AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **47**, 4548 (1967); doi: 10.1063/1.1701666
View online: http://dx.doi.org/10.1063/1.1701666
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/47/11?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 47, NUMBER 11 1 DECEMBER 1967

Mass-Spectrometric Study of Photoionization. VIII. Dicyanogen and the Cyanogen Halides*

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(Received 3 July 1967)

Photoionization-yield curves are obtained for the molecule and selected radical ions of C_2N_2, FCN, ClCN, BrCN, and ICN from threshold to 600 Å. Vibrationally excited states of ions and autoionization of Rydberg levels in the molecules are observed and discussed briefly. The X^+ ion thresholds in the heavier cyanogen halides are used to obtain: $\Delta Hf_0°(\mathrm{CN}) = 101.5$ kcal mole^{-1}, $\Delta Hf_0°(\mathrm{CN}^+) = 430.0$ kcal mole^{-1}, and $I(\mathrm{CN}) = 14.2$ eV. These are applied to compute $\Delta Hf_0°(\mathrm{FCN}) = 5.6$ kcal mole^{-1}, $D(\mathrm{F{-}CN}) = 5.0$ eV, $I(C_2) = 12.15$ eV, and other thermodynamic properties. The formation of CN^+ from dicyanogen apparently includes about 0.6 eV excess energy near the threshold.

INTRODUCTION

The heat of formation of the cyanogen radical and its relation to bond dissociation energies in dicyanogen and other cyanogen compounds has been the subject of several recent studies. Berkowitz,[1] using a mass spectrometer to analyze the vapor in equilibrium with graphite and nitrogen at high temperature, obtained $\Delta Hf_0°(\mathrm{CN}) = 109 \pm 3$ kcal mole^{-1} which results in about 145 kcal mole^{-1} for $D(\mathrm{NC{-}CN})$. This is identical with the results of an earlier study by Knight and Rink[2] who measured total gas density of shocked samples of dicyanogen. The agreement, together with a re-examination by Berkowitz of some previous studies, notably electron impact,[3-6] resulted in a considerable degree of confidence in the value. Almost simultaneously, however, Tsang, Bauer, and Cowperthwaite[7] had published another shock-tube study of the dissociation energy of dicyanogen with the result, $D(\mathrm{NC{-}CN}) = 125 \pm 8$ kcal mole^{-1}, from which we may calculate, $\Delta Hf_0°(\mathrm{CN}) = 99 \pm 8$ kcal mole^{-1}. Although in agreement within the combined large uncertainties, Tsang *et al.* posed interesting criticisms of the earlier "high" value for $D(\mathrm{NC{-}CN})$.

In view of the considerable uncertainty remaining in the above, we have re-examined the ionization processes in the cyanogen halides and in dicyanogen using a nearly monoenergetic photon beam to avoid some of the errors inherent in the electron-impact method and to provide a greater precision in the determination of thresholds. Although cyanogen fluoride was available for this study, the heat of formation has only been estimated[8] to be 3 ± 5 kcal mole^{-1} using a correlation method due to Glockler.[9] Also, because of the controversy regarding the state or energy content of CN or CN^+ in dicyanogen,[1] we have chosen to discuss first the observations on ClCN, BrCN, and ICN, applying the conclusions to the interpretation of the remaining members of the series.

EXPERIMENTAL

Measurements were made by means of a combined vacuum-ultraviolet monochromator and mass spectrometer differing in minor respects from that described in detail in the first paper of this series.[10] A gold-coated grating having 1200 grooves/mm is used in the monochromator with optical slits of 0.1 mm, thus providing a resolution of about 1 Å. Photon sources and intensities of photons and of ions were substantially those described in the preceeding paper of this series.[11] The following conversion factors are used: 1 eV = 8065.73 cm^{-1}, 1 eV per molecule equals 23.0609 kcal mole^{-1}, 1 cal = 4.1840 J.

Dicyanogen and cyanogen chloride were commercial materials with minimum purities of 98.5% as stated by the supplier. Samples held at liquid-nitrogen temperature were pumped on to remove noncondensibles. The chloride was also pumped on briefly at dry-ice temperature. Mass spectra indicated a trace of dicyanogen in the cyanogen chloride compound. Cyanogen bromide and cyanogen iodide were also commerical samples with stated minimum purities of 95% to 99%. These were also pumped on at dry-ice temperatures and used without further purification. Mass spectra of each showed only trace amounts of the other halogen compounds. Cyanogen fluoride was synthesized by W. J. Lafferty of the Infra-red and Microwave Spectroscopy Section. According to our mass-spectral data, the stock material contained about 5 mole % dicyanogen and possibly a trace of methyl cyanide. Unfortunately, the amount available was too small to permit fractional distillation and simple bulb-to-bulb distilla-

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* This work was supported in part by the U.S. Atomic Energy Commission.

