

## The Raman and Infra-red Studies of Polycrystalline Potassium dicyanocuprate at Room and Low Temperature.

D. A. LONG, B. M. CHADWICK, \*S. U. QURESHI  
School of Chemistry, University of Bradford, Bradford (U. K.).

(Received 25th May 1982)

**Summary:** The infra-red and Raman spectra of  $\text{KCu}(\text{CN})_2$  have been assigned in terms of the known structure. There are no coincidences, and in the CuC stretching and CuCN bending regions there is evidence of factor group splittings at room temperature. On cooling the solid to  $15^\circ\text{K}$  there is no evidence of a phase change, but there is significant increase in the signal-to-noise ratio which allows confirmation of the assignments made from room temperature data. Assignments were made for the four components of eight out of the ten fundamentals. No assignments were possible for  $\nu_4$ , the totally symmetric CCuC bending vibration and  $\nu_{10}$ , the interionic CuN stretching vibration.

### Introduction

Over 50 years ago, Bassett and Corbet<sup>1</sup> made a phase rule study of the system  $\text{CuCN-KCN-H}_2\text{O}$  at  $298^\circ\text{K}$  and reported solid phases,  $\text{KCu}(\text{CN})_2$ ,  $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ ,  $\text{K}_3\text{Cu}(\text{CN})_4 \cdot \text{H}_2\text{O}$ . More recent investigations<sup>2, 3, 4</sup> however, indicated that the last compound is not hydrated.

Much of the early work on the  $\text{Cu}(\text{CN})_2^-$  ion in aqueous solution has proved to be either inconclusive or incorrect. One of the difficulties encountered was that of measuring the e.m.f of a copper or copper amalgam electrode against a high pH solution containing Cu(I) and an alkali metal cyanide. For example, Penneman and Jones<sup>5</sup> have calculated from the early electro-chemical work of Spitzer<sup>6</sup> values for the  $\text{Cu}(\text{CN})_2^-$  stability constant ranging from  $\sim 5 \times 10^{-24}$  to  $\sim 10^{-16}$  as the Cu(I) concentration is reduced from 0.1M to 0.00025 M. It has proved difficult to obtain the wavenumber of the symmetric and antisymmetric CN stretching vibrations in aqueous solution.

Penneman and Jones<sup>5</sup> in an infra-red spectroscopic study of the systems  $\text{CuCN-KCN-H}_2\text{O}$  and  $\text{NaCN-CuCN-HNO}_3\text{-H}_2\text{O}$ , have argued that in solution having  $[\text{CN}^-]/[\text{Cu(I)}] \ll 3.00$ , there is an appreciable amount of  $\text{Cu}(\text{CN})_2^-$  but that its detection is difficult because of the low value of the absorption coefficient of the anti-symmetric CN stretching vibration. In the KCN system they were unable to detect the anti-symmetric CN stretching vibration even at the minimum  $[\text{CN}^-]/[\text{Cu(I)}] = 2.8$  and for  $[\text{Cu(I)}] = 0.200$  and a path length

of 20-34  $\mu\text{m}$ . Only the antisymmetric CN stretching vibration of the  $\text{Cu}(\text{CN})_3^{2-}$  ion was observed at  $2094\text{ cm}^{-1}$ . When the  $[\text{CN}^-]/[\text{Cu(I)}]$  ratio was increased to 3.5 by increasing  $[\text{CN}^-]$ , the only changes observed were that the intensity of the band at  $2094\text{ cm}^{-1}$  decreased a new band at  $2076\text{ cm}^{-1}$  appeared and increased in intensity so that at  $[\text{CN}^-]/[\text{Cu(I)}] = 35$  it was more intense than that at  $2094\text{ cm}^{-1}$ . The band at  $2076\text{ cm}^{-1}$  is attributed to the antisymmetric CN stretching vibration ( $f_2$ ) of the tetrahedral  $\text{Cu}(\text{CN})_4^{3-}$  ion. In the NaCN system, Penneman and Jones<sup>5</sup> observed a broad band at  $2125\text{ cm}^{-1}$  for  $[\text{CN}^-]/[\text{Cu(I)}] = 2.56$ ,  $\text{Cu(I)} = 0.063$  and  $\text{HNO}_3 = 0.06$ . They attributed this band to  $\text{Cu}(\text{CN})_2^-$  ion and by implication assigned it the antisymmetric stretching vibration of a presumably linear  $\text{Cu}(\text{CN})_2^-$  ion.

