[CONTRIBUTION NO. 579 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Remarks on the Spectra of Methyl Cyanide and Methyl Isocyanide[1]

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The infra-red spectrum of liquid methyl cyanide was investigated several years ago by Coblentz,[2] using rather low dispersion, and more recently Raman studies[3] have been made on this substance and on methyl isocyanide. The data obtained appear never to have been interpreted completely but attention was called by Dadieu[4] to the presence of a frequency shift of around 2200 cm.$^{-1}$ in the Raman spectra of both substances. This he took as evidence for the presence of a triple bond between carbon and nitrogen in both cyanide and isocyanide. Lechner[5] made a simplified normal coördinate treatment of the molecules in which he assumed that in two of the vibrations the methyl group would behave as a rigid unit, and by the use of two observed frequencies calculated two of the force constants in each. The values of the larger constants so obtained are probably quite reliable and their magnitude is conclusive evidence for a carbon–nitrogen linkage which at least approaches very closely to triple bond in character. The calculation gave less reliable values for the single bond constants of the C–C and C–N linkages, respectively, since there are two vibrations in which both single bond and methyl group participate to a considerable extent, causing Lechner's values to be somewhat too small.

However, at the present time it is not possible to make a much more satisfactory calculation. The authors have attempted a complete normal coördinate treatment of all parallel vibrations, but when using the so-called "valence force" potential function there appear to be no real and probable values of the force constants which yield the observed frequencies. From this it is evident that additional interaction terms must be added to the potential function, but at present there is no very reliable method of estimating their magnitude.

It is the purpose of this paper to discuss in further detail the analysis of the spectra of methyl cyanide and methyl isocyanide, pointing out some facts of special interest, and to present some new data on harmonic bands in the photographic infra-red.

In the Raman spectrum of methyl isocyanide all fundamental frequencies appear and no overtones or combinations have been observed. In the cyanide one frequency (1040 cm.$^{-1}$) is absent in the Raman spectrum but may be supplied from the infra-red where it occurs strongly. By comparison with other molecules, particularly the methyl halides, it is possible to make what appears to be a unique assignment of the fundamentals. This is done in Table I in which the vibration types are given an approximate description, and in which a classification is made as to parallel or perpendicular type. This classification of course only has an exact significance in case the molecules in question have an axis of symmetry.

TABLE I

IDENTIFICATION OF THE FUNDAMENTALS IN THE SPECTRA OF METHYL CYANIDE AND METHYL ISOCYANIDE

ν(cm.$^{-1}$)			
Cyanide	Isocyanide	Type	Approximate description
2996	3003	⊥	Vibrations principally confined to methyl group
2942	2951	∥	
1417	1456	⊥	
1370	1414	∥	
2250	2161	∥	$C\equiv N$ vibration
917	928	∥	C—C vibration in cyanide, C—N vibration in the isocyanide
1040	1041	⊥	Swinging of methyl group with respect to remainder of molecule
376	290	⊥	Bending of $C-C\equiv N$ group in cyanide and $C-N\equiv C$ group in isocyanide

The possession of a threefold axis of symmetry will depend presumably only on whether the $C-C\equiv N$ and $C-N\equiv C$ groups are linear or not. In the case of the cyanide there seems no reason to doubt that the group is linear since it has been shown that hydrogen cyanide is definitely a linear

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[1] The experimental work described in this paper is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

[2] William W. Coblentz, "Investigations of Infra-Red Spectra," Carnegie Institution, 1905.

[3] For references see K. W. F. Kohlrausch, "Der Smekal-Raman-Effekt," Julius Springer, Berlin, 1931.

[4] A. Dadieu, *Wien Ber.*, **139**, 629 (1930).

[5] F. Lechner, *ibid.*, **141**, 291 (1932).

molecule,[6] but in the isocyanide there might possibly be some doubt on this point. Lechner's values for the "triple bond" force constants are 1.733 and 1.630 megadynes per cm. for the cyanide and isocyanide, respectively. These may be slightly in error, and their significance is not quite simple since they include certain interaction constants, but they are at least useful in comparing the two molecules which are so similar in many respects. It is evident that the carbon–nitrogen bond is appreciably weaker in the isocyanide than in the cyanide, suggesting that in the former the linkage may not be completely triple bond in character.

