

Determination of Bond Dissociation Energies in Hydrogen Cyanide.* Cyanogen and Cyanogen Halides by the Photodissociation Method

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The photodissociation process yielding $CN B^2\Sigma^+$ from various cyanogen compounds has been studied in the vacuum ultraviolet. Threshold energies of incident photon to produce the $CN B^2\Sigma^+$ are measured by monitoring the fluorescence due to the transition $CN B^2\Sigma^+ - X^2\Sigma^+$. The upper bounds of bond energies can be obtained from these thresholds and the electronic energy of $CN B^2\Sigma^+$. The heat of formation of CN, $\Delta H_f^\circ(CN)$, is computed using these bond energies together with various ΔH_f° . $\Delta H_f^\circ(CN)$ of 101 ± 1 kcal mole⁻¹ (422 kJ mole⁻¹) is obtained from the lowest two values measured. This value is within an estimated error in excellent agreement with the photoionization value recently obtained by Dibeler and Liston. The bond energies based on $\Delta H_f^\circ(CN) = 101$ kcal mole⁻¹ for various cyanogen compounds are $D(H-CN) = 120$, $D(Cl-CN) = 97$, $D(Br-CN) = 83$, $D(I-CN) = 73$, $D(NC-CN) = 128$, $D(C-N) = 184$ all in kilocalories per mole with an over-all estimated error of ± 1 kcal mole⁻¹. Because of the weak fluorescence intensity, no reliable bond energy was obtained for CH_3CN . Other values obtained are $D(F-CN) \leq 111$ kcal mole⁻¹ and $\Delta H_f^\circ(FCN) \geq 7.4$ kcal mole⁻¹. A correlation of the dissociation process with the absorption spectrum is briefly discussed. A comparison is made of bond energies obtained by the photodissociation, photoionization, and electron-impact methods. Limitations of the photodissociation method to determine bond energies are discussed.

INTRODUCTION

Bond dissociation energies in diatomic molecules may be determined spectroscopically by the measurement of band convergences or long-wavelength limits of absorption continua. However, in the case of polyatomic molecules, band convergences are extremely rare and no clean-cut example has yet been observed. Furthermore, long-wavelength limits of continua may not always represent corresponding dissociation limits. In fact in most cases observed limits are considerably higher than the calculated limits.¹

Bond energies may be obtained more precisely by measuring appearance potentials of fragment ions produced in ionization processes, provided ionization potentials of fragments are accurately known. The recently developed technique of mass-spectrometric study of photoionization processes has been successfully applied to a number of compounds to obtain bond energies. Alternatively, bond energies may be determined if threshold energies of incident photons producing fragments can be precisely measured. Since it is possible to form electronically excited species in the vacuum ultraviolet as a result of photodissociation, the threshold energies can be measured by monitoring the appearance of the fluorescence due to these species as a function of incident wavelength. This technique apparently was first applied by Terenin and his co-workers in 1936² to obtain the bond energy $D(H-OH)$ of H_2O by measuring the threshold energy to produce $OH A^2\Sigma^+$.

Unfortunately, no clear-cut limit of dissociation was obtained because they used a hydrogen continuum as a light source. This paper reports the results of the determination of bond energies of seven cyanogen compounds, HCN, FCN, ClCN, BrCN, ICN, C_2N_2 , and CH_3CN by measuring threshold energies of incident photons yielding the $CN B^2\Sigma^+ - X^2\Sigma^+$ fluorescence. Cyanogen compounds were chosen since there have been conflicting values of the heat of formation of CN on which bond energies of these compounds must be based. The generally accepted value of 109 ± 3 kcal mole⁻¹ by Berkowitz⁴ was obtained by the mass-spectrometric analysis of the vapor in the equilibrium $C + \frac{1}{2}N_2 \rightleftharpoons CN$ at high temperature. However, more recent work by Dibeler and Liston⁵ provides $\Delta H_f^\circ(CN) = 101 \pm 1$ kcal mole⁻¹ which has been obtained by the measurements of threshold energies to form halogen ions by photoionization of halogen cyanides. In view of this large discrepancy it appears worthwhile to report our value obtained by an entirely different method.

