Absorption of the Alkyl Cyanides in the Vacuum Ultraviolet

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The effect of hyperconjugation weakening in the C$-$H bond in C_2H_6 as compared with that in CH_4 has been estimated at 7 kcals.[11] A detailed discussion of the disparity between this value and that obtained for para-xylene seems premature in view of the inaccuracy of the results obtained up to date. But we would like to emphasize that in the case of the weakening of C$-$H bonds in para-xylene as compared with meta-xylene we can see no other possible explanation than hyperconjugation, whereas in the

case of the weakening of the C$-$H bond in ethane as compared with methane, the proximity of the two interacting methyl groups offers additional possibilities—for example, steric effects or dipole interactions—of an explanation.

[11] E. C. Baughan, M. G. Evans, and M. Polanyi, Trans. Faraday Soc. 37, 377 (1941).

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The vacuum ultraviolet spectra of methyl and ethyl cyanide have been determined in the region 1000A to 1800A. Three members of a Rydberg series were found for methyl cyanide starting at 1292A, the limit of the series corresponding to an ionization potential of 11.96 ev. Vibrational band changes which have been found to accompany the first two members have been assigned to fundamental frequencies of the molecule by comparison with Raman data. The electronic transition, expressed by the Rydberg series, was ascribed to excitation of a π electron in the triple bond. At higher pressures, a continuous absorption appeared which was followed only to 1600A. No structure could be observed in the spectrum of the ethyl cyanide, although it paralleled that of methyl cyanide in having a stronger absorption starting at 1342A and a weaker one appearing at higher pressures and spreading to longer wave-lengths.

INTRODUCTION

THE following communication contains a study of the absorption spectra of methyl and ethyl cyanides in the vacuum ultraviolet. Previously, Herzberg and Scheibe[1] studied the spectrum of methyl cyanide down to about 1540A, finding a weak band extending from 1820A to 1600A with a maximum at about 1670A. Below 1600A, there was an indication of the beginning of a stronger absorption which would extend to shorter wave-lengths. They also

observed the same indications in the spectra of the methyl halides. Price[2] extended this work on the halides to shorter wave-lengths and found discrete Rydberg series, assigning the excitation to the $p\pi$ electrons on the halide. From this it was felt that if the work on methyl cyanide were also extended to shorter wave-lengths, a Rydberg series might be identified.

EXPERIMENTAL

The far ultraviolet spectra were photographed on a Lyman continuum as a background, using hydrogen as the inert gas, by means of a vacuum spectrograph at nearly normal incidence. A lightly ruled glass grating was used, of focal length 1 meter, with 30,000 lines per inch, ruled by R. W.

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[1] G. Herzberg and G. Scheibe, Zeits. f. physik. Chemie B7, 390 (1930).

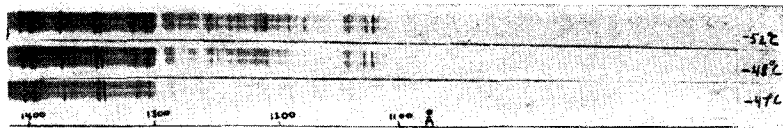[2] W. C. Price, J. Chem. Phys. 4, 539 (1936).

FIG. 1. Spectrum of methyl cyanide.

Wood. The dispersion was about 8.43A per mm. Eastman Kodak III-O, ultraviolet sensitized plates and Ilford Q1 plates were used. The Eastman plates were made on x thin glass so that they could be bent to fit the Rowland circle. Three exposures could be made on one plate, each exposure covering 500A. Discrete bands were measured from microphotometer traces using the strong Si and O lines in the source as standards. The spectrum of MeI was taken as a test plate for the region 1900–1300A since Price[2] has published an illustration of the sharp bands found in that region. The absorption spectra of the compounds were taken with the vapor filling the entire spectrograph, thus producing a total absorbing path of 2 meters. The concentration of the vapor was controlled by the temperature of an acetone bath cooled by dry ice, surrounding the distilling flask leading into the spectrograph.

METHYL CYANIDE

The material supplied by the Eastman Kodak Company was dried for several days over calcium chloride and then distilled in air in an all glass still. The main fraction came over from 81 to 81.5°C. The methyl cyanide was immediately put into a distilling apparatus connected to the spectrograph and redistilled in vacuum before being vaporized into the spectrograph.