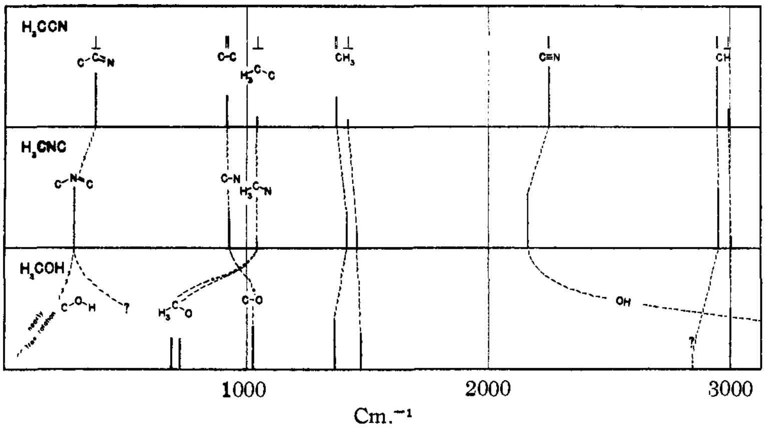

Fig. 1.—Comparison of the Raman spectrum of liquid methyl cyanide and isocyanide (data of Dadieu, etc.) with the infra-red spectrum of methyl alcohol vapor (data of Bartholomé and Sachsse). Missing fundamentals are supplied from the corresponding infrared or Raman spectrum, as the case may be.

It is interesting to compare the vibrations of lowest frequency in the two molecules. The motion in this case is pretty largely a bending of the C—C≡N or C—N≡C groups, and since the mass distribution is so nearly the same in the two cases we can get a rough estimate of the ratio of the force constants involved from the ratio of the squares of the frequencies. We find that the isocyanide bending constant is about 0.6 (or a little less than $^2/_3$) that of the cyanide. At present it is not possible to make any very general statement regarding the bending constants of molecules, but from a recent compilation of data by Penny and Sutherland[7] it appears that they are more or less proportional to the product of the stretching constants of the two bonds involved in the bending. Thus in this deformation oscillation the nitrogen–carbon bond in the isocyanide appears to behave as a double bond. This is probably to be expected since if a double bond structure contributes anything to the ground state of the isocyanide it would be likely to predominate more and more as the molecule is forcibly bent. The question now is whether this trace of double bond character which the bond appears to possess may cause any deviation from linearity in the C—N≡C group in the vibrationless state of the molecule.

Now if we have a bent structure in either the cyanide or isocyanide we should expect a splitting of those frequencies designated as perpendicular in Table I which correspond to degenerate vibrations in a molecule possessing a threefold axis of symmetry. The splitting would undoubtedly be too small to observe in the fundamentals of the internal vibrations of the methyl group, since these are little affected by the remainder of the molecule, but in the two others the separation should be appreciable. The extreme effect would of course be found in the splitting of the low frequency vibration corresponding to the deformation of the cyanide or isocyanide group, since in this case one of the components would take on the character of a torsional motion which would either be of very low frequency or would go over into a more or less free rotation. In order to show what effect may be expected in the absence of a symmetry axis we reproduce in Fig. 1 the infrared spectrum of methyl alcohol vapor, from the data of Bartholomé and Sachsse,[8] together with the Raman spectra of methyl cyanide and isocyanide for the sake of comparison.

By the investigation of both methanol and methanol-*d*, Bartholomé and Sachsse were able to identify a number of fundamental frequencies without uncertainty. They found a separation of 35 cm.$^{-1}$ between the two components of the vibration corresponding to the 1040 frequency in the cyanide and isocyanide, but in the case of the oscillations resulting from the splitting of the vibration analogous to that of lowest frequency in the other substances, neither component could

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(6) Badger and Binder, *Phys. Rev.*, **37**, 800 (1931).

(7) Penny and Sutherland, *Proc. Roy. Soc.* (London), **A156**, 654 (1936).

(8) Bartholomé and Sachsse, *Z. physik. Chem.*, **B30**, 40 (1935).

be identified. From an investigation which the authors have recently made on certain harmonic bands of methyl alcohol[9] it appears probable that one of them has indeed gone over into a nearly free rotation which introduces a new complexity in the rotational structure of the bands.

