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Walter Gordy and Dudley Williams

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The Infrared Absorption of Cyanides and Thiocyanates

WALTER GORDY AND DUDLEY WILLIAMS, *Physics Department, University of North Carolina*

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Aqueous solutions of seven inorganic cyanides, two thiocyanates, and one cyanate were studied in the region from 1.2μ to 7.5μ . Two organic cyanides and an organic thiocyanate were studied in the same region. In all the materials a characteristic absorption band was observed in the region from 4.38μ to 4.90μ . The exact position of the band was found to be different for the various substances. This characteristic absorption was attributed to changes in

the vibrational energy of the bound CN group. An additional band appearing only in the highly ionized cyanide solutions was attributed to the free CN ions. In the cyanate solution a double band appeared in the region of 7μ which was not characteristic of the cyanide or thiocyanate solutions. Hydrolysis and solvation effects were observed in some of the solutions.

PREVIOUS work has been done on the infrared absorption of organic cyanides and thiocyanates by Coblenz.¹ In other studies² Coblenz also gives infrared data for the potassium ferrocyanide crystal. Choi and Barker³ have made a careful investigation of gaseous HCN and have recorded a number of bands in the region 3μ to 15μ . Recent studies^{4, 5} of the infrared absorption spectra of solutions of certain hydroxides have revealed intense bands in the region 3μ to 6μ . These bands were attributed to changes in the energy levels of the hydroxide molecules attached to the molecules of the solvent. A strong band⁶ has also been observed in aqueous solutions of alkaline hydroxides at 2.3μ and has been attributed to changes in the vibrational energy of the OH ions. The present study was undertaken to ascertain whether similar hydration and dissociation effects could be observed in the case of cyanides and thiocyanates. In addition to these compounds, one cyanate solution was studied, and, for more accurate determination of the position of the bands, some of the earlier measurements of Coblenz on organic cyanides and thiocyanates were repeated.

A Hilger infrared spectrometer was used as a resolving instrument. A fluorite prism was employed for the entire region studied and the cell

windows were likewise of fluorite. In any particular region the cell thickness was maintained constant for all the materials studied, thicknesses being 0.11 mm for the range 1.2μ to 2.5μ and 0.03 mm for the range 2.5μ to 7.5μ . Washers of these thicknesses were made of mica, the same washers being used for all the materials. Concentrations for the various solutions are given in Table I.

In Fig. 1 are shown the results obtained with the solutions in the region from 2.5μ to 7.5μ . No absorption which might be attributed to cyanides or thiocyanates was detected in the region from 1.2μ to 2.5μ , and this part of the spectrum is omitted from the figure. As may be readily seen from this set of curves, all the solutions are strongly absorbing in the region 4.6μ to 4.9μ , the position of maximum absorption varying with the solution. The curve for the NaCN solution is typical of the other cyanides listed in Table I, which are not shown in Fig. 1, in all

TABLE I. Location of observed bands.

SUBSTANCE	CHEMICAL FORMULA	MOLAR CONCENTRATION	CHARACTERISTIC BAND*	ADDITIONAL BANDS*
Hydrocyanic acid	HCN	0.8	4.75	
Sodium cyanide	NaCN	5.0	4.78	5.20
Potassium cyanide	KCN	5.0	4.80	4.44 5.20 4.44
Barium cyanide	Ba(CN) ₂	2.5	4.78	
Potassium silver cyanide	KAg(CN) ₂	1.0	4.66	5.20
Sodium ferrocyanide	Na ₄ Fe(CN) ₆	0.5	4.90	5.20
Potassium ferricyanide	K ₃ Fe(CN) ₆	1.0	4.70	5.20
Potassium thiocyanate	KCNS	7.0	4.84	
Ammonium thiocyanate	NH ₄ CNS	7.0	4.84	3.46 6.94
Potassium cyanate	KCNO	5.0	4.62	7.10 7.40
Methyl cyanide	CH ₃ CN	Pure liquid	4.38	3.24
Benzyl cyanide	C ₆ H ₅ CH ₂ CN	Pure liquid	4.40	3.24
Methyl thiocyanate	CH ₃ CNS	Pure liquid	4.62	3.32

* Wave-lengths are given in microns.