Typical spectra of methyl cyanide are reproduced in Fig. 1 where they are enlarged about three times. This compound has a set of strong, discrete bands which start abruptly at 1292A at the lower vapor pressures studied. As the pressure is increased these discrete bands widen, and a continuous absorption appears to spread from the short wave-length end. The continuum is believed to be caused by the absorption of methane and ethane in this region, starting at 1300A and 1350A, respectively.[3, 4] As the pressure is increased, the absorption no longer starts

abruptly at 1290A, but a continuous absorption occurs which travels to the longer wave-lengths. At the highest temperature used, −25°C, this continuous absorption extends to 1600A. The weak band from 1820A to 1600A reported by Herzberg and Scheibe was not observed, probably because the vapor pressure was never high enough.

The spectrum of methyl cyanide (see Figs. 1 and 2) is not an ideal one for measurement and interpretation. The bands are not very sharp, and it is impossible to find indications of structure which might facilitate in the analysis. In this respect the spectrum of methyl cyanide resembles the shorter wave-length spectrum of HCN as reported by Price.[5, 6] The overlapping continua extending from the shorter wave-lengths are a serious difficulty, obscuring the shorter members of the discrete banded systems. Nevertheless, it seems very probable that a Rydberg series is represented by the strongest bands 1, 7, and 10. These bands can be represented by the formula

$$\nu_0^n = 96,426 - [R/(n+0.40)^2].$$

The constants were chosen to fit the first member, $n = 2$, since the measurement of the member corresponding to $n = 3$ is made difficult by interfering O III emission lines, and the band corresponding to $n = 4$ is quite broad. The agreement between observed and calculated values is shown in Table I. The convergence limit, 96,426 cm^{-1} ≡ 1035A, is obscured in the C—C and C—H continua; the corresponding ionization potential is 11.96 volts.

The strong bands 1 and 7 are accompanied on

TABLE I.

	Observed cm^{-1}	Calculated cm^{-1}
$n=2$	77,374	77,374
$n=3$	86,953	86,933
$n=4$	90,853	90,757

[3] A. B. F. Duncan and J. P. Howe, J. Chem. Phys. 2, 851 (1934).
[4] W. C. Price, Phys. Rev. 47, 444 (1935).

[5] W. C. Price, Phys. Rev. 46, 529 (1934).
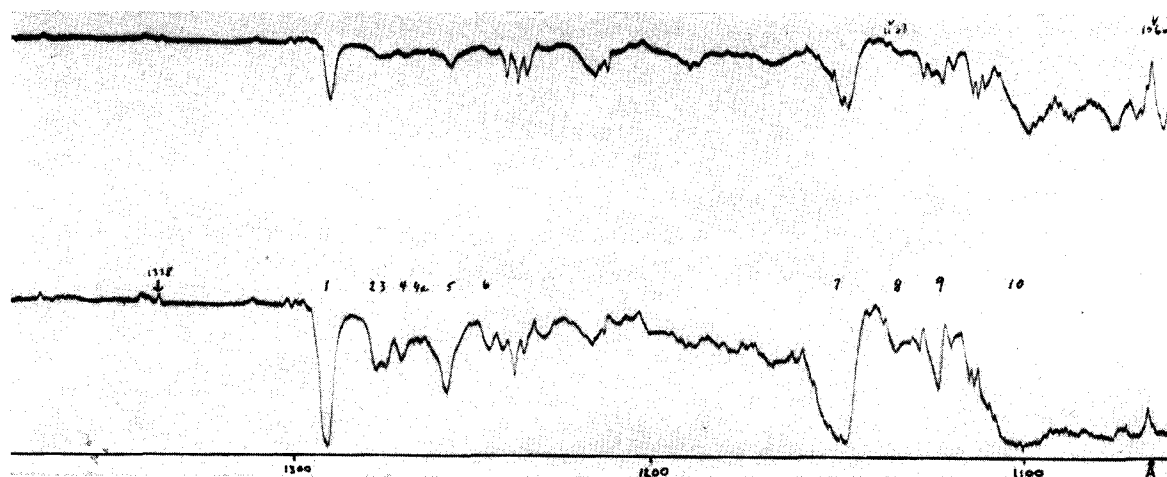[6] W. C. Price, and A. D. Walsh, Trans. Faraday Soc. 41, 381 (1945).

Fig. 2. Microphotometer tracing of methyl cyanide spectrum.

the short wave-length side by weaker bands which represent transitions to vibrating electronic states. The differences of the main bands of the 1292A group are listed in Table II.

