid phase are so weak that the intense bands of solid TCNE are correlated with the fundamental vibrational modes of the vapor molecules.

Raman Spectrum.—The Raman spectrum of solid TCNE was recorded photoelectrically by using a Cary model 81 spectrometer and photographically by using a Yuki Gosei model RL-II spectrometer. Several lumps of crystals prepared in the same way as those for the infrared polarization measurement were used as samples. The observed frequencies and their relative intensities are summarized in Table I. Attempts to determine the depolarization ratios by using the polarized incident-light technique were unsuccessful.

The Symmetry of Molecule and Selection Rule

According to X-ray analysis by Bekoe and Trueblood,[12] a TCNE molecule in crystal should have the site symmetry of C_i; in fact, slight difference is found between two C–C bond lengths of one wing of the molecule, and also between two bond angles formed by the two C–C bonds and the C=C bond (the C–C bond lengths: 1.454±0.007 Å and 1.443±0.006 Å; the C–C=C bond angles: 120.2° and 122.4°). However, it is reasonable to assume that the vibrational spectra of the crystal can virtually be treated under the molecular point group V_h for the following reasons: (1) The difference between the two C–C bond lengths, as well as that between the two C–C=C bond angles, is very small, as has been described above, and the planarity of the molecule is fairly

13) Since it was shown[11] that TCNE slowly evolves hydrogen cyanide when exposed to moist air even at room temperature, the gas cell was evacuated before heating, but weak bands due to hydrogen cyanide were still observed at ca. 3320 and 712 cm^{-1}.

TABLE II. SYMMETRY COORDINATES* FOR TETRACYANOETHYLENE

Species	Symmetry coordinate	Mode
A_g	$S_1=\Delta R$	C=C stretching
	$S_2=1/2(\Delta r_2+\Delta r_3+\Delta r_4+\Delta r_5)$	C-C stretching
	$S_3=1/2(\Delta l_6+\Delta l_7+\Delta l_8+\Delta l_9)$	C≡N stretching
	$S_4=1/\sqrt{3}\{(\Delta\alpha_0+\Delta\alpha_1)-1/2(\Delta\beta_2+\Delta\beta_3+\Delta\beta_4+\Delta\beta_5)\}$	C-C-C bending
	$S_5=1/2(\Delta\theta_6+\Delta\theta_7+\Delta\theta_8+\Delta\theta_9)$	C-C≡N bending
B_{1g}	$S_6=1/2(\Delta r_2-\Delta r_3+\Delta r_4-\Delta r_5)$	C-C stretching
	$S_7=1/2(\Delta l_6-\Delta l_7+\Delta l_8-\Delta l_9)$	C≡N stretching
	$S_8=1/2(\Delta\beta_2-\Delta\beta_3+\Delta\beta_4-\Delta\beta_5)$	C-C-C rocking
	$S_9=1/2(\Delta\theta_6-\Delta\theta_7+\Delta\theta_8-\Delta\theta_9)$	C-C≡N bending
B_{2u}	$S_{10}=1/2(\Delta r_2-\Delta r_3-\Delta r_4+\Delta r_5)$	C-C stretching
	$S_{11}=1/2(\Delta l_6-\Delta l_7-\Delta l_8+\Delta l_9)$	C≡N stretching
	$S_{12}=1/2(\Delta\beta_2-\Delta\beta_3-\Delta\beta_4+\Delta\beta_5)$	C-C-C rocking
	$S_{13}=1/2(\Delta\theta_6-\Delta\theta_7-\Delta\theta_8+\Delta\theta_9)$	C-C≡N bending
B_{3u}	$S_{14}=1/2(\Delta r_2+\Delta r_3-\Delta r_4-\Delta r_5)$	C-C stretching
	$S_{15}=1/2(\Delta l_6+\Delta l_7-\Delta l_8-\Delta l_9)$	C≡N stretching
	$S_{16}=1/\sqrt{3}\{(\Delta\alpha_0-\Delta\alpha_1)-1/2(\Delta\beta_2+\Delta\beta_3-\Delta\beta_4-\Delta\beta_5)\}$	C-C-C bending
	$S_{17}=1/2(\Delta\theta_6+\Delta\theta_7-\Delta\theta_8-\Delta\theta_9)$	C-C≡N bending

