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The Vibration Spectra and Structure of the Cyanogen Halides

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The Raman spectra of the cyanogen halides in the liquid state or in alcoholic solution contain 3 frequencies ν_1 , ν_2 , and ν_3 . In the order chloride, bromide, iodide, $\nu_1 = 2201, 2187, 2158 \text{ cm}^{-1}$; $\nu_2 = 729, 580, 470$; $\nu_3 = 397, 368, 321$; the order of intensities of Raman transitions is $\nu_1 > \nu_2 > \nu_3$. The relative

values of the frequencies indicate a linear arrangement of the nuclei in the lowest electronic state of these molecules, and the data are in accord with the structure $\text{X}-\text{C}\equiv\text{N}$ rather than $\text{X}-\text{N}=\text{C}$.

THE following report contains the results of experiments designed to establish the fundamental vibration frequencies of the unsymmetrical triatomic molecules, the cyanogen halides, by investigating the Raman spectra of these compounds, and the evidence on the debated matter of their structure afforded by a knowledge of these frequencies.

EXPERIMENTAL

Cyanogen chloride was easily obtained in a pure condition by passing chlorine into the double cyanide of zinc and potassium according to Mauguin and Simon's modification of Held's method.¹ The bromide was a commercial product, while the iodide was prepared by the action of mercuric cyanide on iodine in ether solution.² The chloride and bromide were examined in the liquid state. The chloride, whose boiling point is 15°C , was condensed in a well cooled scattering tube, which was sealed off when filled. The spectrum was examined at room temperature (18°C). The bromide, which melts at 52° and boils at 61° , was examined in a tightly stoppered tube 2 inches long, placed in a bath of acetone vapor (B.P. 56°).

The iodide melts only under pressure. There is, however, sufficient decomposition of the substance at the melting point, about 146° , to color the liquid dark red, and it was impossible to obtain the spectrum of the pure liquid. The substance was investigated dissolved in methyl alcohol, in which it is very soluble in the cold without undergoing chemical change.

¹ Mauguin and Simon, *Ann. Chim.* **15**, 18 (1921).

² Linnemann, *Annalen* **120**, 36 (1862).

The source of light was a Hanovia 220 volt quartz mercury arc, focussed by a large glass condensing lens on the scattering tube, and the spectrograph was a Hilger constant deviation instrument with a dispersion of about 100 cm^{-1} per mm in the blue and violet. Spectra were photographed both with the lines of wave-length 4047A and the group about 4358A as exciting lines and with the former line removed by means of a filter composed of two plates of Noviol O glass. A solution of *p*-nitro toluene in alcohol is also very suitable for removing 4047 without appreciably dimming 4358, and was used in the later experiments. The substances gave relatively strong Raman spectra with comparatively little background.

TABLE I.

ClCN			BrCN			ICN		
$\nu \text{ cm}^{-1}$	Source	$\Delta \nu \text{ cm}^{-1}$	$\nu \text{ cm}^{-1}$	Source	$\Delta \nu \text{ cm}^{-1}$	$\nu \text{ cm}^{-1}$	Source	$\Delta \nu \text{ cm}^{-1}$
22541	e	397	22572	e	368	22617	e	321
22501	a	2202	22516	a	2187	22549	a	2156
22321	b	2195	22360	e	580	22468	e	470
22263	d	732	20754	e	2186	20780	e	2158
22219	e	729						
22129	e	809						
20848	c	2191						
20786	d	2201						
20736	e	2200						

The results are summarized in Tables I and II, and microphotometer curves are reproduced in Fig. 1. The column headed source refers to the line in the Hg spectrum causing the Raman line. The wave-lengths of Hg lines concerned are a, 4047; b, 4078; c, 4339; d, 4348; e, 4358a. The figures in parenthesis after the vibration frequencies in Table II give a rough estimate of the relative intensities of the Raman transitions. The