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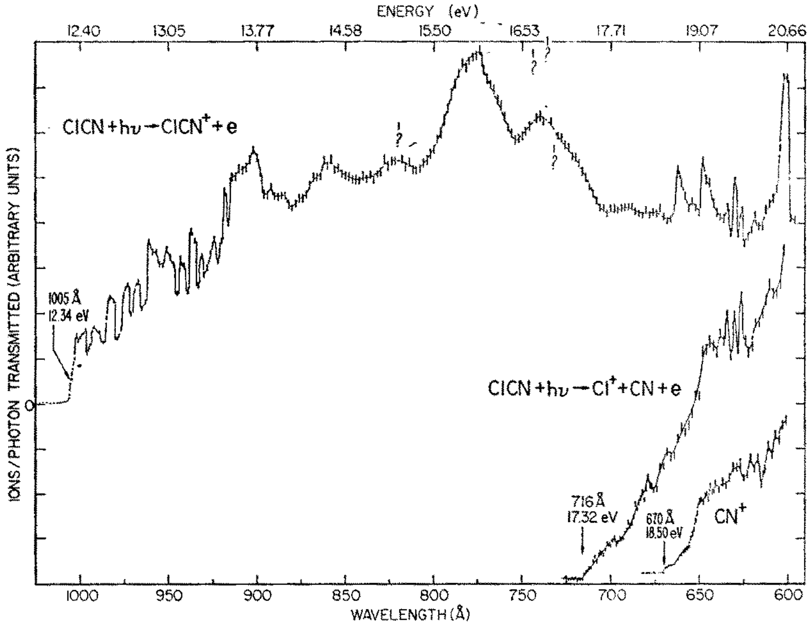

FIG. 1. Photoionization-yield curves for the $ClCN^+$, Cl^+, and CN^+ ions of cyanogen chloride.

tion at low temperatures did not remove the dicyanogen. Therefore, it was used without further purification.

RESULTS AND DISCUSSION

ClCN

The abundances of the cyanogen chloride fragment ions relative to the molecule ion are given in the summary, Table I. The abundances of the isotopic halogen ions are added to provide the "monoisotopic" spectrum. Relative intensities of other ions are less than 1% and there is no evidence for negative ions formed by ion-pair processes. With the latter exception, the photon spectrum at 21 eV is quite similar to the electron-impact spectrum[6] at 70 eV.

Typical photoionization-yield curves for the $^{35}ClCN^+$, $^{35}Cl^+$, and the CN^+ ions are plotted in Fig. 1. Abscissa scales are given in angstroms with the equivalent energy in electron volts at selected wavelengths. In arbitrary units, the ordinate scales for the Cl^+ and CN^+ ions are one-tenth that of the molecule ion. Error bars at each point represent the estimated uncertainty, due principally to the uncertainty in the photon-intensity measurement.

TABLE I. Relative abundances of cyanogen halide ions by photon impact.

	Relative abundance			
Ion	FCN[a]	ClCN[b]	BrCN[b]	ICN[b]
XCN^+	1.00	1.00	1.00	1.00
CX^+	0.32	0.018	0.006	0.008
X^+	···	0.083	0.11	0.25
CN^+	0.08	0.063	0.002	···

[a] At 600 Å (20.66 eV).

[b] At 584 Å (21.23 eV).

The initial threshold of the $ClCN^+$ ion-yield curve rises abruptly. The slope of the onset is approximately that expected from the optical resolution and we select the midpoint, 1005 Å (12.34 eV) as the onset with an estimated uncertainty of ±0.01 eV. The familiar peaks due to autoionization of Rydberg levels in the molecule appear immediately thereafter and we are not able to identify vibrationally excited states of the ion or to observe evidence for the $^2\Pi$ components resulting from spin–orbit coupling of the $p\pi$ electrons. The latter may not be expected in ClCN as studies of ultraviolet absorption[12] and nuclear quadrupole coupling constants[13] indicate considerable electron delocalization and a high degree of conjugation of the halogen and CN electrons. Also, there is not a close correlation between the above threshold and the value of 13.01 eV for the ionization energy of atomic chlorine.[14]

The initial onset is in good agreement with a tentative value of 12.36 eV obtained by photoelectron spectroscopy[15] but is appreciably below the electron-impact value[6] of 12.49±0.04 eV. Obviously, a systematic error several times the quoted imprecision must be involved in the latter measurement or the minimum threshold was not reached by electron impact. There is evidence for a second onset at about 946 Å (13.1 eV) followed by several bands of unresolved autoionization in the wavelength region 900 to 825 Å and perhaps another onset at about 15.3 eV. Several bands of autoionization

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[12] G. W. King and A. W. Richardson, J. Mol. Spectry. **21**, 339, 353 (1966).

[13] J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).

[14] C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. No. 467 (1952).

[15] W. C. Price (private communication).

TABLE II. Summary of threshold observations and some derived thermodynamic values.