EXPERIMENTAL

Experimental arrangements to measure threshold energies of incident photons to form $CN B^2\Sigma^+$ from cyanogen compounds were similar to those which have been described.⁶ The light source was a hydrogen discharge tube operated on a high-voltage ac power supply. A 0.5-m Seya-Namioka monochromator was used to obtain monochromatic light in the wavelength region 1200–2100 Å. A reaction vessel, 4 cm in length, was

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¹ G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N. J., 1966), p. 482.

² H. Neuimin and A. Terenin, *Acta Physicochim. URSS* **5**, 465 (1936).

³ Estimated over-all limits of error, unless otherwise noted.

⁴ J. Berkowitz, *J. Chem. Phys.* **36**, 2533 (1962).

⁵ V. H. Dibeler and S. K. Liston, *J. Chem. Phys.* **47**, 4548 (1967); **48**, 4765 (1968).

⁶ H. Okabe, *J. Chem. Phys.* **47**, 101 (1967).

placed behind the exit slit of the monochromator. Since the fluorescence intensity was weak a resolution of 7 Å had to be used. The intensity of the fluorescence was monitored by a 13-stage photomultiplier with "S"(Q) spectral response in conjunction with a filter which transmitted radiation in the region 2300–4200 Å. In a separate series of experiments a reaction vessel was placed in front of the entrance slit of an $f/4.4$ -grating monochromator and the spectrum of the fluorescence excited by strong resonance lamps⁷ (Kr, Xe, and Hg) was observed at right angles to the incident beam with an 11-stage photomultiplier (spectral response S-20) located behind the exit slit. The resolution was about 20 Å.

The C_2N_2 and ClCN each with a stated purity of 98% were obtained commercially. Each gas was transferred from its cylinder to the gas-handling system via a P_2O_5 drying tube and was stored in a 1-liter Pyrex flask fitted with a greaseless vacuum stopcock. A mass-spectrometric analysis of C_2N_2 showed 0.4% HCN and 1.2% CO_2 . It was used without further purification. The ClCN was frozen out at $-90^\circ C$ and pumped on for approximately 5 min to reduce impurities. A mass-spectrometric analysis showed 0.1% CO_2 , 0.1% C_2N_2 , and 0.2% HCN. No additional purification was carried out.

The BrCN and ICN were obtained commercially. Each compound was degassed three times at $-90^\circ C$ and then dried by passage over P_2O_5 . The solid was then sublimed into a blackened Pyrex vessel. An analysis of BrCN by mass spectrometry showed 0.2% CO_2 , 1.5% HCN, and 0.3% C_2N_2 . It was used without further purification. The ICN contained 0.1% CO_2 , 1.2% HCN, 0.2% C_2N_2 , and 0.8% I_2 . The I_2 impurity in ICN was further reduced by pumping on the solid for approximately 4 min at room temperature. An analysis of the sample after this treatment indicated less than 0.1% I_2 . The HCN was kindly supplied to us by D. Milligan and M. E. Jacox of the National Bureau of Standards. The gas was prepared by reaction of NaCN with H_3PO_4 . A mass-spectrometric analysis showed 0.2% CO_2 and 0.3% C_2N_2 . No additional purification was performed. The FCN was kindly supplied to us by W. J. Lafferty of the National Bureau of Standards. The gas was prepared by the thermal decomposition of cyanogen trifluoride and purified by bulb-to-bulb distillation. The major impurities were reported to be C_2N_2 , CF_3CN , and CO_2 . Because of the limited amount of the sample no attempt was made to remove these contaminants. In an actual experimental run, however, FCN was always taken from the storage at $-116^\circ C$. This procedure should have greatly minimized the level of C_2N_2 in the reaction cell. The CH_3CN , obtained from the Eastman Kodak Company was of spectrograde. It was used without further purification.