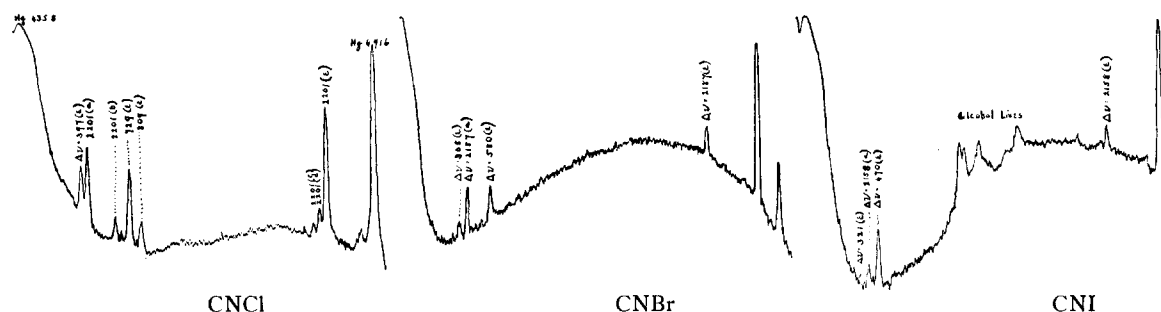


FIG. 1. Raman spectra of cyanogen halides.

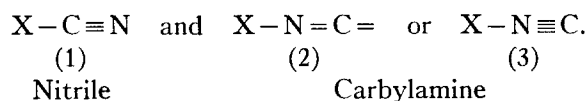
feeble Raman line in the spectrum of ClCN of $\Delta\nu$ 809 cm^{-1} seems most probably to originate in a transition involving the oscillation of fundamental frequency 397 in which the vibrational quantum number increases by 2.

TABLE II. Fundamental vibration frequencies of cyanogen halides.

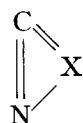
	$\nu_1 \text{ cm}^{-1}$	$\nu_2 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$
ClCN	2201 (10)	729 (5)	397 (3)
BCN	2187 (10)	580 (5)	368 (2)
ICN	2158 (10)	470 (2)	321 (1)

DISCUSSION

Although the cyanogen halides have been known for over a century, there is still uncertainty as to their constitution, the choice being, in the symbolism of organic chemistry between the structures



Gutman³ has also proposed a cyclic formula



which, however, with trivalent halogen, seems inherently improbable and is excluded by the results we have obtained.

The weight of opinion on the side of organic chemists seems to incline to the carbylamine formula (2),⁴ modified by arguments that the

chloride is a carbylamine, the iodide a nitrile, and the bromide a tautomeric mixture of the two.⁵ The cyanogen halides in fact show the chemical behavior neither of typical compounds containing a well-defined nitrile group nor yet of those containing a nitrogen-halogen linkage—they are much more stable than any compound which we have been able to find reference to as definitely containing a nitrogen halogen linkage. Nor, it must be admitted at the outset, do the results we have obtained on the fundamental vibrations of the compounds, permit a completely definitive answer to be made as to their linkages, though there is no suggestion that the linkages are not of the same nature in all three compounds.

In the first place it is to be noted that the comprehensive work of Dadiou and Kahlrausch on organic C—N compounds shows that the great differences in chemical behavior which exist between authentic nitriles and authentic carbylamines is not well expressed by the distinction between a triple and a double bond between C and N as indicated in formulae (1) and (2).⁶ The Raman spectra of the alkyl nitriles show a remarkably constant frequency of 2245 cm^{-1} which is undoubtedly due to the vibration between the C and N atom, and which is about the magnitude to be expected for the vibration of the triple bonded group $\text{C}\equiv\text{N}$. The alkyl carbylamines have a different, but not markedly different frequency at 2180 cm^{-1} ; and it is impossible to ascribe such a small change in vibration frequency to a change in linkage represented

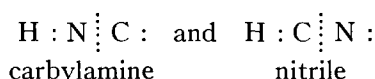
⁵ C. V. Zappi, *Bull. Soc. Chim.* **47**, 453, 537 (1930); **49**, 397 (1931).

⁶ Kahlrausch, *Der Smekal-Raman-Effekt*, p. 319 et seq. (Julius Springer, Berlin, 1931).

³ Gutman, *Ber.* **42**, 3623 (1909).