¹ W. W. Coblenz, *Investigations of Infrared Spectra*, p. 60, Carnegie Institution of Washington, 35 (1905).

² W. W. Coblenz, *Investigations of Infrared Spectra*, p. 26, Carnegie Institution of Washington, 65 (1900).

³ K. N. Choi and E. F. Barker, *Phys. Rev.* **42**, 777 (1932).

⁴ E. K. Plyler and W. Gordy, *J. Chem. Phys.* **2**, 420 (1934).

⁵ E. K. Plyler and F. D. Williams, *J. Chem. Phys.* **2**, 565 (1934).

⁶ Walter Gordy, *J. Chem. Phys.* **2**, 621 (1934).

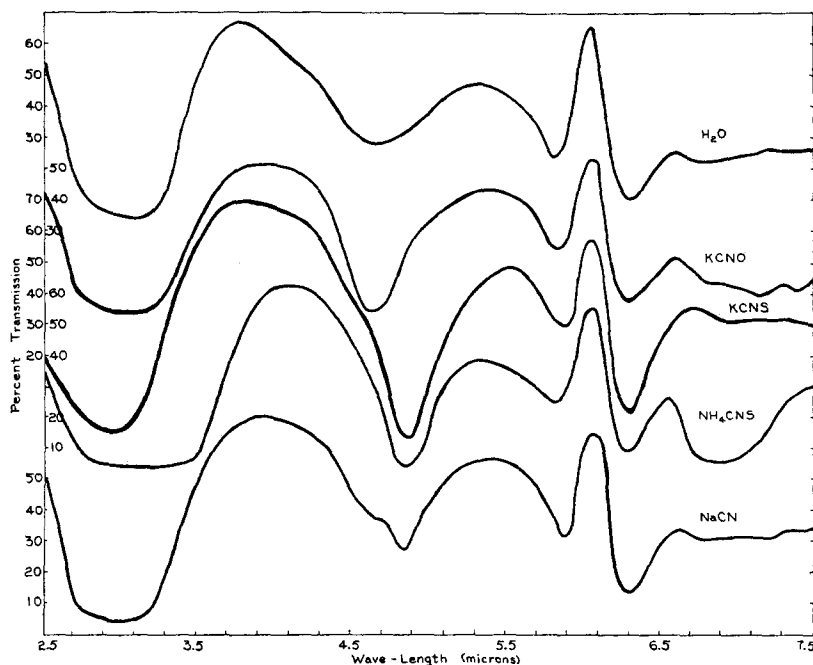


FIG. 1. The percent transmission of typical cyanides, cyanates, and thiocyanates in aqueous solution in the region from 2.5μ to 7.5μ .

parts of the spectrum except 4.6μ and 4.9μ . Their transmissions in this region are given in a different figure. In the case of the thiocyanates the 3μ water band seems to be definitely shifted to shorter wave-lengths. Since this shift was not observed in any of the other compounds studied, it is probably due to a solvation effect in which the linkage is between the sulphur and the water. Another evidence of solvation is the marked increase in the transmission of water in certain regions, which is evident from the figure. This solvation effect is somewhat masked in the case of ammonium thiocyanate by the absorption of the NH_4 group. Reinkober⁷ in a study of aqueous solutions of ammonium salts has recorded absorption bands in the regions from 3.09μ to 3.57μ , 4.66μ to 4.85μ , and 6.90μ to 7.12μ . Ammonium thiocyanate was not investigated by Reinkober. Our data reveal the position of the NH_4 bands for this salt to be 3.46μ and 6.94μ . Other bands

occurring in the region from 4.6μ to 4.9μ prevented an exact determination of the position of the third NH_4 band.