Molecule	Ion	Threshold (eV)	Remarks
ClCN	$\mathrm{ClCN^+}$	12.34 ± 0.01	
		15.3 (?)	
		$>18.$	
	$\mathrm{Cl^+}$	17.32 ± 0.02	$\Delta Hf_0{}^\circ$ (CN) $\leq 103.3_6\pm0.05$ kcal mole^{-1}
	$\mathrm{CN^+}$	18.50 ± 0.02	$\Delta Hf_0{}^\circ$ ($\mathrm{CN^+}$) $\leq 430.7_5\pm0.05$ kcal mole^{-1} I (CN) $\geq 14.20\pm0.02$ eV
BrCN	$\mathrm{BrCN^+}$	11.84 ± 0.01	$^2\Pi_{3/2}$
		11.9_3	$\nu_1=735$ cm^{-1}
	$\mathrm{Br^+}$	15.52 ± 0.02	$\Delta Hf_0{}^\circ$ (CN) $\leq 102.6_0\pm0.5$ kcal mole^{-1}
ICN	$\mathrm{ICN^+}$	10.87 ± 0.02	$^2\Pi_{3/2}$
		11.48 (?)	$^2\Pi_{1/2}$
		12.94	
	$\mathrm{I^+}$	13.62 ± 0.02	$\Delta Hf_0{}^\circ$ (CN) $\leq 101.5_6$ kcal mole^{-1}
FCN	$\mathrm{FCN^+}$	13.32 ± 0.01	
		13.43	$\Delta\nu\approx800$ cm^{-1}
		13.52	
		14.4	
	$\mathrm{CN^+}$	19.21 ± 0.02	$\Delta Hf_0{}^\circ$ (FCN) $=5.6\pm1.0$ kcal mole^{-1} D (F–CN) $=5.0_0$ eV
	$\mathrm{CF^+}$	16.35	$\Delta Hf_0{}^\circ$ ($\mathrm{CF^+}$) <270.0 kcal mole^{-1}
		18.8 (?)	$\Delta Hf_0{}^\circ$ (CF) <43.9 kcal mole^{-1}
		20.1 (?)	
$\mathrm{C_2N_2}$	$\mathrm{C_2N_2{}^+}$	13.374 ± 0.008	
		13.64	$\Delta\nu=2178$ cm^{-1}
		15.46	
	$\mathrm{C_2{}^+}$	17.46 ± 0.02	$\Delta Hf_0{}^\circ$ ($\mathrm{C_2{}^+}$) $=476.0\pm0.5$ kcal mole^{-1} I ($\mathrm{C_2}$) $=12.15\pm0.05$ eV
	$\mathrm{CN^+}$	20.42 ± 0.02	Excess energy of 0.6 eV

again appear at 775 to 715 Å, probably representing Rydberg levels converging above 18 eV. A final band is apparent in the region 660 to 600 A suggesting a threshold above 21 eV. Except for the latter, these observations are generally in agreement with the results of photoelectron spectroscopy.[15]

The initial threshold for the $\mathrm{Cl^+}$ ion appears at 716 Å (17.32 ± 0.02 eV). The ion-yield curve shows structure, some of which may be correlated with structure in the molecule–ion curve. The threshold value is equivalent to a heat of reaction $\Delta Hf_0{}^\circ=399.4_1$ kcal mole^{-1} for the process $\mathrm{ClCN}+h\nu\rightarrow\mathrm{Cl^+}+\mathrm{CN}+e$. From the heats of formation,[16] $\Delta Hf_0{}^\circ(\mathrm{ClCN})=32.804$ kcal mole^{-1} and $\Delta Hf_0{}^\circ(\mathrm{Cl^+})=328.86$ kcal mole^{-1}, we calculate the heat of formation of the cyanogen radical, $\Delta Hf_0{}^\circ(\mathrm{CN})=103.3$ kcal mole^{-1}. It should be noted that in the event of excess energy in the dissociative-ionization process, this value represents an upper limit and we estimate the uncertainty in the present result to be less than ±0.5 kcal mole^{-1}. The discrepancy between our value and 109 ± 3 kcal mole^{-1} [1,2] is greater than the combined uncertainties but well within the range of 99 ± 8 kcal mole^{-1}.[7]

The initial onset of the $\mathrm{CN^+}$ ion appears at 670 Å (18.50 ± 0.02 eV) and corresponds to a $\Delta H_0{}^\circ=426.6_3$ kcal mole^{-1} for the process $\mathrm{ClCN}+h\nu\rightarrow\mathrm{CN^+}+\mathrm{Cl}+e$. From the heat of reaction, the $\Delta Hf_0{}^\circ(\mathrm{ClCN})$ and $\Delta Hf_0{}^\circ(\mathrm{Cl})=28.68$ kcal mole^{-1},[16] we calculate $\Delta Hf_0{}^\circ(\mathrm{CN^+})=430.7_5$ kcal mole^{-1}. Subtracting the above heat of formation of cyanogen radical gives the ionization energy, $I(\mathrm{CN})=327.4\pm0.5$ kcal mole^{-1}, or 14.20 ± 0.02 eV. This is identical to, but more precise than, the direct measurement reported by Berkowitz.[1] Of course, this assumes no excess energy in either dissociation process. However, the agreement with the

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[16] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. Tech. Notes 270-1, 2, and 3.

