

Effects of Isomerism on Infrared Absorption Spectra

Walter Gordy and Dudley Williams

Citation: [The Journal of Chemical Physics](#) **4**, 85 (1936); doi: 10.1063/1.1749804

View online: <http://dx.doi.org/10.1063/1.1749804>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Effect of porosity on infrared absorption spectra of silicon dioxide](#)

J. Appl. Phys. **77**, 1805 (1995); 10.1063/1.358877

[The Far Ultraviolet Absorption Spectra of Selected Isomeric Hexenes](#)

J. Chem. Phys. **22**, 1266 (1954); 10.1063/1.1740362

[The Far Ultraviolet Absorption Spectra of the Isomeric Butenes](#)

J. Chem. Phys. **22**, 599 (1954); 10.1063/1.1740132

[Infrared Absorption Spectra](#)

Phys. Today **4**, 26 (1951); 10.1063/1.3067075

[Near Ultraviolet Absorption Spectra of the Isomeric Picolines](#)

J. Chem. Phys. **17**, 587 (1949); 10.1063/1.1747337



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

FEBRUARY, 1936

NUMBER 2

Effects of Isomerism on Infrared Absorption Spectra

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

(Received November 7, 1935)

The absorption spectra of four organic cyanides, two organic thiocyanates, and the corresponding isomers have been studied in the region from 1.0μ to 6.5μ . The intense band appearing near 4.4μ in the normal cyanides appears at a longer wave-length and with doubled intensity in the isocyanides, the variation in wave-length and intensity being nearly constant for all compounds. In the case of the thiocyanates the variation in wave-length of the 4.6μ

band for the two configurations is less than in the cyanides, whereas the intensity differences are greater. No other bands in these organic compounds were appreciably affected by isomerism. In the absorption spectrum of aqueous solutions of hydrocyanic gas there appears an intense band at 4.75μ and also a less intense band at 4.95μ . The band at 4.95μ can be attributed to a small amount of the isomer HNC.

COBLENTZ¹ in his studies of the infrared absorption of isomeric organic compounds found that differences in the structure of the molecules are accompanied by differences in spectra, the effects being more pronounced in the region of longer wave-lengths. In many cases the spectra of isomers are identical up to about 6μ , at which point marked shifts begin to appear. Other studies² made by Weniger on alcohols, acids, and esters show that the greater the difference in structure between isomers, the greater the difference in their spectra.

Recently the authors have investigated the absorption spectra of thirteen cyanides and thiocyanates.³ For each of these compounds a well-defined band was observed in the region between 4.4μ and 4.9μ , the exact position of the band being different for different compounds. The absorption in this region was attributed to fundamental frequencies of the cyanide and thio-

cyanate molecules in which a CN vibration is active. It was the purpose of the present investigation to ascertain the effects of isomerism on this characteristic vibration. The isocyanides are different from isomers previously studied in that the carbon is divalent in the isocyanides and tetravalent in the normal cyanides.

The experimental method was the same as that used in the previous investigation.³ A Hilger spectrometer with a fluorite prism was used for the entire region from 1.0μ to 6.5μ . Cell windows were of fluorite, and the thickness of the absorbing layer was 0.03 mm for all materials studied unless otherwise specified.

Absorption curves for four cyanides and the corresponding isocyanides are shown in Fig. 1. The solid lines represent the percent transmission of the cyanides; the broken lines, that of the isocyanides. The band in the region of 3.25μ is characteristic of the group associated with the cyanide group and is found in other methyl, ethyl, butyl, and phenyl compounds.^{2, 4} Within the limits of experimental error the position and

¹ W. W. Coblentz, *Investigations of Infrared Spectra* 1-2, (Carnegie Institution of Washington, 35, 1905), pp. 101-102.

² W. Weniger, *Phys. Rev.* **31**, 388 (1910).

³ W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935).

⁴ E. K. Plyler and T. Burdine, *Phys. Rev.* **35**, 605. (1930).