The transmission curve for potassium cyanate shows absorption in the region of 7μ , which is not characteristic of the other potassium salts nor of the other cyanides and thiocyanate solutions. Plotting the ratio of the absorption of this solution to that of water in this region reveals a broad double band with absorption maxima at 7.1μ and 7.4μ . No similar absorption occurs for the other salts, and these bands are to be attributed to the cyanate radical. Nitrate crystals⁸ show characteristic bands near 7.2μ and carbonate crystals⁹ at 6.9μ . Since the double band observed in the case of the cyanates is not a characteristic cyanide vibration, it is possible that the components of the band at 7.1μ and 7.4μ are due to other

⁸ C. Schaeffer and M. Schubert, *Ann. d. Physik* **50**, 283 (1916).

⁹ C. Schaeffer, C. Bormuth and F. Matossi, *Zeits. f. Physik* **39**, 648 (1926).

⁷ O. Reinkober, *Zeits. f. Physik* **35**, 179 (1925).

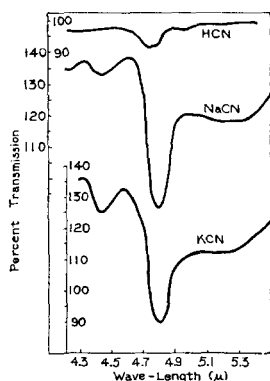


FIG. 2. The ratio of the transmission of HCN, NaCN, and KCN solution to that of water from 4.1μ to 5.5μ .

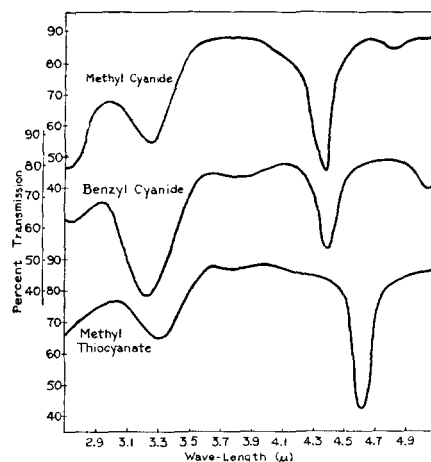


FIG. 3. The percent transmission of two organic cyanides and one organic thiocyanate in the region 2.7μ to 5.1μ .

fundamental frequencies of the CNO group in which a CO vibration and an NO vibration are active.

The HCN, NaCN, and KCN solutions were found to have bands at 4.75μ , 4.78μ , and 4.80μ , respectively, while NaCN and KCN showed less intense bands at 4.44μ and 5.20μ , as may be seen from Figs. 2 and 3. Methyl cyanide shows an intense band at 4.38μ , and benzyl cyanide at 4.40μ . These are shown in Fig. 3. Since this absorption is not characteristic of the organic groups,¹⁰ it is to be attributed to the CN group. There is a striking dissimilarity between the absorption of the KCN and NaCN solutions and that of other substances containing the CN group in that they show three well resolved bands. The absorption at 5.20μ is doubtless due to NaOH and KOH formed by hydrolysis, a band at this position having been previously reported by Plyler and Gordy.⁴ The presence of the band at 4.44μ can be attributed to the CN ion liberated by these highly ionized salts. No band was observed at 4.44μ in the HCN solution. The absence of this band is explained by the extremely low degree of ionization of hydrocyanic acid. The bands at 4.75μ , 4.78μ , and 4.80μ in the HCN, NaCN, and KCN, respectively, are due to vibrational energy changes of the CN group in the molecule. The shift between the bands in KCN and NaCN is not as great as would be expected from considerations of atomic

weights. In this case the shift to be expected from the differences in atomic weight is probably counteracted by a change in the binding force produced by the two metals.