* Redundant coordinates are excluded.

good.[12] (2) The correspondence of the infrared bands among vapor, solution, and solid is fairly good. (3) The infrared bands of the crystal are classified into three groups according to their dichroic properties. Thus, the normal vibrations of TCNE divide into symmetry species as follows:

$$\Gamma = 5A_g(R) + 4B_{1g}(R) + 4B_{2u}(IR) + 4B_{3u}(IR) + 2A_u(\text{inactive}) + 2B_{1u}(IR) + 2B_{2g}(R) + B_{3g}(R)$$

where the first four are the in-plane vibrations, and the rest are the out-of-plane vibrations.

Normal Coordinate Treatment for In-plane Vibrations

The ***GF*** matrix method developed by Wilson[14] was used. A representative of each type of internal coordinate is shown in Fig. 2, while the symmetry coordinates are shown in Table II. The equilibrium bond lengths adopted are those determined from X-ray analysis by Bekoe and Trueblood:[12] $R_0=1.317$ Å, $r_0=1.449$ Å,[15] and $l_0=1.15$ Å. For the bond angles, $\alpha_0=\beta_0=120°$ and $\theta_0=180°$ were assumed for the sake of simplicity. In order to solve the secular equation, the symmetrization of the ***GF*** matrix was made according to the usual method.[16-18]

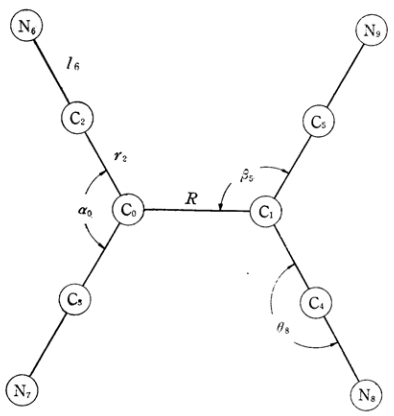

Fig. 2. Internal coordinates for tetracyanoethylene.

The numerical calculations were carried out by using the KDC-1 electronic digital computer constructed in the Faculty of Engineering of Kyoto University.

The basic UBFF[4,5] was used at first as the potential function for TCNE. Then, three bond-stretching (K(C=C), K(C-C), and K(C≡N)), three angle-bending (H(C-C-C), H(C-C=C), and H(C-C≡N)), and four non-bonded repulsion force constants (F(C-C-C), F(C-C=C), F(C-C≡N), and C) were necessary. The constants, C, represents the repulsion between two

14) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).
15) The average of the individual bond lengths (see above).
16) T. Miyazawa, *J. Chem. Phys.*, **29**, 246 (1958).
17) T. Shimanouchi, "Jikken-Kagaku Koza," 3, Maruzen, Tokyo (1957), Chap. 5.
18) W. J. Taylor, *J. Chem. Phys.*, **18**, 1301 (1950).

carbon atoms in the cis-position.[9,19,20] Since Urey-Bradley force constants transferable to conjugated nitriles have not been reported, for the first calculation the force constants were assumed to have the values found for alkylnitriles,[21,22] tetrahalogenoethylenes,[20] and methyl-substituted ethylenes.[23] Repetitions of the calculation with several sets of force constants were then carried out by the trial-and-error method by the use of the Jacobian matrix.[24] The final set of force constants thus obtained is shown in Column I of Table III, and the frequencies calculated with these constants are compared in Column I of Table IV with the observed values. The agreement is satisfactory except in the case of the frequency 679 cm^{-1} (ν_3) of the A_g species.