There seems little doubt that the strongest vibrational band associated with the Rydberg transition of longest wave-length, with a frequency difference of 2001 cm^{-1} from the O→O band, originates in the excitation of the C≡N valence vibration (ν_2),*** of frequency 2249 in the normal state, as determined by the Raman spectrum.[7] The diminution in frequency in the excited state from its value in the normal state, indicating a diminution of bonding strength, is a common occurrence, being analogous, for example, to the change in the symmetrical C=C vibration in ethylene from its value of 1623 cm^{-1} in the ground state to 1370 cm^{-1} in its first

TABLE II.

Band	cm^{-1}	Differences from O→O
1, O→O	77,374	
2	78,187	813
3	78,342	968
4	78,613	1239
4a	78,934	1560
5	79,375	2001
6	80,098	2724

*** Notation in G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 333.

[7] A. W. Reitz and R. Skrabal, Monats. F. Chem. **70**, 398 (1937).

Rydberg excited state.[8] Similarly, the band displaced by 2724 cm^{-1} from the O→O band is probably the symmetrical C−H vibration of frequency 2942 cm^{-1} (ν_1) in the ground state. The band displaced 1239 cm^{-1} from the O→O band may represent the symmetrical deformation frequency of the methyl group, 1376 cm^{-1} in the ground state (ν_3). The ground state has a totally symmetrical "C−C" frequency ν_4, at either 916 cm^{-1} or 1124 cm^{-1},*** more likely the former, and it therefore seems probable that the frequency interval 813 cm^{-1} or 968 cm^{-1}, more likely the former, represents this vibration in the excited state. Herzberg assigns the second of the frequencies just mentioned in the normal state to the degenerate rocking frequency of the methyl group (ν_7), and it is possible that the 968 cm^{-1} band represents this frequency in the excited state, although the intensity seems unusually large for a degenerate vibration. The very weak band 4a (Fig. 2), with a frequency separation of 1560 cm^{-1} from the O→O band, may be $2\nu_4$, and a weak band at about 4000 cm^{-1} from the O→O band may be $2\nu_2$.

The vibrational transitions associated with the second Rydberg member at 1150A are less certain because of difficulties of measurements imposed by interfering emission lines in the source. A strong band displaced 2009 cm^{-1} (band 9) from the O→O band doubtless repre-

[8] W. C. Price and W. T. Tutte, Proc. Roy. Soc. London **A174**, 207 (1940).

sents the $C \equiv N$ vibration (ν_2), and the frequency interval of 1107 cm^{-1} (band 8) may represent the methyl deformation vibration (ν_3).

ETHYL CYANIDE

No discrete bands could be found for ethyl cyanide. A diffuse absorption starts at 1342A and extends to shorter wave-lengths. This absorption occurs at low pressures similar to those at which the Rydberg type of absorption was predominant in methyl cyanide. At higher pressures the continuous absorption extends to longer wave-lengths similar to the continuous absorption of methyl cyanide.

DISCUSSION

The discrete Rydberg band series starting at 1292A in the case of methyl cyanide is assigned to an excitation of one of the four π electrons making up the $C \equiv N$ bond. The fact that the $C \equiv N$ vibration is most strongly excited lends support to this assumption. This excited electron, however, can set up methyl and $C-C$ vibrations since its excited orbital will probably extend, to some extent, into the rest of the molecule. As in the case of methyl iodide (where the excited electron has been proved to be the $p\pi$ electron on the iodine),[2] symmetrical methyl vibrations in another part of the molecule accompany the early Rydberg members. Since only the $0 \rightarrow 1$ vibrations are excited strongly in each Rydberg transition, we may conclude that the relative positions of the atoms in the molecule do not change very much by excitation.

It is interesting to note that one of the Rydberg series found by Price and Walsh[6] for methylacetylene,

$$\nu_0{}^n = 91,240 - [R/(n+0.48)^2],$$

has a constant in the term value denominator (0.48) which is similar to that found for methyl cyanide. Price and Walsh showed that it was a π electron from the triple bond of methylacetylene which was excited. The term values observed for methylacetylene and methyl cyanide are compared in Table III.

Although the term value for the ground state in methylacetylene is 91,240 cm^{-1} as compared with 96,430 cm^{-1} for methyl cyanide, the term values for the corresponding higher states of the

TABLE III.