Two years later, Cromer<sup>7</sup> reported the structure of  $\text{KCu}(\text{CN})_2$ . Remarkably,  $\text{KCu}(\text{CN})_2$  did not contain the expected discrete linear  $\text{Cu}(\text{CN})_2^-$  ions but polymeric ions  $[\text{Cu}(\text{CN})_2^-]$  in the form of helical chains in which the individual  $[\text{Cu}(\text{CN})_2^-]$  ions were bent with  $\text{C-Cu-C} = 134 \pm 1^\circ$ . Each Cu(I) is three-coordinated, being surrounded by a C atom of an unshared  $\text{CN}^-$  ion and a C atom and a N atom of shared  $\text{CN}^-$  ions. The two CuC bond lengths are  $1.92 \pm 0.02\text{ \AA}$  and the CuN bond length is  $2.05 \pm 0.02\text{ \AA}$ . The CN bond lengths are  $1.15 \pm 0.03\text{ \AA}$  (protruding) and  $1.13 \pm 0.03\text{ \AA}$  (in the chains). The CuCN angles are in the range  $175 \pm 3^\circ$ ,  $\text{CuNC} = 139 \pm 2^\circ$ . The copper atom and the three

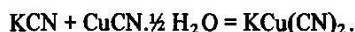
\*Present Address: Institute of Chemistry, University of Sind, Jamshoro (Sind) Pakistan.

light atoms bonded to it are approximately coplanar; there is a relatively short "non-bonded" Cu-Cu distance of  $2.84 \text{ \AA}$  between adjacent chains. The space group of the unit cell is  $P2_1/C$  ( $C^5_2h$ ) and there are four formula units per primitive unit cell. The site symmetry of all the atoms is  $C_1$ .

This paper presents the spectroscopic studies of  $KCu(CN)_2$  at room and low temperature. The Raman vibrational spectroscopic studies at low temperature has not been investigated, and does not appear to have been published yet.

### Experimental

#### Preparation of Potassium Dicyanocuprate $KCu(CN)_2$ .



KCN (B.D.H. AnalaR; 20g) was dissolved in minimum amount of  $H_2O$  (40 ml), this solution was further diluted by adding 100 ml, of  $H_2O$ .  $CuCN \cdot \frac{1}{2}H_2O$  (B.D.H. 26g) was gradually added along with constant stirring. The mixture was heated to boiling. When the volume of the solution was reduced to 30 ml, it was cooled in ice. The white crystals produced were filtered at the water pump, followed by washings of ethanol and ether. The yield was 19.8g i.e. 62% based on  $CuCN$ .

#### Infrared Spectroscopy

The infrared spectra ( $4000-250 \text{ cm}^{-1}$ ) which are presented in Figs 1 and 2 were obtained as nujol mulls between KBr and CsI plates using Perkin-Elmer 475 and 521 spectrophotometers. The latter PE 521 was calibrated with water vapour. The observed corrected wavenumbers are listed in Table-1.

#### Raman Spectroscopy.

The Raman spectra reported in this paper were obtained using a spex 1401/II double monochromator, an E.M.I 4789/Q/A photomultiplier, a photon counter and an Oxford Instrument series 3000 recorder.

The Raman spectra of polycrystalline  $KCu(CN)_2$  at room temperature was recorded using 488.0 nm exciting radiation from a Spectra Physics argon ion laser (1200 mW and 600 mW ex-laser) and a spectra slit width

of  $1 \text{ cm}^{-1}$ . The maximum uncertainty of the Raman wavenumber reported in the Table-3 is  $\pm 1 \text{ cm}^{-1}$ .