⁷ H. Okabe, *J. Opt. Soc. Am.* **54**, 478 (1964).

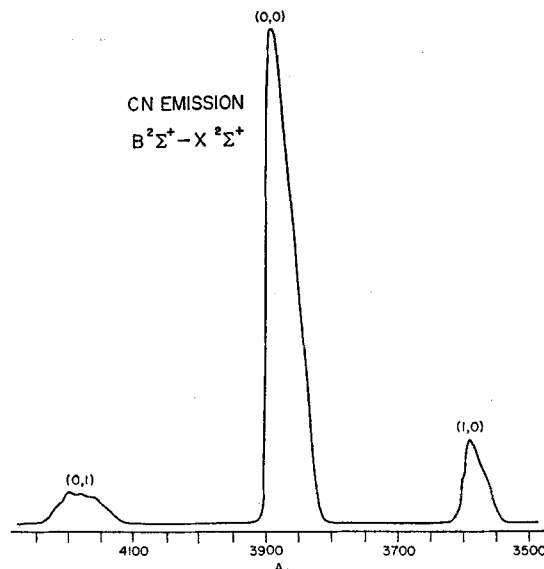


FIG. 1. The CN violet system ($B^2\Sigma^+ - X^2\Sigma^+$) from 1 torr HCN excited by the Kr lines; resolution approximately 20 Å.

RESULTS

The fluorescence spectrum from 1 torr HCN excited by the Kr lines is shown in Fig. 1. No other fluorescence was observed in the region 2000–7000 Å. Three bands (0, 0), (0, 1), and (1, 0) of the CN violet system⁸ $B^2\Sigma^+ - X^2\Sigma^+$ were observed. Since the CN red system $A^2\Pi - X^2\Sigma^+$ lies mainly in the region above 7900 Å⁸ it would not be possible to detect this system if present. Jakovleva reported similar observations when ICN,⁹ BrCN,⁹ and C_2N_2 ¹⁰ were illuminated by a hydrogen continuum. The CN $B^2\Sigma^+$ molecule was reported to be highly rotationally excited. Other cyanogen compounds tested, FCN, ClCN, BrCN, ICN, and C_2N_2 all produced the CN violet system. When ICN was excited by the Hg line at 1849 Å only the (0, 0) and (0, 1) bands were observed. Besides this violet system a continuum was observed for this compound in the spectral region 3100–3400 Å with a maximum at about 3240 Å. This may be due to the I_2 C-X emission bands reported by Venkateswarlu.¹¹ The I_2 in this system may be formed from ICN in contact with the wall. The I_2 emission in the ultraviolet and blue regions from ICN has been reported by Jakovleva.⁹ For the measurement of the fluorescence threshold for ICN, therefore, an appropriate filter to transmit light of wavelength only above 3600 Å was used to eliminate the emission in the region 3100–3400 Å due to the impurity. When a filter transmitting light of wavelength 2200–4200 Å was used the threshold shifted from 1970 to about 2100 Å.

⁸ R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (John Wiley & Sons, Inc., New York, 1963).

⁹ A. Jakovleva, *Acta Physicochim. URSS* **9**, 665 (1938).

¹⁰ A. Jakovleva, *Acta Physicochim. URSS* **10**, 433 (1939).

¹¹ P. Venkateswarlu, *Phys. Rev.* **81**, 821 (1951).