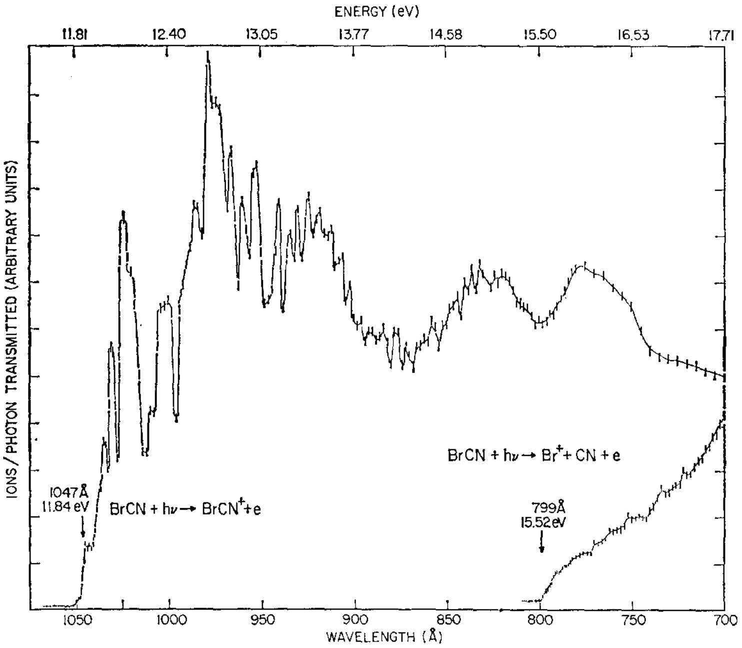

FIG. 2. Photoionization-yield curves for the $BrCN^+$ and Br^+ ions of cyanogen bromide.

directly measured value gives strong support to that value and to our ΔHf_0°(CN). Observed and calculated values are summarized in Table II.

BrCN

The relative intensities of the measurable ions are listed in Table I. As in the case of the chloride, intensities of isotopic bromine ions are added to obtain the "monoisotopic" spectrum. There is no evidence for negative ions; otherwise, there is general agreement with the electron-impact spectrum.[6]

The ion-yield curves for $BrCN^+$ and Br^+ ions are plotted in Fig. 2 in a manner similar to that of Fig. 1. The data are shown down to 700 Å although measurements were made to 600 Å. In the region not shown, the curves are apparently featureless and of nearly constant intensity.

The $BrCN^+$ ion has a sharp onset with a midpoint in the initial segment at 1047 Å (11.84±0.01 eV). This is nearly identical with the ionization energy of atomic bromine[14] and we assume it represents excitation of a halogen-localized $p\pi$ electron. Thus, we ascribe it to the $^2\Pi_{3/2}$ component of the spin–orbit doublet. The separations of the doublet components in HBr^+ and CH_3Br^+ have been reported[17] to be 2653 and 2540 cm^{-1}, respectively. This interval of approximately 0.3 eV is completely masked by the intense autoionization in the region below 1035 Å. However, a step is apparent with an onset midpoint at 1039 Å (11.9_3 eV). This $\Delta\nu = 735$ cm^{-1} is very near the zeroth-order $\nu_1 = 700$ cm^{-1} (C–Br stretch) estimated by King and Richardson[12] for the *C* state of BrCN.

Our minimum threshold value for $BrCN^+$ is again lower than the electron-impact threshold, 11.98±0.08 eV, by an amount somewhat greater than the combined uncertainties.[6] However, it is higher than the tentative photoelectron spectroscopy value[15] of 11.76 eV. The latter observations also indicate inner ionization thresholds at 13.4, 14.2, and about 17.9 eV. Although our curve gives considerable evidence of autoionizing Rydberg levels possibly converging to these limits, we are not able to make accurate identification of the onsets.

The Br^+ ion has an abrupt threshold at 799 Å (15.52±0.02 eV). This is equivalent to a $\Delta Hf_0^\circ = 357.9_0$ kcal $mole^{-1}$ for the process $BrCN + h\nu \rightarrow Br^+ + CN + e$. From the heats of formation,[16] $\Delta Hf_0^\circ(BrCN) = 46.07$ kcal $mole^{-1}$ and $\Delta Hf_0^\circ(Br^+) = 301.368$ kcal $mole^{-1}$, we calculate $\Delta Hf_0^\circ(CN) = 102.6_0 \pm 0.5$ kcal $mole^{-1}$. This is in agreement with the heat of formation obtained from ClCN, within the estimated uncertainty, but suggests that some excess energy may be included in the dissociative ionization processes of the molecule.

ICN

Relative intensities of the three measurable ions are again given in Table I. The partial mass spectrum is similar to that obtained by electron impact[6] except for the absence of negative ions by ion-pair processes.

Figure 3 shows the ion-yield curves for the ICN^+ and I^+ ions plotted to 700 Å. Data obtained down to 600 Å are omitted as the curves are quite featureless and of nearly constant intensity below 700 Å. The ICN^+ ion-yield curve shows a rapid rise at onset with a midpoint of the initial linear segment at 1140 Å (10.87±0.02 eV). This is in agreement with the elec-

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[17] W. C. Price, Proc. Roy. Soc. (London) **A167**, 216 (1939).