The Raman spectra of polycrystalline  $KCu(CN)_2$  at 15K were also obtained with 488.0 nm (500 mW ex laser). The sample was cooled by using an Air Products Displex CS-202 closed cycle helium gas refrigerator. The solid was held between two glass plates mounted in a 19 mm diameter holder made of nickel plates copper. Indium gaskets were used to ensure reasonable thermal contact between holder and glass plates. The sample holder was screwed into the cold tip of the Displex refrigerator. An indium gasket between the cold tip and the sample holder ensured good thermal

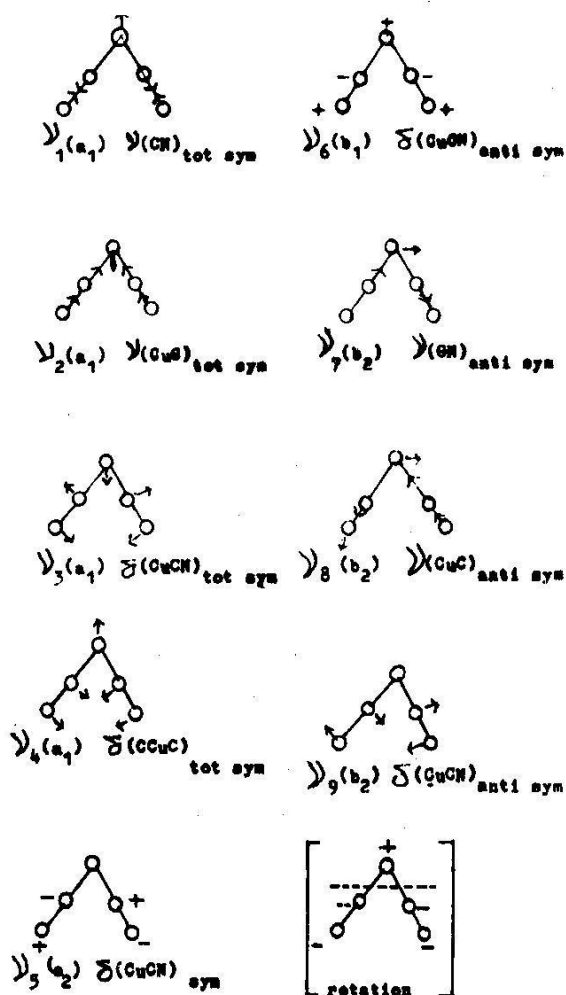


Fig. 1: Normal modes of vibration of a  $C_{2v}$   $Cu(CN)_2^{-1}$  ion.

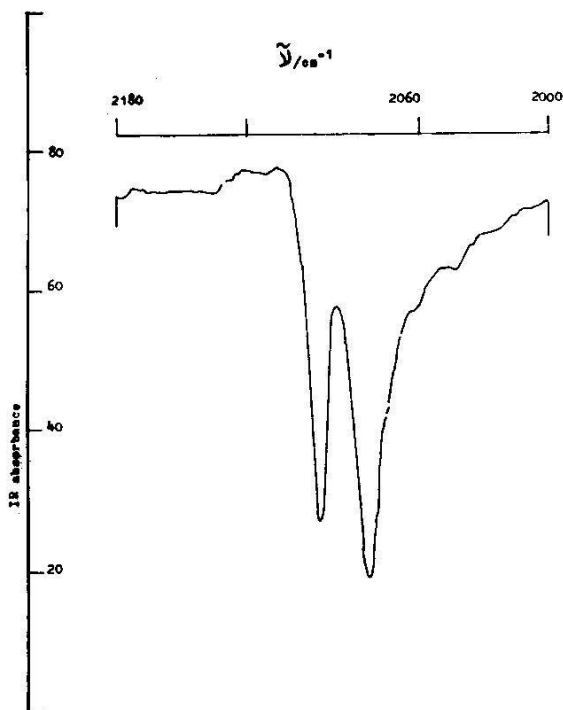


Fig. 2: Infra-red spectrum of polycrystalline  $\text{KCu}(\text{CN})_2$  at room temperature in the CN stretching region.

contact. The temperature of the cold tip was measured with a hydrogen vapour bulb thermometer and also with a chromel vs gold with 0.07 atomic % iron thermocouple used in conjunction with a Doric digital temperature readout device. The sample holder was maintained in a vacuum of  $10^{-6}$  torr<sup>7,8</sup>.

