

The Intensities of Several of the InfraRed Absorption Bands of Cyanogen and Cyanogen Chloride

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the force constants f_{CC} and f_{CCl} were found to vary by $\pm 0.7 \times 10^5$ and $\pm 0.3 \times 10^5$ dynes/cm respectively. Effects due to other cross terms were not investigated, but it is to be expected that they will cause much smaller variations in f_{CCl} than the above term. We may somewhat arbitrarily select a value of 5.0×10^5 dynes/cm as a reasonable lower limit to f_{CCl} ; this corresponding to a positive interaction constant and allowing for small variations from other sources.

VI. DISCUSSION

For an essentially covalent carbon-chlorine bond (in a molecule such as CH_3Cl) the carbon-chlorine stretching force constant has a value $\sim 3.6 \times 10^5$. The value of $f_{CCl} \geq 5.0 \times 10^5$ in chloroacetylene, therefore, indicates considerable stiffening of the bond. We ascribe this to resonance between the covalent structure and the double-bonded $\text{H}-\text{C}^-=\text{C}=\text{Cl}^+$. We might also expect

a corresponding softening of the carbon-carbon bond, and the value of 14.9×10^5 for f_{CC} is rather lower than its value in acetylene and other molecules where such resonance cannot occur. However, it must be noted that the uncertainty in the values of the interaction terms puts the true value of f_{CC} in considerable doubt, and no valid deductions can be made from it. It is also to be expected that for a molecule which is a resonance hybrid of the above type the stretch-stretch interaction terms will be positive and at least for the one term investigated this leads to higher values of f_{CC} .

VII. ACKNOWLEDGMENT

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The Intensities of Several of the Infra-Red Absorption Bands of Cyanogen and Cyanogen Chloride*

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Measurement of the absolute intensities of several infra-red absorption bands of cyanogen and cyanogen chloride gives the following values in cycles per cm at N.T.P.

Cyanogen	Band 2150 cm^{-1}	Intensity 90×10^{10}
Cyanogen chloride	Band 714 cm^{-1} 2214 cm^{-1}	Intensity 17×10^{10} 220×10^{10}

Values of the variation in bond moments with change in bond length are calculated on the basis of bond moment additivity. This leads to widely different values of this derivative for the CN bond in the two molecules.

The infra-red spectrum of cyanogen chloride from 2 to 20 microns is reported.

INTRODUCTION

RECENTLY Wilson and Wells¹ have described an experimental method by which the intensities of infra-red absorption bands may be determined to a fair degree of accuracy even with a spectrometer of ordinary resolution. This method has been used here to

measure the intensities of the 2150 cm^{-1} band of cyanogen and the 714 cm^{-1} and 2214 cm^{-1} bands of cyanogen chloride. Errors in the measurements are estimated as less than \pm ten percent.

In the Wilson-Wells method (and using their terminology) the integrated apparent absorption, \mathcal{B} , given by the equation

$$\mathcal{B} = pLB = \int (\ln T_0/T) d\nu \quad (1)$$

is measured for a given band at a series of values of the product pL . In this expression p is the pressure of the absorbing gas; L is the cell length; T_0 the light transmitted by the empty cell; T the light transmitted by the sample cell; and the integration is carried over the

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¹ E. Bright Wilson, Jr. and A. J. Wells, *J. Chem. Phys.* 14, 578 (1946).

width of the band. If the fine structure of the band is satisfactorily eliminated by pressure broadening and corrections are made for any atmospheric absorption or stray light, the true band intensity is then the value of B obtained by extrapolation to $pL=0$.

In a first approximation the true intensity A_k of the k th fundamental vibrational band is related to the molecular parameters by the expression

$$A_k = (N\pi/3c) |\partial \mathbf{u} / \partial Q_k|^2, \quad (2)$$

in which N is the number of molecules per unit volume, c is the velocity of light, \mathbf{u} is the dipole moment of the molecule and Q_k is the normal coordinate for the particular vibrational mode. If it is assumed that bond moments are additive and depend only upon bond lengths and if the normal coordinates are known in terms of internal coordinates, it is then possible to reduce band intensities to values of either the individual bond moments μ_i , or rates of change of bond moments with internuclear distances $(\partial \mu / \partial r)_i$.

The instrument used in this investigation was a Perkin-Elmer Spectrometer Model 12B, modified by a double beam arrangement, which allowed rapid comparison of the transmission of the filled and empty cells.

CYANOGEN

The cyanogen was prepared by the thermal decomposition of mercuric cyanide. A charge of Mallinckrodt Analytical Reagent $Hg(CN)_2$ was preheated to assure dryness, then decomposed at $550-600^\circ$. The gas evolved was passed through P_2O_5 and condensed in a dry ice trap; the crystalline condensate was twice fractionally sublimed, each time the bottom fraction (about 30 percent) being discarded.