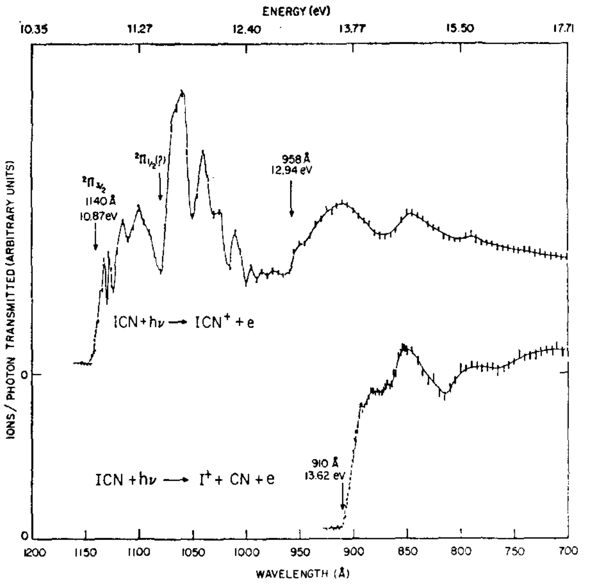

FIG. 3. Photoionization-yield curves for the ICN^+ and I^+ ions of cyanogen iodide.

tron-impact value,[6] of 10.98 ± 0.05 eV provided the uncertainty in that measurement is somewhat greater than quoted. Our value is in excellent agreement with the photoelectron value of 10.89 eV communicated by Price.[15] The comparison with the ionization energy of atomic iodine,[18] 10.448 eV, is not so striking as in BrCN. However, we ascribe the initial onset to the $^2\Pi_{3/2}$ component. Price observes a second onset at 11.45 eV, presumably the $^2\Pi_{1/2}$ component. There is evidence for such an onset in Fig. 3 at 1080 Å (11.48 eV), although the autoionization of the Rydberg levels converging to this limit partially obscure the threshold.

A second band of autoionizing Rydberg levels is observed in the region 1060 to 970 Å. These are apparently converging at about 958 Å (12.94 eV). The spacings of the peaks in this region are nearly constant at about 20 Å (1800 cm^{-1}). This is approximately equal to the ν_3 (C–N stretch) vibrational frequency of 1953 cm^{-1} reported for the *C* state of ICN.[12]

The significant increase in the ion-yield curve at 12.94 eV is nearly identical with the threshold observed by Price[15] at 12.97 eV. Several other broad peaks which may be unresolved bands of autoionization are apparent from 940 to 790 Å. However, no further increase in the ion yield is observed down to 600 Å, although Price reports thresholds at 13.5, 16.64, and 20.4(?) eV.

The I^+ ion has a very sharp onset at 910 Å (13.62 ± 0.02 eV). There is some indication of unresolved structure in the curve, particularly from 860 to 820 Å. This may correspond to autoionization also observed in the molecule–ion curve. The threshold value gives a $\Delta H_0{}^\circ = 314.1$ kcal $mole^{-1}$ for the process $ICN+h\nu\rightarrow I^+ + CN + e$. From the heats of formation[16] and ionization energy of atomic iodine,[18] $\Delta Hf_0{}^\circ(ICN) = 54.04$ kcal $mole^{-1}$ and $\Delta Hf_0{}^\circ(I^+) = 266.571$ kcal $mole^{-1}$, we calculate $\Delta Hf_0{}^\circ(CN) = 101.5_6\pm0.4$ kcal $mole^{-1}$. This is in good agreement with the heat of formation obtained from the chloride and the bromine, although lower than either.

The possibility of excess energy in the dissociative ionization processes used to evaluate $\Delta Hf(CN)$ and the apparent trend suggest that the lowest value is the most nearly correct. In addition, the present uncertainty in heats of formation of the cyanogen halides relative to each other and to dicyanogen is estimated to be 0.2–0.3 kcal $mole^{-1}$. This added to the uncertainty in threshold measurements (0.4–0.5 kcal $mole^{-1}$), strongly suggests use of the minimum value with a total uncertainty of about 1 kcal $mole^{-1}$. Thus, we adopt: $\Delta Hf_0{}^\circ(CN) = 101.5\pm1.0$ kcal $mole^{-1}$, $\Delta Hf_0{}^\circ(CN^+) = 430.0\pm1.0$ kcal $mole^{-1}$, and $I(CN) = 14.2_5\pm0.05$ eV.

FCN

The relative intensities of the FCN^+, CN^+, and CF^+ ions are calculated from observations at 600 Å (20.66 eV) instead of 584 Å to avoid a possibly significant contribution from cyanogen impurities to the CN^+ ion intensity. The relative abundances are given in Table I at that wavelength. Other ions are immeasurably small and there was no evidence for negative ions. Fawcett and Lipscomb[13] report the abundance of the CN^+ and CF^+ relative to FCN^+ to be 0.18 and 0.15, presumably at 70 V. Apparently the relative abundance of the CN^+ ion increases rapidly below 600 Å.

The photoionization-yield curves for the molecule and fragment ions of FCN are plotted in Fig. 4 in the same manner as above. The ordinate scales for the CF^+ and the CN^+ ions are, respectively, one-fifth and one-twentieth that of the FCN^+ ion. The FCN^+ ion shows a rapid rise with a midpoint at 931 Å (13.32 ± 0.01 eV). This is in reasonable agreement with a tentative value[15] of 13.6 eV obtained by photoelectron spectroscopy. The first onset is followed by one clearly defined step at 923 Å (13.43 eV) and a second partially resolved step at 917 Å (13.52 eV). Apparently the Franck–Condon factors for the initial vibrationally excited states are relatively weak. The $\Delta\nu$ of about 0.1 eV or 800 cm^{-1} is ascribed to the C–F stretching frequency, ν_1, of the ions as this frequency in the neutral molecule has been reported[19] to be 1077 cm^{-1}. The $\Delta\nu$ is apparently too large to be ascribed to the spin–orbit coupling components of the ion. As an estimate of this interval, we use the $^2P_{3/2}$–$^2P_{1/2}$ interval of 404 cm^{-1} (0.05 eV) of the atomic fluorine atom. Very likely, the degree of conjugation of the halogen and CN π electrons is greater in FCN than in ClCN and the absence of the spin–orbit components of the $^2\Pi$ state is not surprising.