## Results and Discussion

### The vibrational spectra of solid $\text{KCu}(\text{CN})_2$ .

#### a) The predicted spectrum.

A centrosymmetric linear isolated  $\text{Cu}(\text{CN})_2^-$  ion has  $D_{\infty h}$  symmetry and would have ten degrees of vibrational freedom and seven vibrational wavenumbers (see Table 1) of which three are Raman-active and the remaining four are infra-red active.

$$\Gamma_{\text{vib}} = 20_g^+ + 2\sigma_u^+ + \pi_g + 2\pi_u$$

A bent  $C_{2v}$  isolated  $\text{Cu}(\text{CN})_2^-$  ion would have nine degrees of vibrational freedom and nine vibrational wavenumbers (Table 2 and Figure 1).

$$\Gamma_{\text{vib}} = 4a_1 + a_2 + b_1 + 3b_2$$

Table-1  $D_{\infty h}$  to  $C_{2v}$  correlation for the  $\text{Cu}(\text{CN})_2^-$  ion.

Fundamental	Approximate Description	Symmetry species	Symmetry Species	Approximate Description	Symmetry species.
$\nu_1$	$\nu(\text{CN})_{\text{tot sym}}$	$\sigma_g^+$	$a_1$	$\nu(\text{CN})_{\text{tot sym}}$	$\nu_1$
$\nu_2$	$\nu(\text{CuC})_{\text{tot sym}}$	$\sigma_g^+$	$a_1$	$\nu(\text{CuC})_{\text{tot sym}}$	$\nu_2$
$\nu_3$	$\nu(\text{CN})_{\text{tot sym}}$	$\sigma_u^+$	$a_1$	$\delta(\text{CuCN})_{\text{to sym}}$	$\nu_3$
$\nu_4$	$\nu(\text{CuC})_{\text{anti sym}}$	$\sigma_u^+$	$a_1$	$\delta(\text{CCuC})_{\text{tot sym}}$	$\nu_4$
$\nu_5$	$\delta(\text{CuCN})_{\text{sym}}$	$\pi_g$	$a_2$	$\delta(\text{CuCN})_{\text{sym}}$	$\nu_5$
$\nu_6$	$\delta(\text{CuCN})_{\text{anti sym}}$	$\pi_u$	$b_1$	$\delta(\text{CuCN})_{\text{anti sym}}$	$\nu_6$
$\nu_7$	$\delta(\text{CCuC})_{\text{anti sym}}$	$\pi_u$	$b_2$	$\nu(\text{CN})_{\text{anti sym}}$	$\nu_7$
			$b_2$	$\nu(\text{CuC})_{\text{anti sym}}$	$\nu_8$
			$b_2$	$\delta(\text{CuCN})_{\text{anti sym}}$	$\nu_9$

All nine modes are Raman-active i.e. two CN stretching vibrations ( $\nu_1, \nu_7$ ), two CuC stretching vibrations ( $\nu_2, \nu_8$ ), four CuCN bending vibrations ( $\nu_3, \nu_5, \nu_6, \nu_9$ ) and one C Cu C bending vibration ( $\nu_4$ ). Relative to the  $D_{\infty h}$   $\text{Cu}(\text{CN})_2^-$  ion, the Ramanactive CuCN bending vibration splits into  $\nu_5(a_2)$  and  $\nu_9(b_2)$ , the two infra-red-active stretching vibrations become Raman-active, the infra-red-active CuCN bending vibration splits into  $\nu_3(a_1)$  and  $\nu_6(b_1)$  and the doubly degenerate, infra-red active C Cu C bending vibration becomes the non-degenerate  $\nu_4(a_1)$  (Table 1). One CN stretching one CuC stretching one CuCN bending, and one C Cu C stretching vibration will be polarised.

For the  $C_{2v}$  isolated  $\text{Cu}(\text{CN})_2^-$  ion eight of the nine modes are infra-red-active as one of the four CuCN bending vibrations  $\nu_5(a_2)$  is infra-red-inactive. Relative to the  $D_{\infty h}$   $\text{Cu}(\text{CN})_2^-$  ion, the infra-red-active CuCN bending vibration splits into  $\nu_3(a_1)$  and  $\nu_6(b_1)$ , the infra-red-active doubly degenerate C Cu C bending vibrations become the non-degenerate  $\nu_4(a_1)$ , the two Raman-active stretching vibrations become infra-red active, the doubly degenerate Raman active CuCN bending vibration becomes the non-degenerate  $\nu_9(b_2)$  (Table 2).

The isolated ion group to site group to unit cell group correlation for the internal modes is given in (Table 2). The precise details of the structure adopted by  $\text{K}[\text{Cu}(\text{CN})_2]$  are unusual in that none of the atoms occupies a special position. Consequently, in the site group approximation there are nine coincidences. In other words,  $\nu_5(a_2)$  becomes infra-red active.