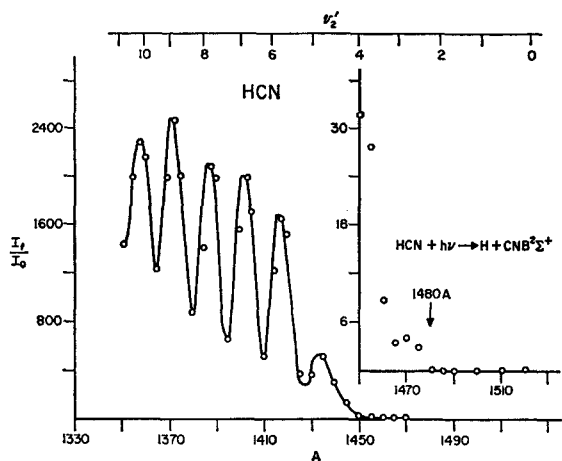


FIG. 2. The intensity of the fluorescence, I_f , from 0.25 torr HCN, normalized to that of the incident light, I_0 , as a function of the incident wavelength. The peaks of the curve approximately correspond to the v_2' vibrational progression of the γ -X system indicated at the top; predissociation to produce CN $B^2\Sigma^+$ takes place from $v_2' = 3$.

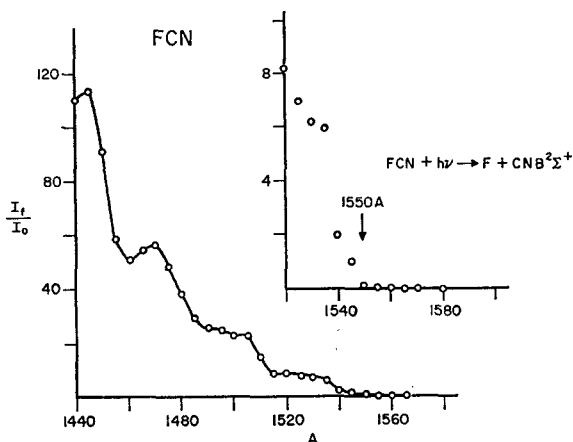


FIG. 3. The normalized fluorescence intensity curve from 0.45 torr FCN as a function of the incident wavelength.

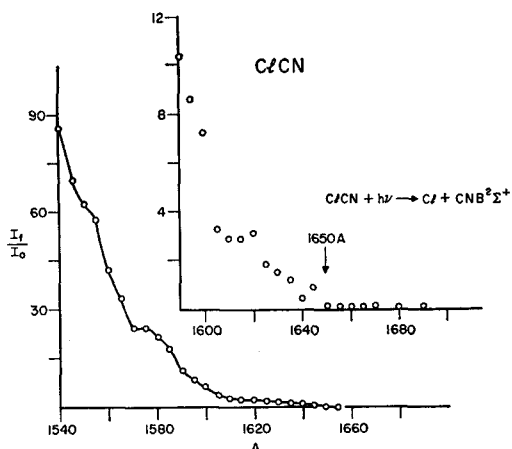


FIG. 4. The normalized fluorescence intensity curve from 0.25 torr ClCN as a function of the incident wavelength.

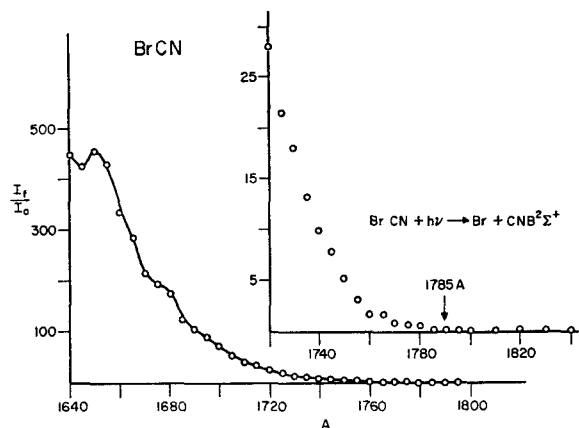


FIG. 5. The normalized fluorescence intensity curve from 0.50 torr BrCN as a function of the incident wavelength.

