

The InfraRed Absorption of Silver Cyanide

W. David Stallcup and Dudley Williams

Citation: *The Journal of Chemical Physics* **10**, 199 (1942); doi: 10.1063/1.1723707

View online: <http://dx.doi.org/10.1063/1.1723707>

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was reported by Bell and Davey. Further studies were made, demonstrating the fact that impure radiation can give rise to a secondary peak at small angles. It is suggested that it may be possible that this is the origin of Bell and Davey's secondary peak, caused by a slight unbalance of their balanced filters.

Using the Geiger-Mueller counter method, as Bell and Davey did, but with pure radiation and with geometrical conditions at least as good as in their work, no fine structure could be obtained. Slight fluctuations of the observed points about a smooth curve are not large enough to establish

fine structure, and these fluctuations are considered to be wholly statistical.

It is concluded, further, that the extensive deductions made by Bell and Davey are without experimental foundation.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge that this work was supported in part by grants from the Rumford Fund of the American Academy of Arts and Science, the American Association for the Advancement of Science, and the Elizabeth Thompson Science Fund.

APRIL, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

The Infra-Red Absorption of Silver Cyanide

W. DAVID STALLCUP AND DUDLEY WILLIAMS

University of Florida, Gainesville, Florida

(Received January 17, 1942)

The spectrum of powdered AgCN has been studied in the region $2500\text{--}1800\text{ cm}^{-1}$. Intense absorption at 2178 cm^{-1} is attributed to an oscillation involving the CN group. The CN frequency for AgCN is almost 100 cm^{-1} higher than the CN frequencies of NaCN and KCN.

INVESTIGATIONS of the infra-red and Raman spectra of the organic cyanides have revealed the existence of a vibrational frequency of approximately 2245 cm^{-1} which is characteristic of the CN groups, while similar studies of the organic isocyanides indicate that the NC group has a characteristic frequency of $2146\text{--}2161\text{ cm}^{-1}$. The simpler inorganic cyanides, NaCN and KCN, have CN frequencies of approximately 2080 cm^{-1} , while in the complex cyanides such as $\text{KAg}(\text{CN})_2$ and $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ the characteristic frequencies are in the neighborhood of 2150 cm^{-1} .^{1,2} It has been suggested by several workers³ that in inorganic cyanides the CN frequency increases when there

is an increase in the homopolar nature of the M-CN binding.

It seemed desirable to test this hypothesis by determining the CN frequency for a simple cyanide in which the M-CN bond possesses some homopolar properties. As the existing data provide only comparisons of NaCN and KCN with double cyanides and with complex cyanides of the type mentioned above, the study of the infra-red spectrum of AgCN for comparison with NaCN immediately suggested itself, since the homopolar properties of the silver salts are well known.⁴

The silver cyanide used in the present work was prepared by adding an equimolecular amount of potassium cyanide solution to an approximately $0.1M$ solution of silver nitrate with constant and vigorous stirring. After precipitation was complete, the supernatant liquid was decanted and the precipitate was placed in a two

¹ Summary of the Raman data: K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931), p. 320; J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold, New York, 1939), p. 452.

² Infra-red data: W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935); **4**, 85 (1936); F. K. Bell, *J. Am. Chem. Soc.* **57**, 1023 (1935).

³ P. Krishnamurti, *Ind. J. Phys.* **5**, 651 (1930); R. Samuel and M. J. Khan, *Zeits. f. Physik* **84**, 87 (1933); Volkenshtein, *Acta Physicochim.* (U. S. S. R.) **7**, 315 (1937).

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940), p. 73.

and a half foot large glass test tube. A fine jet of water was then directed into the precipitate. In this manner the precipitate was continuously washed for two days. The precipitated silver cyanide was then collected and dried.