In the unit cell group approximation each of the nine modes split into a quartet which consists of two sets of non-coincident doublets, one set which is Raman-active and the other infra-red-active.

#### b) The Raman and Infrared results.

The Raman and infra-red results (Table 3 Fig 2 to 7). are significant for several reasons. First, seven fundamentals are expected in this region of the Raman spectrum, two CuC stretching and four CuCN bending vibrations (see table 1) and one interionic CuN stretching vibration. Secondly, only four bands of similar intensity are obtained in the corresponding region of the infra-red spectrum (Fig. 3). Thirdly, it is tempting to attribute each of the six Raman bands to the six  $a_g$  factor

group components of each fundamental and the six Raman shoulders or incompletely resolved bands to the corresponding six  $b_g$  components e.g. the band at  $279 \text{ cm}^{-1}$  and the incompletely resolved band at  $272 \text{ cm}^{-1}$  would be the  $a_g$  and  $b_g$  components respectively of one of the three CuCN bending vibrations or the CuN stretching vibration. If this interpretation is correct, then this region of the vibrational spectra of  $\text{KCu}(\text{CN})_2$  provides definite evidence of factor group doublets which were both based on the isolated ion of  $C_{2v}$  symmetry.

Table-2 Isolated ion group to site group to unit cell group for the internal modes of  $\text{Cu}(\text{CN})_2^-$  in  $\text{KCu}(\text{CN})_2^-$ .

Isolated Ion	Site	Unit Cell
	$C_{2v}$	$C_{2h}$
$\nu_1, a_1$	a	$a_g + b_g$ $a_u + b_u$
$\nu_2, a_1$	a	$a_g + b_u$ $a_u + b_u$
$\nu_3, a_1$	a	$a_g + b_g$ $a_u + b_u$
$\nu_4, a_1$	a	$a_g + b_g$ $a_u + b_u$
$\nu_5, a_2$	a	$a_g + b_g$ $a_u + b_u$
$\nu_6, b_1$	a	$a_g + b_g$ $a_u + b_u$
$\nu_7, b_2$	a	$a_g + b_g$ $a_u + b_u$
$\nu_8, b_2$	a	$a_g + b_g$ $a_u + b_u$
$\nu_9, b_2$	a	$a_g + b_g$ $a_u + b_u$

Table 3. Raman and infra-red spectra and assignments for  $\text{Cu}(\text{CN})_2^-$  ion in solid  $\text{KCu}(\text{CN})_2$ 

Mode	Approximate Description	Symmetry species	Wavenumber/ $\text{cm}^{-1}$		
			Raman (a)	Raman (b)	Infra-red
$\nu_1$	$\nu(\text{CN})_{\text{tot sym}}$	$a_1$	2113(vs)	2115(vs) 2114 (sh)	2109.5(s)
$\nu_2$	$\nu(\text{CuC})_{\text{tot sym}}$	$a_1$	432(w) 426 (s)	438(m) 429 (m)	420(w) 419 (vs)
$\nu_3$	$\delta(\text{CuCN})_{\text{tot sym}}$	$a_1$	345(m) 337(sh)	348(m) 338(vw)	342.5(m) 331.5(w)
$\nu_4$	$\delta(\text{CCuC})_{\text{tot sym}}$	$a_1$	—	—	—
$\nu_5$	$\delta(\text{CuCN})_{\text{sym}}$	$a_2$	357.5(w)	363(m) 358(vw)	Inactive
$\nu_6$	$\delta(\text{CuCN})_{\text{anti sym}}$	$b_1$	279(s) 272(sh)	280(m) 265(w)	286(sh)
$\nu_7$	$\nu(\text{CN})_{\text{anti sym}}$	$b_2$	2091(vs)	2090(vs) 2089(s)	2088(vs)
$\nu_8$	$\nu(\text{CuC})_{\text{anti sym}}$	$b_2$	388(m) 373(sh)	389(s) 382(vw)	377.5(s)
$\nu_9$	$\delta(\text{CuCN})_{\text{anti sym}}$	$b_2$	315(m) 291(sh)	315(m) 296(w)	305(s)

(a) Recorded by the present author at room temperature.