⁴ Chattaway and Wadmore, *J. Chem. Soc.* **81**, 192 (1902).

by the difference between a triple and a double bond; the bond $C=N$ would in fact have a frequency near 1700 cm^{-1} . It is possible to write electronic formulae for the two classes of compounds which are completely analogous.



and these are probably a better representation of the state of binding in the unexcited state of the 2 molecules than the conventional bond formulae.

Returning to the evidence provided by a knowledge of the vibration frequencies of the cyanogen halides on the alternative structures, one finds that, if not absolutely conclusive, it is strongly in favor of the nitrile constitution for all three compounds. The carbon-nitrogen frequency in the chloride, 2201 cm^{-1} , is decidedly higher than the value for the aliphatic carbylamines, 2180 cm^{-1} . True, it is lower than the value 2245 cm^{-1} , characteristic of the aliphatic nitriles, but it is likely enough, and in accord with experience in similar cases, that substitution of a heavy Cl atom for the one or two C atoms in the alkyl group which alone influence the $C-N$ vibration should lower the value of this frequency, as is shown by its progressive diminution in the bromide and iodide. The observed value of the frequency for $CN\text{I}$ is only 12 cm^{-1} lower than that for methyl carbylamine whereas substitution of a heavy iodine atom for the CH_3 group would have been expected to diminish it much more considerably, probably by about 80 or 90 cm^{-1} . In the conclusion that all three halides have the same structure we are in agreement with that of Badger and Sho-Chow Woo⁷ who, as a result of their study of the continuous ultra-violet absorption spectra of these compounds, advance cogent reasons based on a discussion of binding energies for preferring the nitrile structure.

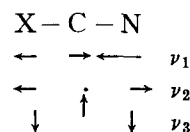
SHAPE OF THE MOLECULE

It may first be relevant to refer to the conclusive proof given by Barker and Kya Nam

⁷ Badger and Woo, *J. Am. Chem. Soc.* **53**, 2542 (1931).

Choi⁸ in their rotational analysis of the infrared absorption bands of HCN that this molecule is linear.

In the following discussion we shall assume that the linkage is $X-C-N$ where X is the halogen. A triatomic molecule will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom if bent and $3 \times 3 - 5 = 4$ degrees if linear. In the latter case, two of the frequencies, those corresponding to the bending of the molecule in two perpendicular planes, are equal if the binding forces are axially symmetrical. Three fundamental frequencies will therefore exist, all of which appear in the Raman spectra in the case of the cyanogen halides. Anticipating the result that the frequencies observed for these compounds are in accord with a linear molecule, we may represent the vibrations as follows:



The solution of the mechanical problem of the motion of 3 point masses under the action of "valence" forces has been given by Lechner⁹ who finds the condition that for a linear arrangement of the masses, m_1 , m_2 and m_3 .

$$\frac{\nu_1}{\nu_2} + \frac{\nu_2}{\nu_1} > 2k, \text{ where } k = 1 - \frac{\mu_{12}\mu_{23}}{m_2^2},$$

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}, \quad \mu_{23} = \frac{m_2 m_3}{m_2 + m_3}.$$

The values for $\nu_1/\nu_2 + \nu_2/\nu_1$ and $2k$, respectively, are: chloride, 3.36, 2.60; bromide 4.00, 2.74; iodide 4.84, 2.80. The observed frequencies are compatible with a linear arrangement of the atoms.

It is of some interest to calculate the force constants, the restoring force for 1 cm displacement of the atoms in the various vibrations when the latter remain simple harmonic. According to Lechner, these are given for the unsymmetrical linear three-point-mass model by

$$n_1^2 + n_2^2 = f_{12}/\mu_{12} + f_{23}/\mu_{23},$$

⁸ Barker and Choi, *Phys. Rev.* **42**, 777 (1932).