Strong peaks in the region 910 to 862 Å are due to autoionization of Rydberg levels apparently converging at about 860 Å (14.4 eV). Thereafter, the con-

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[18] L. Minnhagen, Arkiv Fysik **21**, 415 (1962).

[19] R. E. Dodd and R. Little, Spectrochim. Acta **16**, 1083 (1960).

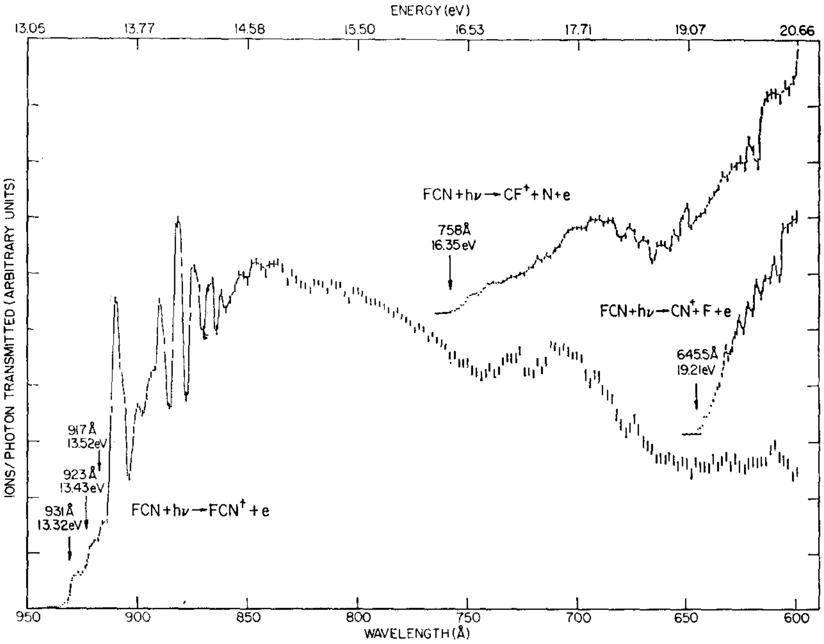

FIG. 4. Photoionization-yield curves for the FCN^+, CN^+, and CF^+ ions of cyanogen fluoride.

tinuum is quite smooth with some indication of further autoionization in the wavelength region of 730 to 700 Å. Thresholds for ionization energies above 14.4 eV are not apparent. However, a tentative report on photoelectron studies[15] indicates such thresholds at 15.6 and 16.8 eV.

The CN^+ ion-yield curve rises very rapidly at a threshold of 645.5 Å (19.21 eV). Thus, the heat of reaction for $FCN+h\nu \rightarrow CN^+ + F + e$ is 442.8 kcal mole^{-1}. As this threshold is about 50 Å below that of CN^+ from dicyanogen there is no difficulty due to possible dicyanogen impurity. If we apply this threshold, the $\Delta Hf_0°(CN^+) = 430.0$ kcal mole^{-1} as given in the previous section, and $\Delta Hf_0°(F) = 18.38$ kcal mole^{-1} [16] we calculate $\Delta Hf_0°(FCN) = 5.6$ kcal mole^{-1} and $D(F\text{–}CN) = 115.3$ kcal mole^{-1} or 5.00 eV. It is difficult to find corroborating evidence for these values. The only estimate of $\Delta Hf(FCN)$ presently available is that obtained by extrapolation of heats of formation[8] and this is by no means conclusive, particularly with regard to fluorine as the terminal element. The situation is quite reminiscent of that regarding the formerly accepted "high" heat of dissociation of F_2 with subsequent spectroscopic[20] and other equilibrium data leading to the presently accepted value of $D(F_2)$. We are not aware of any previous determination of $D(F\text{–}CN)$.

The minimum threshold for the CF^+ ion is observed at 758 Å (16.35 eV). The slowly rising ion-yield curve shows some evidence for step structure in the initial region as well as interference from partially resolved autoionization peaks at shorter wavelengths. Although there is some indication of higher energy thresholds at about 18.8 and 20.1 eV, these are poorly defined. The onset at 16.35 eV (376.9 kcal mole^{-1}) is taken to be the heat of reaction for the process $FCN+h\nu \rightarrow CF^+ + N + e$. However, the transition to ground states of $CF^+ + N$ is forbidden by spin-conservation rules and the threshold may represent an upper limit to the energy required for the adiabatic process. Nevertheless, if we apply the heats of formation, $\Delta Hf_0°(FCN) = 5.6$ kcal mole^{-1} and $\Delta Hf_0°(N) = 112.5$ kcal mole^{-1}, we calculate $\Delta Hf_0°(CF^+) = 270.0$ kcal mole^{-1}. Johns and Barrow[21] report the ionization energy, $I(CF) = 226.1$ kcal mole^{-1} and Andrews and Barrow[22] report $D(C\text{–}F) = 114$ kcal mole^{-1} from which one may calculate $\Delta Hf(CF^+) = 300$ kcal mole^{-1}. Our threshold value indicates this estimate is too high by at least 30 kcal mole^{-1}. The discrepancy probably results from an error in the spectroscopic determination of the dissociation energy of the diatomic molecule CF as our observation is more nearly in accord with the value of $D(C\text{–}F) = 141$ kcal mole^{-1} obtained by means of shock-tube studies.[23]