The experimental values of the integrated apparent absorption for the 2150 cm^{-1} band are shown in Fig. 1. It can be seen that the addition of one atmosphere of nitrogen as a broadening agent produces only a minor increase in \mathcal{B} . This was taken to mean that for the spectrometer resolution in this spectral region the fine structure of the band is already essentially eliminated in pure cyanogen by self broadening and that the one atmosphere of nitrogen is adequate for the pressure broadening effect. It might be expected that larger values of the integrated apparent absorption would result from the use of smaller slit widths and hence greater resolving power but the scattering of the data due to experimental error obscures such a relation. Because of this scattering of experimental data, the intensity was calculated from values of \mathcal{B} taken from the smooth curve in Fig. 1. These "smoothed" values of \mathcal{B} determine the curve $B = \mathcal{B}/PL$ which extrapolates at $PL=0$ to an intensity of 90×10^{10} cycles per cm at N.T.P. for the 2150 cm^{-1} band.²

² There is a slight complication here in that the band at 2150 cm^{-1} overlaps a weaker one on the low frequency side. Bailey and Carson (J. Chem. Phys. 7, 859 (1939)) report the center of the weaker band at 2093 cm^{-1} and its intensity as 15 percent of that

With a potential function containing only harmonic valence forces, the normal coordinate for the vibrational mode corresponding to this band, which Herzberg³ labels ν_3 , is given by $Q_3 = 2.32 \times 10^{-12}(r_1 - r_2)$ where r_1 and r_2 represent changes in the two C-N distances. The assumptions of bond moment additivity then lead to $(\partial \mu / \partial r)_{CN} = \pm 0.72 \times 10^{-10}$ (c.g.s. units), the ambiguity in sign resulting from the quadratic relation in (2).

CYANOGEN CHLORIDE

Samples of cyanogen chloride were prepared and purified according to the method of Coleman, Leeper and Schulze.⁴

Prior to intensity measurements, the infra-red spectrum of the gas in the region from 2 to 20 microns was investigated. The results of this work are given in Fig. 2 and Table I. A survey in the thallium bromiodide prism range revealed an additional strong absorption band centering at about 390 cm^{-1} , but neither the frequency nor the intensity of this band could be de-

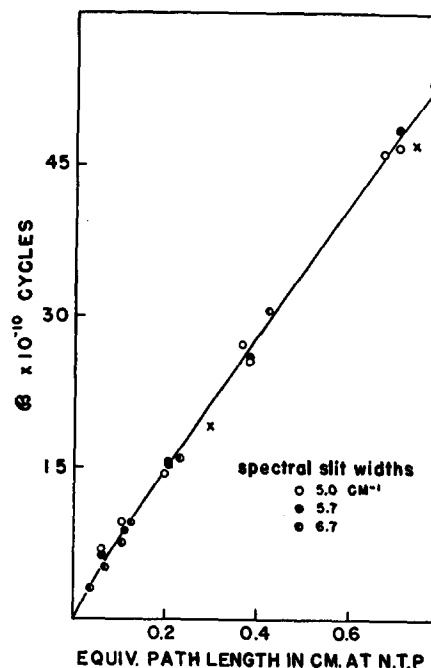


Fig. 1. Experimental values of \mathcal{B} , the integrated apparent absorption, for the 2150 cm^{-1} band of cyanogen as a function of the pressure of cyanogen. The circles represent determinations in which nitrogen was added to give a total pressure of one atmosphere. The x represents cases in which no broadening agent was added.

of the 2150 cm^{-1} band. It is difficult to see from the data given in their paper how they arrived at this value for the relative intensity. The present work indicates that the 2093 cm^{-1} band is much weaker than this and its contribution to the intensity of the 2150 cm^{-1} band has hence been neglected.

³ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 294.

⁴ *Inorganic Syntheses* (McGraw-Hill Book Company, Inc., New York, 1946), Vol. II, p. 90.