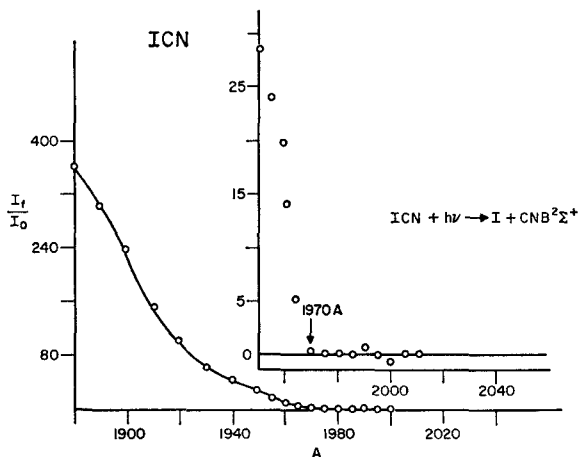


FIG. 6. The normalized fluorescence intensity curve from 0.4 torr ICN as a function of the incident wavelength.

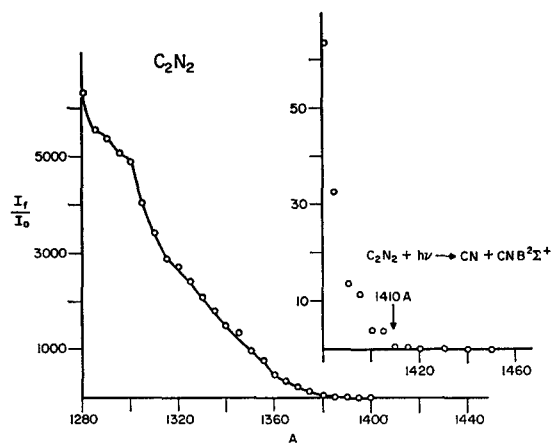


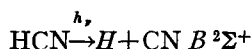
FIG. 7. The normalized fluorescence intensity curve from 0.22 torr C_2N_2 as a function of the incident wavelength.

The intensity of the fluorescence, I_f , in the spectral region 2200–4200 Å, normalized to that of incident photons, I_0 , was measured as a function of the incident wavelength. These fluorescence curves are shown in Figs. 2–7. The CH_3CN yielded a very weak fluorescence in the neighborhood of the expected threshold region (less than 10% in intensity of that from ClCN). Therefore, its threshold could not be determined with certainty. The approximate threshold lies at about 1460 Å. The threshold wavelengths obtained are indicated in Figs. 2–7. Because of the instrumental resolution of 7 Å, the actual threshold are chosen 5 Å below the nominal wavelengths indicated in the figures and are given in Table I with estimated limits of experimental error.

DISCUSSION

Correlation with the Absorption Spectrum

The fluorescence curve for HCN shows several bands indicating that $\text{CN } B^2\Sigma^+$ is produced by predissociation of an electronically excited HCN. These bands approximately correspond to the ν_2' progression of the ν_2' bending vibration of the $\gamma\text{-X}$ system in absorption.^{12,13} This progression is indicated at the top of Fig. 2. It can be seen that the predissociation



sets in at $\nu_2' = 3$, which could be associated with the rapidly increasing diffuseness of the absorption bands of this system. However, the predissociation is apparent even with the $\nu_2' = 0$ bands.¹⁴ Then the (0, 0) and (2, 0) (1, 0) absorption must lead to products other than CN

TABLE I. Threshold energies to form $\text{CN } B^2\Sigma^+$ from cyanogen compounds in photodissociation process.

Molecule	Threshold energies ^a	
	Wavelength (Å)	eV
HCN	1475±10	8.40±0.05
FCN	1545±10	8.02±0.05
ClCN	1645±10	7.53±0.05
BrCN	1780±10	6.97±0.05
ICN	1965±10	6.31±0.04
C_2N_2	1405±10	8.82±0.05
CH_3CN	~1460	~8.5

^a These thresholds are chosen 5 Å below those indicated in the figures because of the 7-Å bandwidth of the incident light.

¹² Reference 1, p. 207.