The transmission of the complex cyanides as compared to water is given in Fig. 4. The $\text{Ba}(\text{CN})_2$ curve shows an absorption band with maximum absorption at 4.78μ . The low intensity of this band is accounted for by the slight solubility of this salt. The double salt $\text{KAg}(\text{CN})_2$ has maximum absorption at 4.66μ . The additional absorption at 5.20μ reveals either hydrolysis effects or the presence of an impurity. In this case there is no band which can be attributed to the CN ion, a result in accord with chemical data which show that $\text{KAg}(\text{CN})_2$ would give on hydrolysis potassium ions and argenti-cyanide ions $(\text{Ag}(\text{CN})_2^-)$ instead of simple K^+ , Ag^+ , and CN^- . The position of the band in the barium salt at the longer wave-length is to be expected from a comparison of the atomic weights of barium and silver. A comparison of the absorption of the complex cyanides $\text{Na}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ shows a marked difference of band position. From chemical data it is known that there is a high degree of ionization, the solutions yielding ions of the type $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively. Since the atomic weight of the metallic constituent is the same for both ions, the shift

¹⁰ E. K. Plyler and T. Burdine, *Phys. Rev.* **35**, 605 (1929).

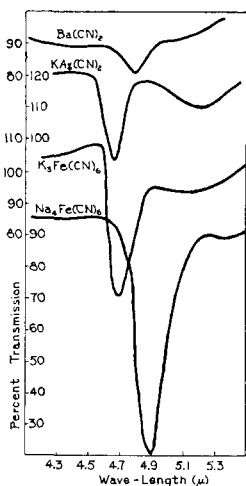


FIG. 4. The percent transmission of solutions of complex cyanides compared to water from 4.1μ to 5.5μ .

can be due only to the variations in the CN binding produced by the difference in valence of the ferrous and ferric iron.

Fig. 5 shows the ratio of the transmission of KCNO, KCNS, and NH_4CNS to that of water in the region 4.1μ to 5.5μ . The strong band appearing in this region is again to be attributed to the CN vibration. The band in KCNO appears at a much shorter wave-length than in KCNS. Since the cation is the same in both cases, this shift is produced by the variation of the atom associated with the CN group in the anion. The shift of the KCNS band from the band attributed to the CN ion is approximately twice that of the KCNO, a fact which is in approximate agreement with the differences in the atomic weights of sulphur and oxygen. This direct dependence upon atomic weight indicates similar binding in the CNO and CNS groups. There is no appreciable shift between the NH_4CNS and KCNS bands at 4.84μ , a result indicating either that the absorption is due to the CNS ion or that the binding force between the metal and the CNS group is extremely weak.

In the case of the organic thiocyanate the characteristic band is at a definitely shorter wave-length than in the inorganic thiocyanates. The reason for this seems to be that the sulphur atom is associated with the organic group as

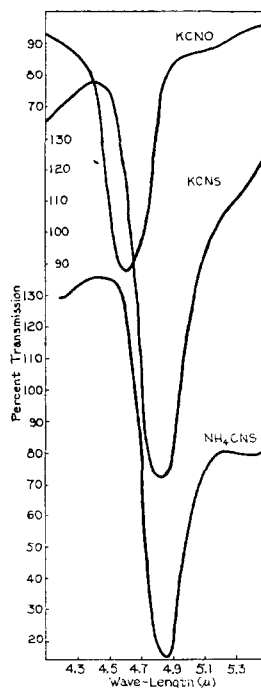


FIG. 5. The ratio of the transmission of some thiocyanate and cyanate solutions to that of water in the region from 4.1μ to 5.5μ .

CH_3S . Other evidence of this association lies in the marked shifts of the methyl band near 3.3μ to a longer wave-length, as will be observed in a comparison of the first and last curves of Fig. 3. In the curves for the organic cyanides the CN band appears at a shorter wave-length than in the inorganic compounds, a fact indicating closer CN binding in these compounds.

From a consideration of the variation of the maxima of the bands occurring near 4.8μ in HCN, KCN, and NaCN, we have concluded that these bands are due to the CN group in the molecule rather than to the CN ion. The appearance of the absorption of the CNS group so near to that of these molecules indicates similar binding in the CNS group and in the simple cyanide molecules.

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