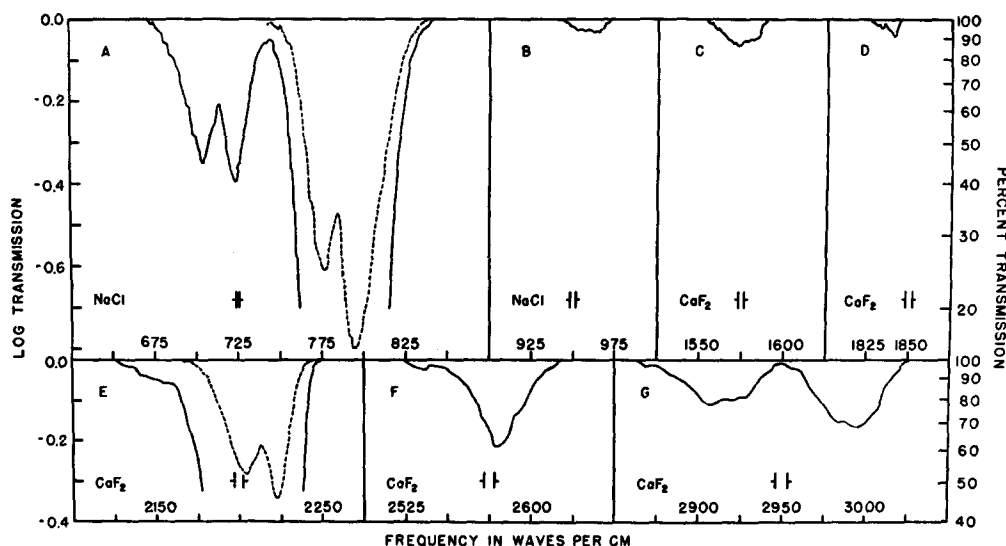


FIG. 2. Infra-red spectrum of cyanogen chloride at 25°, 10-cm path length and pressure of 45.5 cm Hg (solid line). Dashed lines represent 21.0-cm pressure in (A) and 3.3 cm pressure in (E).

TABLE I. Infra-red band centers and assignments in cyanogen chloride.

Frequency (cm ⁻¹)	Assignment
(390)	ν_2
714	ν_1
784	$2\nu_2$
960	?
1573	?
1840	?
2214	ν_3
2580	$\nu_3 + \nu_2$
2915	$\nu_3 + \nu_1$
2995	$\nu_3 + 2\nu_2$

terminated accurately because of the presence of a considerable amount of stray radiation and the lack of a precise prism calibration.

In the Raman spectrum of liquid cyanogen chloride, West and Farnsworth⁵ found strong lines at 397, 729 and 2201 cm⁻¹ which they assigned as the three fundamental vibrations. A very weak line at 809 cm⁻¹ they assumed to be the first overtone of the bending mode. It thus seems reasonable to assign the strong infra-red bands at 390, 714 and 2214 cm⁻¹ as the three fundamentals for the gas. Table I includes these assignments given according to Herzberg's numbering.⁶

Several remarks on the spectrum of cyanogen chloride seem to be in order. First, the appearance of weak bands at 960 and 1573 cm⁻¹ is almost certainly caused by impurities. One sample of the gas was prepared in which there was no trace of absorption at these frequencies. This sample was discarded, however, because it contained an estimated 0.4 percent of CO₂, the result of a slight decomposition. Second, the band at 1840 cm⁻¹, which appeared in all the samples of cyanogen chloride prepared, is unaccounted for but may be due to an impurity not readily removed by the methods of purification employed here. Thirdly, from the pre-

liminary work, the bending fundamental ν_2 (390 cm⁻¹) appears to be no more intense, possibly weaker, than $2\nu_2$ (784 cm⁻¹), but as stated before, estimation of intensities is somewhat uncertain in the 390 cm⁻¹ range. Lastly it should be pointed out that there is the possibility of Fermi resonance between levels ν_1 and $2\nu_2$ and levels $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$. The magnitude of such resonance cannot be determined from the available data and so resonance effects have been neglected in the

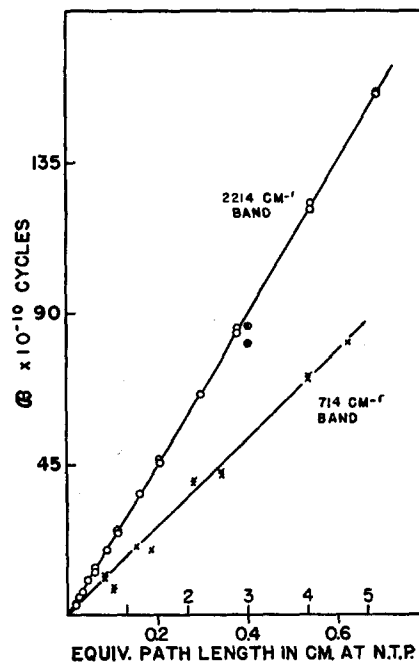


FIG. 3. Experimental values of R , the integrated apparent absorption, for the 714 cm⁻¹ and 2214 cm⁻¹ bands of cyanogen chloride as a function of the pressure of cyanogen chloride. The upper abscissa scale applies to the 714 cm⁻¹ band. The open circle and \times represent experiments in which nitrogen was added to give a total pressure of one atmosphere, the half-filled circle represents the case with one-half atmosphere of nitrogen; the completely filled circle the case with no foreign gas present.

⁵ W. West and M. Farnsworth, J. Chem. Phys. 1, 402 (1933).