(b) Recorded by the present author at 15° K.

In order to obtain confirmatory evidence of these factor group splitting and also to obtain corroborative evidence that each of the two CN stretching bands was, in fact, a doublet, the Raman spectrum of solid  $\text{KCu}(\text{CN})_2$  at 15 K was obtained with 1200 mW ex laser (Table 3 and Fig 4 to 7). The results are in striking agreement with expectations.

Each fundamental will now be taken in turn in order of decreasing wavenumber, an assignment proposed, and the importance of the Raman spectrum emphasised. In every case the assignment of the  $a_g$  vibration and the  $b_u$  vibration is made to the more intense of the pair of components. All the assignments are summarised in Table 3.

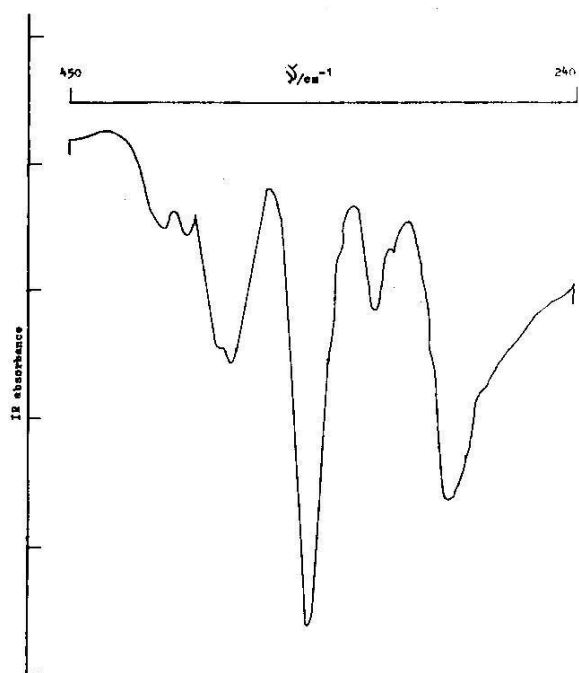


Fig. 3: Infra-red Spectra of polycrystalline  $\text{KCu}(\text{CN})_2$  at room temperature in the  $450\text{-}240\text{ cm}^{-1}$  region.

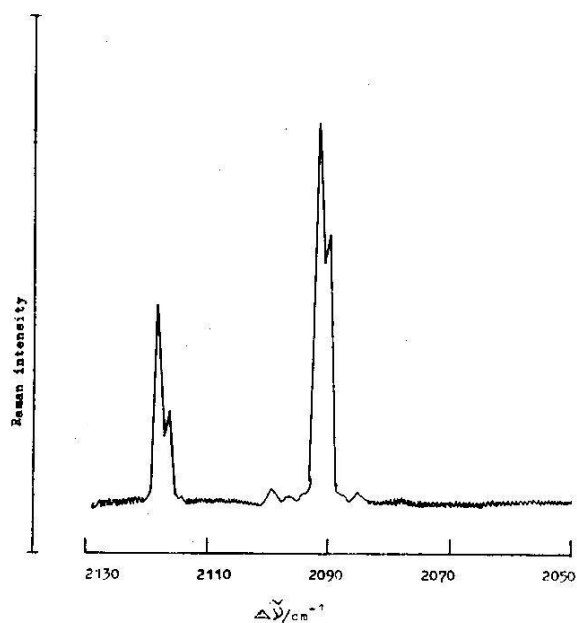


Fig. 5: The Raman spectrum of polycrystalline  $\text{KCu}(\text{CN})_2$  at 15K in the CN stretching region.

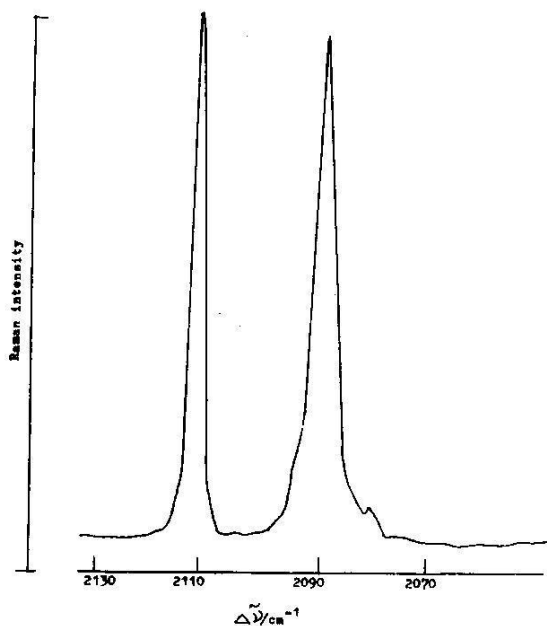


Fig. 4: Raman spectrum of polycrystalline  $\text{KCu}(\text{CN})_2$  at room temperature in the CN stretching region.