In order to obtain a better agreement for this frequency, the basic UBFF was modified by introducing new cross terms between the C-C and C=C bonds to take the presumed resonance interaction into account. The modified potential function is written as:

$$2V_{\text{mod. UBFF}} = 2V_{\text{UBFF}} + 2\rho\sum_{i=2}^{5}(\Delta R)(\Delta r_i)$$

The new cross terms appear only on the A_g factor of the $\boldsymbol{F}$ matrix. Hence, by putting $\rho = 0.75$ mdyn./Å, $K(C{=}C) = 7.79$ mdyn./Å, and other constants equal to those of Set I, considerable improvements were made for the frequencies of the A_g species without any altration of the frequencies for other species. The

TABLE III. FORCE CONSTANTS* FOR TETRACYANOETHYLENE (mdyn./Å)

	I UBFF	II Mod. UBFF
K(C=C)	6.31	7.79
K(C-C)	4.80	4.80
K(C≡N)	16.84	16.84
H(C-C-C)	0.05	0.05
H(C-C=C)	0.16	0.16
H(C-C≡N)	0.13	0.13
F(C-C-C)	1.11	1.11
F(C-C=C)	1.04	1.04
F(C-C≡N)	0.08	0.08
C	0.11	0.11
ρ	—	0.75

* $F' = -0.1\,F$, $C' = -0.1\,C$

TABLE IV. COMPARISON BETWEEN OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR IN-PLANE FUNDAMENTAL VIBRATIONS OF TETRACYANOETHYLENE

Species	No.	Obs. freq. Raman	Obs. freq. Infrared	I Calcd. freq.	I Dev.* %	II Calcd. freq.	II Dev.* %
A_g	ν_1	2250		2250	0.0	2246	−0.2
	ν_2	1573		1573	0.0	1573	0.0
	ν_3	679	Inact.	647	−4.7	659	−2.9
	ν_4	536		525	−2.1	530	−1.1
	ν_5	—		122	—	122	—
B_{1g}	ν_6	2237		2232	−0.2	2232	−0.2
	ν_7	1284	Inact.	1304	+1.5	1304	+1.5
	ν_8	508		503	−1.0	503	−1.0
	ν_9	251		251	0.0	251	0.0
B_{2u}	ν_{10}		2230	2239	+0.4	2239	+0.4
	ν_{11}	Inact.	1155	1152	−0.3	1152	−0.3
	ν_{12}		429	433	+0.9	433	+0.9
	ν_{13}		—	111	—	111	—
B_{3u}	ν_{14}		2262	2257	−0.2	2257	−0.2
	ν_{15}	Inact.	959	980	+2.2	980	+2.2
	ν_{16}		579	591	+2.1	591	+2.1
	ν_{17}		—	157	—	157	—

* $100 \times (\nu_{\text{calcd}} - \nu_{\text{obs}})/\nu_{\text{obs}}$

19) D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957).
20) D. E. Mann, L. Fano, J. H. Meal and T. Shimanouchi, ibid., **27**, 51 (1957).
21) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 513 (1962).
22) T. Fujiyama, I. Nakagawa and T. Shimanouchi, Symposium on Structural Chemistry, Tokyo, October, 1961.
23) S. Mizushima and T. Shimanouchi, "Sekigaisenkyushu to Raman Koka," Kyoritsu, Tokyo (1958).
24) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1132 (1955).

TABLE V. POTENTIAL ENERGY DISTRIBUTIONS (%) FOR IN-PLANE FUNDAMENTAL VIBRATIONS OF TETRACYANOETHYLENE

	A_g				
	ν_1 2246 cm^{-1}	ν_2 1573 cm^{-1}	ν_3 659 cm^{-1}	ν_4 530 cm^{-1}	ν_5 122 cm^{-1}
S_1	0.0	78.0	0.0	1.2*	0.4*
S_2	13.4*	13.2*	83.5	5.1*	0.9
S_3	86.6	0.0*	13.1	0.4*	0.0
S_4	0.0*	8.1	2.4	63.2	32.8*
S_5	0.0*	0.7	1.0	30.0	65.8
	B_{1g}				
	ν_6 2232 cm^{-1}	ν_7 1304 cm^{-1}	ν_8 503 cm^{-1}	ν_9 251 cm^{-1}	
S_6	15.5*	52.0*	26.3	1.7	
S_7	84.0	7.6*	4.8	0.6	
S_8	0.5	39.7	49.3	13.2	
S_9	0.0*	0.6*	19.7*	84.5	
	B_{2u}				
	ν_{10} 2239 cm^{-1}	ν_{11} 1152 cm^{-1}	ν_{12} 433 cm^{-1}	ν_{13} 111 cm^{-1}	
S_{10}	16.3	83.0	0.0	1.5*	
S_{11}	83.6*	14.4	0.2*	0.0	
S_{12}	0.0*	2.2*	50.6*	46.2	
S_{13}	0.0	0.4	49.1	52.3	
	B_{3u}				
	ν_{14} 2257 cm^{-1}	ν_{15} 980 cm^{-1}	ν_{16} 591 cm^{-1}	ν_{17} 157 cm^{-1}	
S_{14}	15.8*	62.8*	16.9*	0.0	
S_{15}	84.1	10.1*	4.1*	0.0	
S_{16}	0.0	23.8	57.3*	23.2	
S_{17}	0.0	3.3	21.6*	76.7*	