⁶ See reference 3, p. 174.

TABLE II. Force constants, normal coordinates and bond moment derivatives of cyanogen chloride as a function of the interaction constant k_{12} .

k_{12}	k_1 (in units of 10 ⁵)	k_2	L_{11}^{-1}	L_{12}^{-1} (in units of 10 ⁻¹²)	L_{11}^{-1}	L_{11}^{-1}	$(\partial\mu/\partial r)_{\text{CCl}}$ (in units of 10 ⁻¹⁹)	$(\partial\mu/\partial r)_{\text{CN}}$ (in units of 10 ⁻¹⁹)
0.0	4.93	17.05	4.96	3.01	0.524	-2.98	0.41	1.84
							0.92	1.03
0.5	4.77	17.71	4.98	2.95	0.407	-3.05	0.47	1.87
							0.86	1.08
1.0	4.63	18.34	4.99	2.86	0.294	-3.11	0.43	1.88
							0.81	1.12
5.0	4.86	22.49	4.97	2.36	0.468	3.51	0.89	2.01
							0.44	1.38

calculation of force constants and bond moment derivatives discussed below.⁷

Experimental data for the intensities of ν_1 and ν_3 are shown in Fig. 3. Again one atmosphere of nitrogen proved to be adequate for the pressure broadening effect. In the same manner as described for cyanogen, "smoothed" values of \mathcal{B} were used in the extrapolation process, leading to 17×10^{10} and 220×10^{10} (cycles per cm at N.T.P.) as the intensities of ν_1 and ν_3 respectively.

The force constants k_1 and k_2 have been calculated for several values of the interaction constant k_{12} on the basis of the potential function

$$V = \frac{1}{2}k_1 r_1^2 + k_{12} r_1 r_2 + \frac{1}{2}k_2 r_2^2, \quad (3)$$

where r_1 and r_2 are respectively the changes in the CCl and CN distances. These calculations are given in Table II, together with values of the coefficients L_{kj}^{-1} for the transformation from internal to normal coordinates.

$$Q_k = \sum_j L_{kj}^{-1} r_j. \quad (4)$$

Calculation of bond moment derivatives in cyanogen chloride again involves sign ambiguity and for each k_{12}

⁷ While the actual extent of resonance and consequent mixing of levels is undetermined, a first-order perturbation calculation, using observed intensities and frequencies, gives $\pm 12.5 \text{ cm}^{-1}$ as the maximum possible Fermi shift for the levels ν_1 and $2\nu_2$. In this extreme case of resonance the "unperturbed" fundamental ν_1 would fall at 727 cm^{-1} and possess zero intensity. Under these conditions force constants and bond moment derivatives would have the following values

$$\begin{aligned} k_1 &= 5.14 \times 10^5 & (\partial\mu/\partial r)_{\text{CCl}} &= \pm 0.32 \times 10^{-10} \\ k_2 &= 16.98 \times 10^5 & (\partial\mu/\partial r)_{\text{CN}} &= \pm 1.74 \times 10^{-10} \end{aligned}$$

for the case in which the interaction constant, k_{12} , of expression (3) is set equal to zero. These values are to be compared with those in the first line of Table II, in which resonance involving ν_1 has been neglected.

two numerical values of each derivative are possible. These are given in Table II, the upper set for the case in which both derivatives have the same sign (either positive or negative), the lower set for the case of opposite signs.

DISCUSSION

It has been pointed out that information aside from intensity data is necessary to establish the sign of bond moment derivatives. In the case of cyanogen chloride, Beach and Turkevich⁸ have suggested that two resonating structures may be written for the molecule.

- (a) $\text{Cl}-\text{C}\equiv\text{N}$
(b) $^+\text{Cl}=\text{C}=\text{N}^-$.

If it is assumed that the CN and CCl bond moments both have their positive ends directed toward the carbon atom, then a CCl stretch, favoring structure (a) and a CN stretch, favoring (b), lead to increased moments and hence positive signs for both derivatives. By this argument we should then adopt the upper set of values in Table II with positive signs for the bond moment derivatives.

Despite any sign considerations, however, it is seen that $(\partial\mu/\partial r)_{\text{CN}}$ has widely different numerical values in C₂N₂ and ClCN. It is reasonable to expect that bond moment derivatives should vary from molecule to molecule since the assumptions of bond moment additivity disregard the effects of induced polarization in neighboring bonds within a molecule. That $(\partial\mu/\partial r)_{\text{CN}}$ in ClCN is much greater than in C₂N₂ would indicate that the CCl bond is more polarizable than the CC bond.

⁸ J. Y. Beach and A. Turkevich, J. Am. Chem. Soc. **61**, 299 (1939). See also C. H. Townes and B. P. Dailey, J. Chem. Phys. **9**, 788 (1949).