¹³ W. C. Price, Phys. Rev. **46**, 529 (1934).

¹⁴ G. Herzberg (private communication).

TABLE II. Comparison of bond dissociation energies $D(\text{R-CN})$ of cyanogen compounds obtained by photodissociation, photoionization, and electron-impact methods.

Molecule	Bond dissociation energies (eV)		
	Photo-dissociation ^a	Photo-ionization ^b	Electron impact ^c
HCN	5.20±0.05	5.20±0.02	5.1±0.2
FCN	4.82±0.05	5.01±0.02	...
ClCN	4.33±0.05	4.31±0.02	4.9±0.1
BrCN	3.77±0.05	3.68±0.02	4.4±0.1
ICN	3.11±0.04	3.17±0.02	3.9±0.1
C_2N_2	5.62±0.05	6.22±0.02	6.2±0.3
CH_3CN	5.3	...	4.8±0.1

^a This work.

^b Reference 4.

^c See Table III; calculated on the basis that CN is produced in the ground state.

$B^2\Sigma^+$. Continuous fluorescence curves for ClCN, BrCN, and ICN can be associated with the continuous absorption, the $\alpha\text{-X}$ system,¹⁵ which produces directly the ground-state halogen atoms and $\text{CN } B^2\Sigma^+$. Another process to produce the excited halogen atoms ($^2\text{Br}_{1/2}$, $^2\text{Cl}_{1/2}$) and $\text{CN } B^2\Sigma^+$ should energetically be possible below 1647 Å for BrCN and below 1627 Å for ClCN but there is no apparent change of the curves (Figs. 5 and 4) near these thresholds. The fluorescence curve for C_2N_2 corresponds to the almost continuous transition beginning at about 1450 Å.¹⁶ A very weak fluorescence from CH_3CN may be due to a small extent of the reaction to form $\text{CN } B^2\Sigma^+$ in analogy with the observation that CN^+ and CH_3^+ forming steps are minor in photoionization of CH_3CN .^{5b} Apparently, this fluorescence is associated with the continuous transitions $\tilde{B}\text{-}\tilde{X}$ of CH_3CN .¹⁷

Determination of Bond Energies

Bond dissociation energies can be obtained from the relation

$$D(\text{R-CN}) \leq h\nu_0 - E, \quad (1)$$

where $h\nu_0$ are threshold energies of incident photon to produce $\text{CN } B^2\Sigma^+$ from cyanogen compounds and E , the electronic energy of $B^2\Sigma^+$ which is equal to 3.198 eV. Bond energies obtained by (1) are given in Table II. Bond energies by the photoionization and electron-impact methods are also listed for comparison with

¹⁵ G. W. King and A. W. Richardson, J. Mol. Spectry. **21**, 339 (1966).

¹⁶ W. C. Price and A. D. Walsh, Trans. Faraday Soc. **41**, 381 (1945).

¹⁷ Reference 1, p. 631.

TABLE III. Values used to obtain bond energies in Table II.

Electronic energies of CN ^a		Ionization potential (eV)	
State	eV		
X ² Σ ⁺	0	F	17.42 ^b
B ² Σ ⁺	3.198	Cl	13.01 ^b
		Br	11.84 ^b
		I	10.45 ^b
		CN	14.20±0.02 ^c 14.2±0.3 ^d
		CH ₃	9.843 ^e

Molecule	Ion	Threshold
Threshold energies for the production of radical ions by photoionization (electron volts). ^g		
HCN	CN ⁺	19.40±0.02
FCN	CN ⁺	19.21±0.02
CICN	Cl ⁺	17.32±0.02
BrCN	Br ⁺	15.52±0.02
ICN	I ⁺	13.62±0.02
C ₂ N ₂	CN ⁺	20.42±0.02
Threshold energies for the production of radical ions by electron impact (electron volts)		
HCN	CN ⁺	19.3±0.2 ^d
FCN
CICN	Cl ⁺	17.9±0.1 ^f
BrCN	Br ⁺	16.2±0.1 ^f
ICN	I ⁺	14.3±0.3 ^g
C ₂ N ₂	CN ⁺	20.4±0.3 ^g
CH ₃ CN	CH ₃ ⁺	14.6±0.1 ^g