* The sign of the corresponding element of $\boldsymbol{L}$ matrix is negative.

results are shown in Column II of Table III and Table IV. The additional introduction of cross terms between the C–C and C≡N bonds improved the situation little. Table V shows the potential energy distribution (for Set II) among the symmetry coordinates calculated from the expression:[25]

$$P_{ij}=L_{ij}^2F_{ii}/\sum_i L_{ij}^2F_{ii}$$

where L_{ij} denotes the element of the $\boldsymbol{L}$ matrix whose columns are the characteristic vectors of the $\boldsymbol{GF}$ matrix.

Vibrational Assignments

In-plane Fundamental Vibrations. — In view of the fact that, in the polarized infrared spectrum of the TCNE crystal, the two medium-strength bands observed at 2262 and 2230 cm^{-1} (due to the C≡N stretching modes) exhibit a ∥ ⊥ and a ∥ dichroism respectively, it is evident that one of the two species, B_{2u} and B_{3u}, should have one of these dichroic properties, and the remaining one, the other.

On the other hand, comparisons of the four C–X stretching frequencies on each tetrahalogenoethylene ($X_2C=CX_2$) belonging to the point group V_h always result in the sequence $\nu(B_{1g})>\nu(B_{2u})>\nu(B_{3u})>\nu(A_g)$,[20] as is shown in Table VI. Therefore, it is reasonable to

TABLE VI. C–X STRETCHING FREQUENCIES (cm^{-1}) OF $X_2C=CX_2$ MOLECULES (POINT GROUP V_h)

Species	X=F*	Cl*	Br*	CN Present work
A_g	778	447	265	679
B_{1g}	1340	1000	880	1284
B_{2u}	1337	908	766	1155
B_{3u}	1186	777	635	959

* Ref. 20.

assume that the four C–C stretching modes of TCNE should be arranged in the same sequence of frequencies. Thus, the two strong infrared bands at 1155(∥) and 959 cm^{-1}(∥ ⊥) are associated with the B_{2u} and B_{3u} C–C stretching modes respectively, while the two medium-strength Raman lines at 1284 and 679 cm^{-1} are associated with the corresponding B_{1g} and A_g modes respectively (Table VI). These assignments are confirmed by the present normal coordinate analysis. In each species, the potential energy of this vibration is predominantly associated with the C–C stretching mode, its magnitude depending upon the species. These assignments are different from those given by Long and George,[3] who attributed the two infrared bands at 1155 and 959 cm^{-1} to the B_{3u} and B_{2u} C–C stretching modes respectively, and the two Raman lines at 1250[26] and 1280 cm^{-1} to the corresponding B_{1g} and A_g modes respectively.

The assignments of the C–C stretching modes reveal that the infrared acitive species B_{2u} and B_{3u} should have a ∥ and a ∥ ⊥ dichroism respectively. Hence, the ∥ ⊥ band at 2262 cm^{-1} is assigned to the B_{3u} C≡N stretching mode, and the ∥ band at 2230 cm^{-1}, to the corresponding B_{2u} mode. Since the two strong Raman lines at 2250 and 2237 cm^{-1} (due to the C≡N stretching modes) have almost the same intensity, it is difficult to assign these lines to the respective species experimentally. Therefore, with the aid of the normal coordinate

25) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952).

26) We could not find this Raman line in our spectrum even in careful measurements (see Table I).