	Methyl cyanide (obs.)	Methylacetylene (obs.)
$n=2$	19,052	17,643
$n=3$	9,473	9,003
$n=4$	5,573	5,488

π electron of the triple bond are very similar. The lowest members are the ones most affected by the immediate configuration of the surrounding molecule. Since the two molecules are isosteric, it is interesting to note the similarity in term values and one may probably conclude that a π electron of the triple bond is also excited in methyl cyanide.

The ionization potential of HCN is given by Sponer as 14.8 ev,[9] as compared with 11.96 ev found for methyl cyanide in these experiments. This reduction is similar to that found by Price and Walsh[6] for methylacetylene as compared with acetylene, and can be accounted for in the same way, by an inductive effect and hyperconjugation. The inductive effect transfers negative charge into the triple bond from the polarizable methyl group. In the case of hyperconjugation, the three $C-H$ bonds behave somewhat as a triple bond and resonance occurs as in ordinary conjugation, resulting in putting more charge into the triple bond. This conjugation can be represented as:

$$H_3 \equiv C - C \equiv N \rightleftharpoons \overset{+}{H_3} = C = C = \overset{-}{N}$$
$$\text{or}$$
$$\overset{+}{H} \atop HC = C = \overset{-}{N} \atop H$$
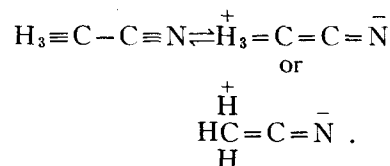
Hurdis and Smyth[10] explained the increase in the dipole moment of methyl cyanide (3.94 Debyes) over that of hydrogen cyanide (2.93 Debyes) on the basis of the hyperconjugation and inductive effect in methyl cyanide. Both effects would put extra negative charge into the $C \equiv N$ and, therefore, the ionization potential would be lowered.

There seems to be some difficulty reconciling

[9] H. Sponer, *Molekulspektren* (Julius Springer, Berlin, 1935), Vol. I.
[10] E. C. Hurdis and C. P. Smyth, J. Am. Chem. Soc. 65, 89 (1943); N. B. Hannay and C. P. Smyth, paper presented at the American Chemical Society meeting in Atlantic City on April 9, 1946.

the value of the ionization potential of methyl cyanide as deduced in these experiments, 11.96 ev, with the value of about 13.8 ev deduced for cyanogen by Price and Walsh[6] from the difficultly measurable absorption spectrum of that compound. Methyl cyanide bears the same relationship to cyanogen as methylacetylene to diacetylene. The ionization potential of methylacetylene, deduced from a well established Rydberg series by Price and Walsh, is 11.36 ev, and that of diacetylene, similarly obtained, is 10.74 ev. This is the relationship to be expected since resonance in the normal conjugated system represented by diacetylene will lower the ionization potential more than in the hyperconjugated system, methylacetylene. Similarly, the ionization potential of cyanogen is expected to be lower than the 11.96 ev of methyl cyanide, which in turn would be lower than that of hydrogen cyanide, 14.8 ev.

The first Rydberg type band in cyanogen is at 1320A as compared with 1292A in methyl cyanide, and this suggests the possibility that the first ionization potential of cyanogen should be lower than that of methyl cyanide. Similarly, the first Rydberg band of diacetylene is at 1630A (I.P. = 10.74 ev) while the first Rydberg band of methylacetylene occurs at 1540A (I.P. = 11.26 ev). If Price and Walsh's value for the ionization potential of cyanogen is taken, then in the light of this experiment, the resonance effects among cyanogen, methyl cyanide, and hydrogen cyanide are different from those among diacetylene, methylacetylene, and acetylene.

The beginning of the absorption of ethyl cyanide at 1342A may represent the limit of the C−C absorption or it may correspond to the first Rydberg member of methyl cyanide. Its shift to longer wave-lengths would indicate a lowering in ionization potential of a few tenths of an electron volt. Since the actual members of a Rydberg series could not be measured, this evaluation is very rough. The lowering of the first ionization potential of ethyl cyanide compared to methyl cyanide may be ascribed to the increase in induction of negative charge into the triple bond from the ethyl group as compared to the methyl group. The dipole moments are 4.00 Debyes and 3.94 Debyes respectively.[10] The lack of structure in the absorption of ethyl cyanide may be due to the relatively stronger C−H and C−C continua (more C−H and C−C bonds) or low frequency vibrations may be present giving the appearance of a quasi-continuum.

In conclusion, it is a pleasure to acknowledge my indebtedness to Dr. William West for his supervision and encouragement during the course of this work and for his helpful suggestions on the preparation of this paper.