^a L. Wallace, *Astrophysical J. Suppl.* **7**, 165 (1962).^b C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (1952).^c Reference 5.^d D. P. Stevenson, *J. Chem. Phys.* **18**, 1347 (1950).^e Reference 1, p. 609.^f J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.* **82**, 1555 (1960).^g C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.* **48**, 1084 (1952).

estimated limits of experimental error. Table III provides various values which are used to obtain bond energies in Table II. It is interesting to note that bond energies for HCN and CICN obtained by photodissociation are in excellent agreement with those obtained by photoionization. Bond energies for FCN, ICN, and C₂N₂ by photodissociation are lower by

0.1 to 0.6 eV than those obtained by photoionization. On the other hand, the bond energy for BrCN by photodissociation gives a slightly higher value. However, values by the electron-impact method are in general 0.6–0.8 eV higher than those by photodissociation implying that excess energies are involved in the ionization process or the method of selecting a threshold is doubtful. $\Delta Hf_0^\circ(\text{CN})$ which is calculated using bond energies and various ΔHf_0° given in Table IV, is given in Table V. On the basis of the lowest two values obtained from HCN and ICN, $\Delta Hf_0^\circ(\text{CN}) = 101 \pm 1$ kcal mole⁻¹ corresponding to 4.38 ± 0.05 eV, is chosen. Photodissociation processes in CICN, BrCN, and C₂N₂ seem to involve some excess energies. Based on $\Delta Hf_0^\circ(\text{CN}) = 101$ kcal mole⁻¹, various thermochemical data are calculated and given in Table VI. These values are generally in excellent agreement with those by photoionization. $\Delta Hf_0^\circ(\text{FCN})$ has not been determined thermochemically and therefore $D(\text{F-CN}) = 111$ kcal mole⁻¹ gives an upper limit. $\Delta Hf_0^\circ(\text{FCN})$ calculated on this basis is 7.4 ± 1 kcal mole⁻¹ and is slightly higher than that by photoionization (5.6 ± 1 kcal mole⁻¹) based on $D(\text{F-CN}) = 5.0$ eV.⁵

Limitations on the Determination of Bond Energies by the Photodissociation Method

It has been demonstrated that the photodissociation method is an excellent technique for the determination

TABLE IV. Heats of formation of molecules and atoms at 0°K^a used to compute $\Delta Hf_0^\circ(\text{CN})$.

Molecule and atom	ΔHf_0°	
	kcal mole ⁻¹	eV
HCN	32.39	1.405
CICN	32.804	1.423
BrCN	46.07	1.999
ICN	54.04	2.344
C ₂ N ₂	73.386	3.184
H	51.626	2.240
F	18.38	0.797
Cl	28.68	1.244
Br	28.189	1.223
I	25.631	1.112
C	169.98	7.374
N	112.534	4.882

^a D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. M. Schumm, *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Std. (U.S.) Tech. Note 270-3 (1968).

TABLE V. Comparison of the heat of formation of CN at 0°K, ΔH_f° , obtained by photodissociation and photoionization methods.

Molecule	Photodissociation ^a		Photoionization ^b	
	kcal mole ⁻¹	eV	kcal mole ⁻¹	eV
HCN	101±1	4.37±0.05	...	
ClCN	104±1	4.51±0.05	103.3 ₀ ±0.5	4.48 ₄ ±0.02
BrCN	105±1	4.55±0.05	102.6±0.5	4.451±0.02
ICN	100.7±0.9	4.37±0.04	101.5 ₆	4.406
C ₂ N ₂	102±1	4.41±0.05	...	

^a This work.