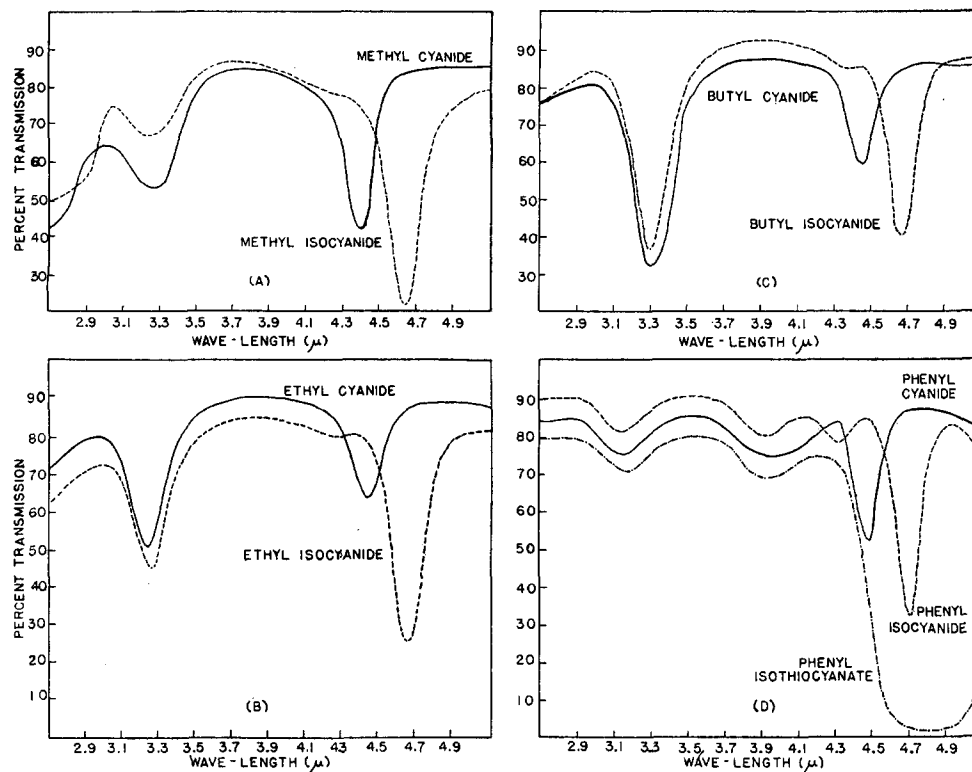


FIG. 1. (a) Transmission of methyl cyanide and methyl isocyanide. (b) Transmission of ethyl cyanide and isocyanide. (c) Transmission of butyl cyanide and isocyanide. (d) Transmission of phenyl cyanide, phenyl isocyanide, and phenyl thiocyanate 2.7μ to 5.1μ .

intensity of this band are the same for both isomeric forms, the band arising from the methyl group being a possible exception. The characteristic cyanide band in the region of 4.6μ is shifted to the longer wave-lengths by about 0.2μ and

TABLE I.

	BAND POSITIONS		VARIATION IN WAVE-LENGTH $\Delta\lambda$	RATIO OF BAND INTENSITY Isocyanide to Cyanide
	Cyanide	Isocyanide		
Methyl	3.25μ	3.25μ	0.00μ	0.7
	4.38	4.58	0.20	2.0
Ethyl	3.22	3.25	0.03	1.0
	4.43	4.63	0.20	2.0
Butyl	3.30	3.30	0.00	1.0
	4.45	4.65	0.20	2.0
Phenyl	3.16	3.14	-0.02	1.0
	4.48	4.71	0.23	1.9
	Thio- cyanate	Isothiocy- anate		
Methyl	3.32	3.32	0.00	1.3
	4.64	4.70	0.06	3.8
Ethyl	3.28	3.29	0.01	1.0
	4.63	4.75	0.12	3.9

its intensity is approximately doubled in the isocyanides. Furthermore, these variations in wave-length and intensity are approximately constant for all the compounds studied. The shift in wave-length is in agreement with the chemical data which indicate divalent carbon in the isocyanides and hence weaker binding forces. Table I gives a numerical comparison of band positions and intensities for corresponding compounds.

The earlier work of Coblenz¹ on two thiocyanates and the corresponding mustard oils was repeated for purposes of intensity comparison and for more accurate determination of band position. The absorption curves for methyl and ethyl thiocyanates and their isomers are given in Fig. 2. As may be seen from the figure, the shifts due to isomerism are different for the two and in both cases are less than the corresponding shift for the cyanides. On the other hand, the intensity variation is much greater than in the case of the cyanides. As before there is no apparent shift in the