The spectrometer used was a rocksalt prism instrument of the Littrow type. The samples used in making the absorption measurements consisted of layers of powder deposited on fluorite plates. The thickness of the absorbing layers varied from 0.02 to 0.05 mm in different samples. As the mean diameter of the particles was approximately three microns, considerable scattering took place in the spectral region studied. In order to minimize this scattering the powder was immersed in carbon tetrachloride in some of the cells.⁵

Figure 1 illustrates the type of transmission curve obtained with powdered AgCN. Curve A represents the transmission of a typical sample, the dotted curve giving the estimated background due to scattering. Curve B shows the transmission of AgCN when corrected for scattering. It will be noted that there is an intense absorption band with maximum at 4.59μ . This band was observed for a number of different

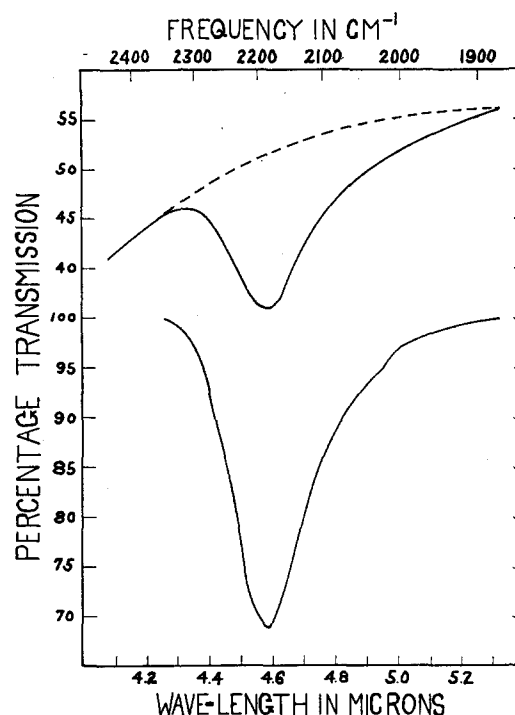


FIG. 1. The transmission of silver cyanide in the 2500–1800 cm^{-1} region.

cells, and the frequency of maximum absorption was found to be 2178 cm^{-1} .

Table I summarizes the pertinent infra-red and Raman data for several types of cyanides. It will be noted that the CN frequency in AgCN is almost 100 cm^{-1} higher than for NaCN and KCN. This result is in accord with the suggestion that increasing homopolarity is accompanied by increases in the CN frequency. It might be mentioned in passing that the AgCN frequency actually falls in the range of the organic isocyanide, NC, frequencies, although many factors render unjustifiable any suggestion of similarity in structure from spectroscopic evidence. Included in the table are data for two divalent cyanides, $\text{Ba}(\text{CN})_2$ and $\text{Hg}(\text{CN})_2$. In this case also the compound having the higher degree of homopolarity has the higher CN frequency. It will be observed from the table that none of the inorganic cyanides yet studied has as great a CN frequency as that characteristic of the organic cyanides.

TABLE I. The CN oscillational frequencies in various compounds.

Compound	Infra-red	Raman
NaCN	2080 GW	2085 K
KCN	2080 GW	2081 P-SG
AgCN	2178 PS	—
$\text{Ba}(\text{CN})_2$	2080 GW	—
$\text{Hg}(\text{CN})_2$	—	2192 K
CH_3NC	2183 GW	2161 B
$\text{C}_2\text{H}_5\text{NC}$	2159 GW	2146 B
CH_3CN	2285 GW	2250 P-SG
$\text{C}_2\text{H}_5\text{CN}$	2258 GW	2246 DK

K—Krishnamurti, Ind. J. Phys. 5, 633 (1930).

P-SG—Pal and Sen Gupta, Ind. J. Phys. 5, 13 (1930).

DK—Dadiou and Kohlrausch, Wien Ber. 139, 165 (1930).

B—Bhagavantam, Ind. J. Phys. 5, 48 (1930).

GW—W. Gordy and D. Williams, J. Chem. Phys. 3, 664 (1935); 4, 85 (1936).

PS—Present study.

⁵ Carbon tetrachloride has no absorption bands in the range 2500–1800 cm^{-1} which was studied.