C_2N_2

The relative intensities of the $C_2N_2^+$, C_2N^+, CN^+, and C_2^+ ions of dicyanogen at 584 Å (21.23 eV) are approximately 1.0, 0.01, 0.07, and 0.2, respectively. There was no evidence for negative ions, and an upper limit for the relative abundance of CN^- is estimated to be 0.002. The ionization-yield curves for the $C_2N_2^+$ and C_2^+ ions are given in Fig. 5. The ordinate scale for the C_2^+ ion is one-half that of the molecule ion. The C_2N^+ ion is immeasurably small in the accessible wavelength region and the CN^+ ion is observed only

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[21] J. W. C. Johns and R. F. Barrow, Proc. Phys. Soc. (London) A71, 476 (1958).

[22] E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London) A64, 481 (1951).

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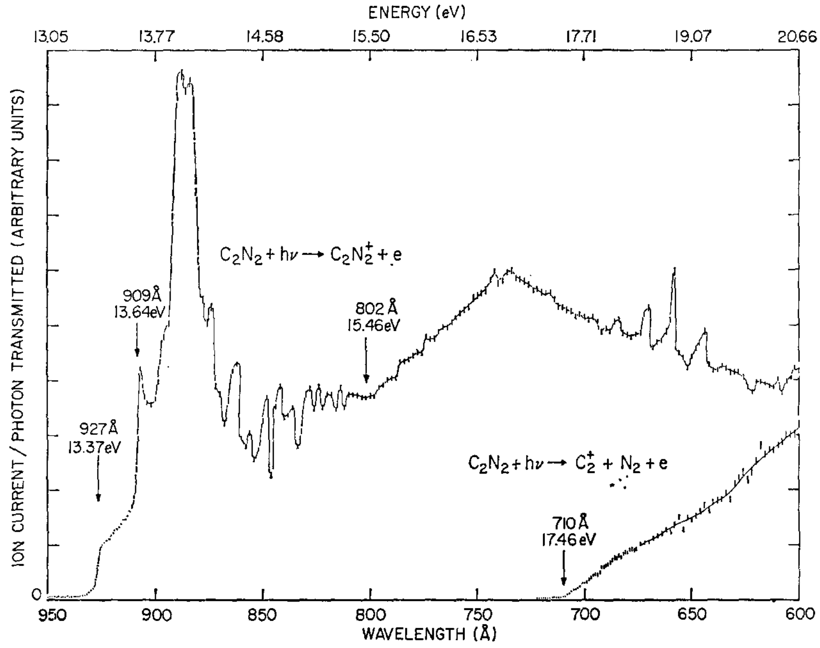

FIG. 5. Photoionization-yield curves for the $C_2N_2^+$ and C_2^+ ions of dicyanogen.

over a very short-wavelength region near 600 Å; therefore both are omitted from the figure.

The rapid onset for the $C_2N_2^+$ ion has an energy spread of approximately 1 Å in the linear segment. The midpoint at 927±0.6 Å (13.374±0.008 eV) is taken as the 0–0 transition. This is considerably below the rough estimate of 13.8 eV obtained by extrapolation of Rydberg levels[24] but is in good agreement with 13.36 eV obtained by photoelectron spectroscopy.[25] It is appreciably below the previously accepted electron-impact value[4] of 13.57±0.02 eV.

A second, rapid onset of great intensity is observed with a midpoint at 909 Å (13.64 eV). The $\Delta\nu = 0.27$ eV or 2178 cm^{-1} is identical with that observed by Turner and Baker[25] and ascribed by them to the C–N symmetrical stretching mode, ν_1. Herzberg[26] gives 2329.9 cm^{-1} as the ν_1 frequency for the $X\,^1\Sigma_g^+$ state of C_2N_2. The diminution in frequency on ionization is about that observed for the ν_2 frequency (C–C stretch) for acetylene[27] upon ionization.

Unlike the photoelectron spectra, the present observations on inner electron thresholds are often obscured by an intense band of peaks in the wavelength region 900 to 810 Å. The observed peaks, ascribed to autoionizing Rydberg levels, apparently correspond to at least two series with average spacings of about 7 Å, converging at about 802 Å. An increase in ion yield is observed at that point (15.46 eV) followed by partially resolved steps at intervals of about 0.2 eV due to vibrational excitation. This structure is quite consistent with the results of photoelectron spectroscopy.[25]

Below 800 Å, the ion-yield curve rises steadily to about 735 Å at which point it again decreases in a nearly linear fashion to the wavelength limit of the present measurements (600 Å). There is clear evidence for another band of Rydberg levels in the wavelength region 680 to 645 Å.