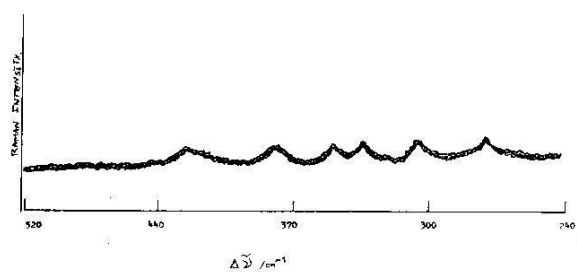


Fig. 6: The Raman spectrum of polycrystalline  $\text{KCu}(\text{CN})_2$  at room temperature in the  $42\text{-}250\text{ cm}^{-1}$  region.

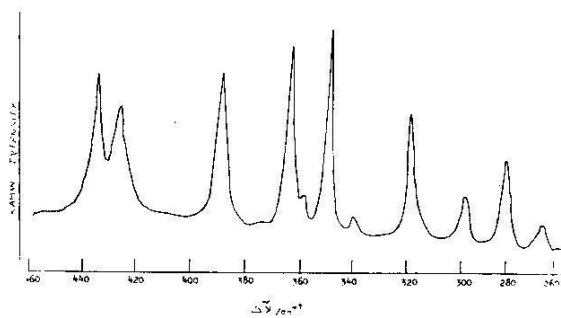


Fig. 7: Raman spectrum of polycrystalline  $\text{KCu}(\text{CN})_2$  at 15K in the  $(460\text{-}260)\text{ cm}^{-1}$  region.

i.  $\nu_1$  the totally symmetric CN stretching vibration (or the CN stretching vibration of the CN group associated with the K ions).

The higher wavenumber CN stretching bands are taken to be the totally symmetric CN stretching vibration because there is no established example of  $\tilde{\nu}$  (CN) anti sym  $\tilde{\nu}$ (CN) tot sym: The  $a_u$  and  $b_u$  components are unseparated at room temperature in the infra-red spectrum at  $2109.5 \text{ cm}^{-1}$ . The  $a_g$  and  $b_g$  components at  $2113 \text{ cm}^{-1}$  in the Raman spectrum at room temperature increased in wavenumber slightly and separate to  $2115 \text{ cm}^{-1}$  and  $2114 \text{ cm}^{-1}$  on cooling to 15 K.

ii.  $\nu_7$ , the anti-symmetric CN stretching vibration, (or the CN stretching vibration of CN group associated with the  $\text{Cu}^1$  atom).

The  $a_u$  and  $b_u$  components are unseparated at room temperature in the infra-red spectrum at  $2088 \text{ cm}^{-1}$ . The  $a_g$  and  $b_g$  components at  $2091 \text{ cm}^{-1}$  in the Raman spectrum at room temperature decrease slightly in wavenumber and separate to  $2090$  and  $2089 \text{ cm}^{-1}$  on cooling to 15 K.

iii.  $\nu_2$ , the totally symmetric CuC stretching vibration.

The higher wavenumber CuC stretching bands are taken to be the totally symmetric CuC stretching vibration because the higher wavenumber band is weaker than the lower wavenumber band in the infra-red. The  $a_u$  and  $b_u$  components are separated at room temperature in the infra-red spectrum at  $420 \text{ cm}^{-1}$  and  $415 \text{ cm}^{-1}$  respectively. The  $b_g$  and  $a_g$  components which are separated at room temperature in the Raman spectrum at  $426 \text{ cm}^{-1}$  and an ill-defined shoulder at  $432 \text{ cm}^{-1}$  increase in wavenumber and occur as two well resolved bands at  $429 \text{ cm}^{-1}$  on cooling to 15 K.

iv.  $\nu_8$ , the antisymmetric CuC stretching vibration.