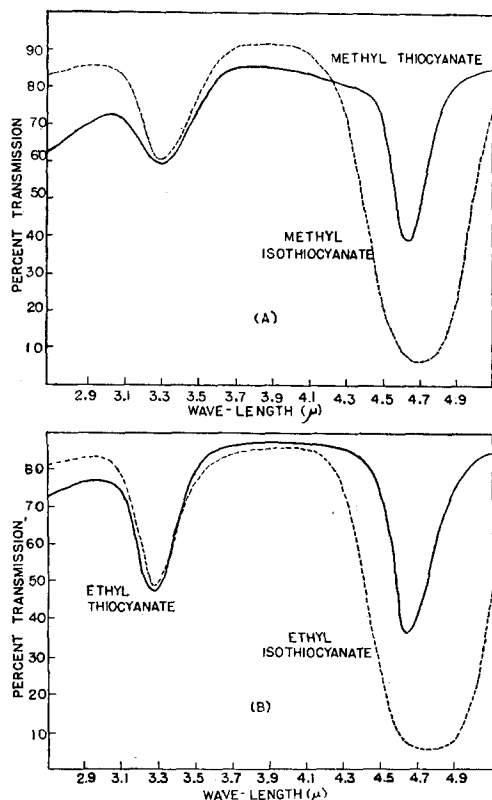


FIG. 2. (a) Transmission of methyl thiocyanate and isothiocyanate. (b) Transmission of ethyl thiocyanate and isothiocyanate. Region: 2.7μ to 5.1μ .

band characteristic of the associated methyl and ethyl groups. The absorption of phenyl thiocyanate was measured and is given in Fig. 1 with the other phenyl compounds.

The fact that the band in the 4.6μ region varies while the 3.25μ band remains constant indicates that both these bands depend primarily on the structure of certain groups rather than upon the structure of the molecule as a whole. Although a survey was made of the whole region from 1.0μ to 6.5μ , no bands were observed which could be classified either as harmonics of the 4.6μ band or as combinations involving this characteristic frequency. This is further indication of a simple type of binding between the carbon and nitrogen atoms, which is only slightly modified by associated groups in the molecule.

Nef⁵ has proposed the two configurations, HCN and HNC, for hydrocyanic gas. If both configurations be present in a given sample, it should be possible to observe two bands in the region of 4.7μ . In the previous investigations,

⁵ J. V. Nef, J. Am. Chem. Soc. **26**, 1549 (1904).

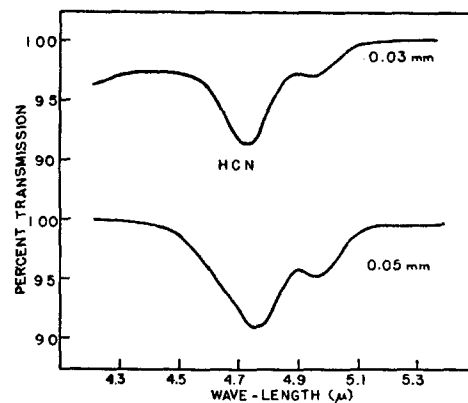


FIG. 3. The ratio of the transmission of hydrocyanic acid solution to that of an equal thickness of water for two cell thicknesses. Region: 4.1μ to 5.5μ .

the authors obtained an absorption curve showing a band at 4.75μ characteristic of HCN in aqueous solution. In this absorption curve there is also a slight depression at 4.95μ . For greater cell thickness this depression becomes deeper and can be interpreted as arising from the isomer HNC. In Fig. 3 are given the transmission curves of hydrocyanic acid for two cell thicknesses. On account of the different absorption coefficients for CN and NC compounds it is impossible to ascertain very accurately the relative abundance of the isomers, but it is evident from the figure that the amount of HNC present is very small, as is to be expected from chemical theory.⁶ Assuming the absorption coefficient of HNC to be twice that of HCN, as is the case for the other isomers studied, we estimate the concentration of HNC to be from two to four percent that of HCN.

Barker⁷ and Choi and Barker⁸ have studied the absorption of gaseous HCN, but have reported no absorption in the region of 4.9μ . This region may have been beyond the range of their investigation, as their published curves for this part of the spectrum extend only from 4.68μ to 4.86μ . A second possibility is that the isomer HNC may be more abundant in aqueous solution than in the gas.

The authors wish to express their thanks to Professor E. K. Plyler for his helpful discussion of the manuscript and to Mr. G. C. Kyker of the Chemistry Department, who prepared the chemicals and offered valuable suggestions.

⁶ J. Schmidt, *Text Book of Organic Chemistry*, (D. Van Nostrand Co., 1932), p. 323.

⁷ E. F. Barker, Phys. Rev. **23**, 200 (1924).

⁸ K. N. Choi and E. F. Barker, Phys. Rev. **42**, 777 (1932).