^b Reference 5.

of bond energies in various cyanogen compounds even though it gives an upper limit for bond energies. It is also possible to examine the degree of excitation of at least one of the products. It is in general much superior to the spectroscopic method in which the detailed interpretation of the spectrum is required. However, there are several cases in which this method may not be applicable for the determination of bond energies.

(1) The fluorescence takes place by secondary reactions

(a) The dissociation process, $N_2O \rightarrow NO B^2\Pi_7 + N^4S$, requires an energy of at least 10.62 eV or photon of wavelength below 1168 Å. However, the fluorescence due to the transition $NO B^2\Pi_7 - X^2\Pi$ is observable even at 1540 Å of incident wavelength.¹⁸ Therefore this fluorescence must be due to secondary reactions the details of which have been previously described.¹⁸

 TABLE VI. Bond dissociation energies and heats of formation on the basis of $\Delta H_f^\circ(CN) = 101$ kcal mole⁻¹.

	Bond energies	
	kcal mole ⁻¹	eV
$D(H-CN)$	120±1	5.10±0.05
$D(F-CN)^a$	≤111.0±0.8	≤4.80±0.04
$D(Cl-CN)$	97±1	4.20±0.05
$D(Br-CN)$	83±1	3.60±0.05
$D(I-CN)$	73±1	3.16±0.05
$D(NC-CN)$	128±1	5.55±0.05
$D(C-N)$	184±1	7.98±0.05
Heats of formation		
CN	101±1 ^b	4.38±0.05
FCN	≥7.4±1	≥0.32±0.05

^a ΔH_f° (FCN) is not available.

^b Average of lowest two values in Table V.

¹⁸ H. Okabe, J. Chem. Phys. **47**, 101 (1967).

(b) The reaction, $HN_3 \rightarrow N_2 A^3\Sigma_u^+ + NH A^3\Pi_i$, should occur below the incident wavelength 1206 Å, whereas the emission due to $NH A^3\Pi_i$ takes place even at 1470 Å. The $NH A^3\Pi_i$ must be formed by secondary processes previously described.¹⁹

(2) The expected reaction is of minor importance and therefore the product is not detectable.

(a) The reaction, $CH_3CN \rightarrow CH_3 + CN B^2\Sigma^+$, should occur below the incident wavelength 1550 Å, whereas the fluorescence is observable only below 1460 Å.

(b) The process, $HN_3 \rightarrow N_2 X^1\Sigma_g^+ + NH c^1\Pi$, should occur below 2130 Å. However, this reaction occurs only to such a small extent that the actual threshold wavelength is about 1660 Å.¹⁹

(c) While the process, $NH_3 \rightarrow NH A^3\Pi_i + H_2$, should occur below the incident wavelength 1627 Å,^{20a} no fluorescence due to the $NH A^3\Pi_i$ has been observed above 1165 Å^{20b} probably because the process is spin forbidden.

(3) Threshold energies cannot be determined precisely because of the presence of impurities.

The bond energy $D(NO-Cl)$ may be determined from the reaction $NOCl \rightarrow NO A^2\Sigma^+ + Cl$. However, since NO, produced from the decomposition of NOCl in the reaction vessel, is also excited to fluorescence by light near the threshold to form $NO A^2\Sigma^+$, it is not possible to determine the threshold precisely.²¹

(4) There are cases in which threshold energies of the photon in order to form fluorescing species may be outside of the experimentally attainable energy range or no emission from excited species has been known.

ACKNOWLEDGMENTS

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¹⁹ H. Okabe, J. Chem. Phys. **49**, 2726 (1968).

²⁰ (a) H. Okabe and M. Lenzi, J. Chem. Phys. **47**, 5241 (1967); (b) J. H. Becker and K. H. Welge, Z. Naturforsch. **19a**, 1006 (1964).

²¹ M. Lenzi and H. Okabe, Ber. Bunsenges Physik. Chem. **72**, 168 (1968).