The  $a_u$  and  $b_u$  components are unseparated at room

temperature in the infra-red spectrum at  $377.5 \text{ cm}^{-1}$ . The  $a_g$  and  $b_g$  components occur as a band at  $388 \text{ cm}^{-1}$  and a weak shoulder at  $373 \text{ cm}^{-1}$  respectively in the Raman spectrum at room temperature and increase in wavenumber slightly to a band at  $389 \text{ cm}^{-1}$  and very weak band at  $382 \text{ cm}^{-1}$  on cooling to  $15^\circ\text{K}$ .

v.  $\nu_5$ , the formally  $a_2$  antisymmetric CuCN bending vibration

This assignment is made on the grounds that the band observed at  $357.5 \text{ cm}^{-1}$  in the Raman spectrum at room temperature is effectively infra-red inactive. The  $a_g$  and  $b_g$  components increase in wavenumbers and separate at  $363 \text{ cm}^{-1}$  and  $358 \text{ cm}^{-1}$  respectively on cooling to  $15^\circ\text{K}$ .

vi.  $\nu_3$ , the totally symmetric CuCN bending vibration.

This assignment is made on the basis of the relative weakness of the infra-red components and the relative strength of the Raman components. The  $b_u$  and  $a_u$  components occur at room temperature in the infra-red spectrum at  $342.5 \text{ cm}^{-1}$  and  $331.5 \text{ cm}^{-1}$  respectively. The  $a_g$  and  $b_g$  components at  $345 \text{ cm}^{-1}$  and as an ill-defined shoulder at  $337 \text{ cm}^{-1}$  respectively in the Raman spectrum at room temperature increase slightly in wavenumber to  $348 \text{ cm}^{-1}$  and a discrete band at  $338 \text{ cm}^{-1}$  on cooling to  $15^\circ\text{K}$ .

vii.  $\nu_6$ , the formally  $b_2$  antisymmetric CuCN bending vibration.

This assignment is made on the basis of the relative strength of the infra-red band and the relative weakness of the Raman components. The  $a_u$  and  $b_u$  components are unseparated at room temperature in the infra-red spectrum at  $305 \text{ cm}^{-1}$ . The  $a_g$  and  $b_g$  components are separated at room temperature in the Raman spectrum at  $315 \text{ cm}^{-1}$  and  $291 \text{ cm}^{-1}$  respectively and increase in wavenumber slightly to  $315 \text{ cm}^{-1}$  and  $298 \text{ cm}^{-1}$  on cooling to  $15^\circ\text{K}$  (A very weak ill-defined shoulder at  $306 \text{ cm}^{-1}$  at room temperature disappears on cooling).

viii.  $\nu_6$ , the formally  $b_1$  antisymmetric CuCN bending vibration.

The  $a_u$  and  $b_u$  components appear unseparated as an ill-defined shoulder at  $286\text{ cm}^{-1}$  in the infra-red spectrum at room temperature. The  $a_g$  and  $b_g$  components are separated at  $279\text{ cm}^{-1}$  and  $272\text{ cm}^{-1}$  respectively in the Raman spectrum at room temperature and decrease in wave number slightly to  $280\text{ cm}^{-1}$  and  $265\text{ cm}^{-1}$  on cooling to  $15^\circ\text{K}$ .

#### Acknowledgements

One of us S.U.Q is thankful to Ministry of Education, Government of Pakistan for providing the financial assistance.

#### References

1. H. Bassett and A. S. Corbet, *J. Chem. Soc.*, **125**, 1660 (1924)
2. K. G. Ashurst, N. P. Finkelstein and L. A. Goold, *J. Chem. Soc. A*, 1899 (1971)
3. H. M. N. H. Irving and A. D. Damodaran, *Anal. Chim. Acta*, **53**, 267. (1971)
4. L. H. Jones, *J. Chem. Phys.*, **29**, 463. (1958)
5. R. A. Penneman and L.H. Jones, *J. Chem. Phys.*, **24**, 293 (1956)
6. F. Spitzer, *Z. Electrochem*, **11**, 345 (1905)
7. D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957)
8. B. R. Carr, Ph. D Thesis, Bradford, 1978.
9. D. G. Cobbold, Ph. D Thesis, Bradford, 1978.