The great similarity between the spectra of the cyanide and the isocyanide will be noted. From this and the absence of any indication of splitting in the degenerate vibrations it seems reasonable to conclude that the C—N≡C group in methyl isocyanide is linear.

Investigations in the Photographic Infra-red

The authors had hoped that it might be possible to photograph the rotational structure of some of the higher harmonic bands of methyl cyanide and isocyanide and to obtain further information about the structure, but this turned out to be impossible at present. The absorption was very weak except beyond 1 μ and in this region it was not possible to get sufficiently clean plates when using high dispersion, to attempt an analysis. The spectra of the liquid substances and also that of methyl cyanide vapor were, however, photographed under low dispersion (about 70 Å. per mm. at λ 9000) using a path length of 7.6 cm. for the liquids, and 3 meters for the vapor under about one atmosphere pressure. The results are presented in Fig. 2 and Table II. The diagrams were drawn with the use of several microphotometer curves as well as the original plates. The intensities of the bands beyond 1μ may be in considerable error since it is difficult to make estimates in a region in which the sensitivity of the photographic plate is dropping off rapidly with increasing wave length. For the same reason the maxima in this region may be slightly in error.

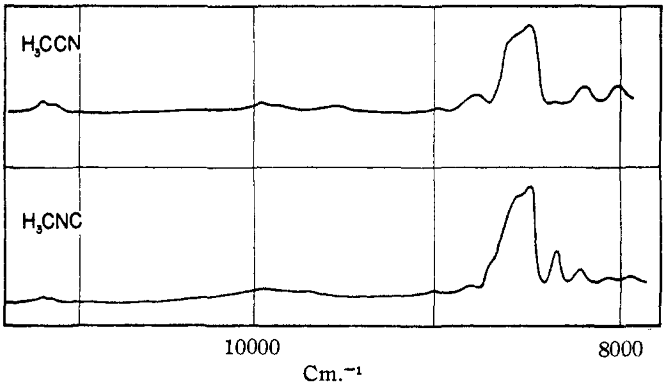

Fig. 2.—Representation of the absorption spectra of liquid methyl cyanide and isocyanide in the photographic infra-red.

Table II

Wave Lengths and Frequencies of Absorption Maxima of Methyl Cyanide and Methyl Isocyanide in the Photographic Infra-red

Methyl cyanide				Methyl isocyanide		Approximate description of band
Vapor		Liquid		Liquid		
λ, Å.	ν, cm.⁻¹	λ, Å.	ν, cm.⁻¹	λ, Å.	ν, cm.⁻¹	
		12373	8080	12560	7960	2ν(C—H) + ν(C≡N)
		12182	8206	12380	8075	
				12138	8236	3ν(C—H)
		12007	8326	11968	8353	
11727	8525	11767	8496	11800	8472	
11602	8617	11626	8598	11628	8597	
				11473	8714	
11360	8801	11405	8765	11327	8826	Possibly H_2O
(11238)	(8896)	11140	8974	11093	9012	
		10490	9530	10310	9697	?
		10145	9854	10157	9843	
		10037	9960	10008	9989	
		8973	11141	8937	11187	4ν (C—H)
		8922	11205	8898	11235	

It does not seem possible to identify all the maxima at present except in a very general way as done in the table. The complexity of the spectrum in the 8500 cm.⁻¹ region is presumably due to the partial removal of the degeneracy in the C-H vibrations in the higher levels.

Summary

A vibrational analysis is made of the spectra of methyl cyanide and methyl isocyanide. Evidence is given which indicates that although the carbon-nitrogen linkage in the isocyanide approaches rather closely to a triple bond it does possess an appreciable amount of double bond character. This, however, does not produce any deviation from linearity in the C—N≡C group and methyl isocyanide appears to possess a threefold axis of symmetry.

The absorption spectra of methyl isocyanide in the liquid state, and of methyl cyanide in the liquid and vapor states have been photographed in the photographic infra-red.

Pasadena, Calif. Received November 27, 1936

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(9) Badger and Bauer, *J. Chem. Phys.*, 4, 469 (1936).