TABLE VIII. ASSIGNMENTS OF OBSERVED BANDS (LINES) DUE TO OVERTONE AND COMBINATION VIBRATIONS OF TETRACYANOETHYLENE

	Freq. cm^{-1}	Intensity	Dichroism	Assignment
Raman line	2313	vw		$1155(B_{2u}) \times 2 = 2310(A_g)$
	2195	vw		$1233(B_{3u}) + 959(B_{2u}) = 2192(A_g)$
	1537	w		$1284(B_{1g}) + 251(B_{1g}) = 1535(A_g)$
				$959(B_{3u}) + 579(B_{3u}) = 1538(A_g)$
Infrared band	1115	m	∥	$679(A_g) + 429(B_{2u}) = 1108(B_{2u})$
	1086	m	∥	$579(B_{3u}) + 508(B_{1g}) = 1087(B_{2u})$
	1021	w	∥	$916(B_{2u}) + 122^*(A_g) = 1038(B_{2u})$
				$1155(B_{2u}) - 122^*(A_g) = 1033(B_{2u})$
	935	m	⊥	$579(B_{3u}) + 360(B_{2g}) = 939(B_{1u})$
	916	m	∥	$555(B_{1u}) + 370(B_{3g}) = 925(B_{2u})$
	825	w	∥	$579(B_{3u}) + 251(B_{1g}) = 830(B_{2u})$
	804	m	⊥	$444(B_{3u}) + 360(B_{2g}) = 804(B_{1u})$
	696	w	∥	$444(B_{3u}) + 251(B_{1g}) = 695(B_{2u})$
				$959(B_{3u}) - 251(B_{1g}) = 708(B_{2u})$
	675	w	∥ ⊥	$429(B_{2u}) + 251(B_{1g}) = 680(B_{3u})$
	444	w	∥ ⊥	$579(B_{3u}) - 122^*(A_g) = 457(B_{3u})$

* Calculated value for ν_5 (see Table IV).

analysis, we attributed the former to the A_g mode and the latter to the B_{1g} mode.

The strongest Raman line, at 1573 cm^{-1}, is undoubtedly to be assigned C=C stretching mode (A_g). In fact, the potential energy of this vibration is primarily associated with the C=C stretching mode (78%), although the contributions of the C–C stretching (13%) and C–C–C bending modes (8%) are appreciable.

A strong infrared band at 579 cm^{-1} and a medium-strength one at 429 cm^{-1} exhibit ∥ ⊥ and ∥ dichroisms and are assigned to the B_{3u} and B_{2u} vibrations respectively. As Table V shows, the band at 579 cm^{-1} (calculated as 591 cm^{-1}) is due to the hybridized mode of the C–C–C bending (57%), C–C≡N bending (22%), and C–C stretching modes (17%). The band at 429 cm^{-1} (calculated as 433 cm^{-1}) is also due to the hybridized mode of the C–C–C rocking (51%)[27] and C–C≡N bending mode (49%). In the region 600∼500 cm^{-1} of the Raman spectrum, three very weak lines are observed at 592, 536 and 508 cm^{-1}. Of these Raman lines, the most intense one, at 536 cm^{-1} (calculated as 530 cm^{-1}), is attributed to the A_g mode involving the C–C–C bending (63%)[28] and C–C≡C bending modes (30%). The line at 508 cm^{-1} (calculated as 503 cm^{-1}) is attributed to the B_{1g} mode involving the C–C–C rocking (49%), C–C≡N bending (20%), and C–C stretching modes (26%). The assignment of the remaining line, at 592 cm^{-1}, will be discussed later.

A weak Raman line at 251 cm^{-1} is assigned to the lowest B_{1g} vibration. The potential energy of this vibration is associated with the C–C≡N bending (85%) and C–C–C rocking modes (13%). The Raman line assigned to the lowest A_g vibration (calculated as 122 cm^{-1}) and two infrared bands assigned to the lowest B_{2u} and B_{3u} vibrations (calculated as 111 and 157 cm^{-1} respectively) could not be observed, because their frequencies are lower than the 200 cm^{-1} limit of the present work. In each species, the potential energy of this vibration of associated predominantly with the C–C≡N bending mode but also partly with the C–C–C bending (or rocking) mode, the distribution of the energy between these two modes depending upon the species.