⁹ Lechner, *Sitz. Wien. Akad. Math.-natur. Classe* **141**, 2a, 291 (1932).

$$n_1^2 n_2^2 = \frac{f_{12}}{\mu_{12}} \cdot \frac{f_{23}}{\mu_{23}} \left\{ 1 - \frac{\mu_{12} \mu_{23}}{m_2^2} \right\},$$

$$n_3^2 = d/\mu_4.$$

If ν is the frequency of vibration in cm^{-1} and m is given in atomic weight units ($\text{Cl} = 35.46$, etc.), n^2 is defined as equal to $4\pi^2 c^2 \nu^2 / N = 5.863 \times 10^{-2} \nu^2$, where N is Avogadro's number. f , the restoring force for stretching displacements and d , the restoring force for the bending displacement are then given in dynes per cm^{10}

d and μ_4 are defined by the relation

$$\frac{1}{\mu_4} = \frac{1}{\mu_{12}} \frac{s^2}{S_{12}^2} + \frac{2}{m_2} \frac{s^2}{S_{12} S_{23}} + \frac{1}{\mu_{23}} \frac{s^2}{S_{23}^2}$$

where S_{12} , S_{23} are the distances between m_1 and m_2 and m_2 and m_3 , respectively, and $d_{12} S_{12}^2 = d_{23} S_{23}^2 = d s^2$. d_{12} is the restoring force for a bending displacement of m_1 , m_3 being fixed and similarly for d_{23} .

The values of the force constants are given in Table III. The calculation of the bending forces

TABLE III.

	f_{12}	f_{23}	d (approx.)
CICN	5.14×10^5 dynes/cm	16.65×10^5 dynes/cm	0.17×10^6 dynes/cm
BrCN	4.16	16.84	0.15
ICN	2.60	16.80	0.11

requires a knowledge of the interatomic distances which are unknown in these compounds. If as a first crude approximation the distances S_{12} and S_{23} are assumed equal, $s_{12} = s_{23} = s$, and $1/\mu_4 = 1/\mu_{12} + 2/m_2 + 1/\mu_{23}$, whence the above values of d are obtained.

Comparison of the frequencies ν_1 and ν_2 in the cyanogen halides with those exhibited by other compounds containing the $\text{C} \equiv \text{N}$ and C^- halogen linkages shows that these molecules are further illustrative of the preservation of "bond fre-

quencies" in polyatomic molecules. The frequency ν_1 has approximately the same value, about 2200 cm^{-1} in all three of the halides, and all compounds containing the linkage $\text{C} \equiv \text{N}$, including the diatomic CN molecule known from spectroscopy, have a frequency not very different from this value. In the same way, the frequency $\nu_2 = 729$ for cyanogen chloride is close to the strong frequency 710 in CH_3Cl ; ν_2 for the bromide is nearly the same as the frequency 594 in CH_3Br , and the value 469 for the iodide is comparable with the frequency 522 in CH_3I . It would therefore be possible to make the statement that the vibration spectra of the cyanogen halides are partially composed of $\text{C} \equiv \text{N}$ and C^- halogen bond frequencies, and to identify these frequencies with ν_1 and ν_2 , respectively. Although the calculation of the force constants is in terms of a dynamical model in which the frequencies ν_1 and ν_2 involve all of the masses, in consequence of which it becomes impossible to attach meaning to $\text{C} \equiv \text{N}$ and C^- halogen vibrations, the experimental fact of the persistence of "bond vibrations" in polyatomic molecules nevertheless suggests the reasonableness of identifying the constant f_{23} as the "force constant for the $\text{C} \equiv \text{N}$ vibration" and the constant f_{12} with the "force constant for the C-halogen vibration." In fact, the constant f_{23} is very close to the constant which is obtained from the experimental value of the frequency in the normal state of the diatomic CN molecule, 2069 cm^{-1} , on the assumption of a simple harmonic oscillation, namely 16.3×10^{-5} dynes/cm. The very small variation of f_{23} in the three halides leads to the conclusion that the carbon-nitrogen linkage is the same in all three compounds, while the steady diminution of f_{12} with increasing atomic weight of the halogen indicates a weakening in this linkage which is in accord with the chemical behavior of the compounds.

Our thanks are due to Mr. Edward Shriver of this department who very kindly obtained the microphotometer curves.

¹⁰ Kohlrausch, *Der Smekal-Raman-Effekt*, pp. 154, 170.