The decrease in the ion-yield curve at about 735 Å (16.8 eV) may mark the onset of a competing process such as dissociative ionization. This point is near to the calculated threshold of 760 Å for the ion pair process $C_2N_2 + h\nu \rightarrow CN^+ + CN^-$, using the electron affinity[28] E.A.(CN) = 85.3 kcal mole^{-1}. However, there is no evidence for the ion-pair process in this or in electron-impact[4] studies. Therefore, dissociation most probably occurs to excited neutral species.

The ion-yield curve for the C_2^+ ion, shown in Fig. 5 has a definite onset at 710 Å (17.46±0.02 eV). The curve rises almost linearly and fairly smoothly to the limit of our measurements. It is interesting to note that taking into account the proper scale and omitting the autoionization peaks, the addition of the C_2^+ ion curve to that of the molecule ion results in a total ionization curve of nearly constant yield from 710 to 600 Å.

The threshold value of 17.46 (402.6 kcal mole^{-1}) is taken to be the heat of reaction for $C_2N_2 + h\nu \rightarrow C_2^+ + N_2 + e$. From $\Delta Hf_0°(C_2N_2) = 73.428$ kcal mole^{-1} [8] and

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$\Delta Hf_0^\circ(C_2) = 195.8 \pm 1.7$ kcal mole^{-1}[29] we obtain the heat of formation of C_2^+, $\Delta Hf_0^\circ(C_2^+) = 476.0$ kcal mole^{-1} and the C_2 ionization energy, $I(C_2) = 280.2$ kcal mole^{-1} (12.15 eV). In the absence of systematic error, the estimated uncertainty is ±0.05 eV, principally due to the uncertainty in the heat of formation of C_2. Our value for the ionization energy is considerably more accurate, but in agreement with the direct measurement[29] of 12.0±0.6 eV.

The initial onset of the CN^+ ion is very abrupt with a threshold at 607 Å (20.42±0.02 eV), in exact agreement with electron-impact results.[4] Step structure is indicated although the curve could only be followed for 20 Å. The threshold value is equivalent to a $\Delta H_0^\circ = 470.9$ kcal mole^{-1} for the process $C_2N_2 + h\nu \rightarrow CN^+ + CN + e$. From the adopted neutral and ion heats of formation, we calculate a $\Delta H_0^\circ = 458$ kcal mole^{-1}. Thus, the observed value indicates excess energy of about 13 kcal mole^{-1}, or 0.6 eV. This is nearly identical with Kandel's measurement[5] of 0.57 eV and in agreement with the qualitative observations by McDowell and Warren.[4] This is not necessarily inconsistent with Stanton's observations[30] that, at 100 eV, principally thermal-energy CN^+ ions are obtained by electron impact on dicyanogen.

ACKNOWLEDGMENTS

We gratefully acknowledge frequent and helpful discussions with W. H. Evans regarding thermodynamic properties of the molecules. We are also indebted to J. A. Walker for continual assistance in maintenance and operation of the apparatus and to W. J. Lafferty for the gift of cyanogen fluoride.

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 47, NUMBER 11 1 DECEMBER 1967

Cancellations Occurring in the Calculation of Transition Energies by a Perturbation Development of Configuration Interaction Matrices

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(Received 7 July 1967)

Two theorems are demonstrated: (1) The coefficients of most of the $(2n+1)$ excited configurations in the nth- order correction to any well separated monoexcited state are [multiplied by a factor $2^{-1/2}$], equal to the coefficients of most of the $2n$ excited configurations in the nth order correction to the wavefunction of the ground state; (2) while the calculation of the nth-order correction to the energy of any state implies $(2n)$-uple summations over the molecular orbitals, the nth-order correction to the transition energy between the ground and a monoexcited state only implies $(2n-1)$-uple summations over the molecular orbitals. These two theorems are only valid when n is smaller than the number of particles in the system.

I. INTRODUCTION

The interest in perturbation techniques to overcome the independant particles model has been recognized a long time ago by Møller and Plesset.[1] This idea has received some practical applications in the field of quantum chemistry.[2–5] The theoretical and numerical superiority of the Rayleigh–Schrödinger expansion over the Brillouin–Wigner development has been recognized by Brueckner[6] and Grimaldi.[5] Within the framework of the Rayleigh–Schrödinger expansion several partitions of the exact Hamiltonian have been proposed by Steiner.[7] Claverie, Diner, and Malrieu have compared the Møller–Plesset and Epstein[8]–Nesbet[2] partitions of the exact Hamiltonian[9,10] and shown that Kelly's procedure[4] was simply a second-order calculation in the Epstein–Nesbet partition of the Hamiltonian. Hereafter we use the Møller–Plesset partition of the Hamiltonian

$$H = H_{\mathrm{SCF}} + V,$$

where H_{SCF} is the self-consistant Hamiltonian. The energy differences between two states involved in the denominators of the perturbation expansion are the differences between the sums of the energies of the molecular orbitals occupied in the two states. In such a case the energy difference between the ground state and a monoexcited state $i \rightarrow j^*$ is the same as the energy difference between any state and the state one gets from it by a supplementary excitation $i \rightarrow j^*$.

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