Out-of-plane Fundamental Vibrations.—Since the B_{2u} and B_{3u} species have been shown to have ∥ and ∥ ⊥ dichroisms, respectively it is apparent that the out-of-plane vibrations of the B_{1u} species give rise to ⊥ bands in the infrared spectrum. For this reason, and also because of its reasonable frequency, the strong infrared band at 555 cm^{-1} (⊥) is assigned to the B_{1u} C–C–C wagging mode. By using a frequency correlation with this mode, the very weak Raman line at 592 cm^{-1} is assigned to

27) Long and George gave a 715 cm^{-1} (medium-strength) infrared band in Table 6 of their paper,[3] and assigned it to the B_{2u} C–C–C rocking mode. This band, however, could be identified neither in their own spectrogram (Fig. 3 of Ref. 3) nor in that obtained by Looney and Downing (Fig. 1 of Ref. 2). No band was observed at this frequency in our spectrum either (see Fig. 1 and Table I).

28) Long and George[3] assigned the Raman line at 678 cm^{-1} to the A_g C–C–C bending mode. In the present work, however, this line (679 cm^{-1}) was attributed to the A_g C–C stretching mode as mentioned above.

the corresponding B_{2g} mode.

In the region 400~300 cm^{-1} of the Raman spectrum, a pair of very weak lines are observed at 370 and 360 cm^{-1}. Each of these lines may be associated with one of the B_{2g} and B_{3g} C–C≡N (out-of-plane) bending modes, because these correlate well with the corresponding modes of malononitrile, which have been observed at 371 and 337 cm^{-1}.[22] Here, the line at 370 cm^{-1} is tentatively assigned to the B_{3g} mode, and the line at 360 cm^{-1}, to the B_{2g} mode, in consideration of the assignments for combination vibrations mentioned below. No infrared ⊥ band to be assigned to the B_{1u} C–C≡N (out-of-plane) bending mode was observed in the region higher than 200 cm^{-1}. The results obtained for the out-of-plane fundamental vibrations are summarized in Table VII.

TABLE VII. ASSIGNMENTS OF OBSERVED BANDS (LINES) DUE TO OUT-OF-PLANE FUNDAMENTAL VIBRATIONS OF TETRACYANOETHYLENE

	Freq. cm^{-1}	Intensity	Assignment
Infrared band	555 (⊥)	s	C–C–C wagging (B_{1u})
	—		C–C≡N bending (B_{1u})
Raman line	592	vw	C–C–C wagging (B_{2g})
	360	vw	C–C≡N bending (B_{2g})
	370	vw	C–C≡N bending (B_{3g})

Overtone and Combination Vibrations.—Besides the bands (lines) assigned to the fundamental vibrations, there remain three weak Raman lines and a number of infrared bands, including five medium-strength ones, which are attributable to the overtone or combination vibrations. According to the selection rule, these Raman lines and infrared bands were assigned as is shown in Table VIII. It may be noticed that all the Raman lines are exclusively associated with the A_g mode. Since the A_u frequencies have not yet been established, the overtones and combinations involving the A_u vibrations were not considered. Nevertheless, for each of the observed frequencies, one or two possible assignments were found, and the agreement between the calculated and observed values is satisfactory, as Table VIII shows.

Summary

The polarized infrared spectrum of a highly-oriented crystal of TCNE have been measured, tegether with the Raman spectrum of a sample consisting of several lumps of the crystals. The infrared spectra of the powedered solid, solution, and vapor have also been observed for comparison. Under the assumption of the V_h symmetry, the normal vibrations of TCNE have been calculated for the in-plane modes by the use of the ***GF*** matrix method. The basic UBFF, as well as the modified one containing cross terms between the C=C and C–C bonds, has been used as the potential function for this molecule. The frequencies calculated with the modified UBFF agree well with the observed values. The potential energy distributions have also been calculated, and the nature of the in-plane fundamental vibrations has been elucidated. The tentative assignments have been made to the out-of-plane fundamental vibrations and to the overtone and combination vibrations.

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