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Photodissociation of NCN_3 in the Vacuum-Ultraviolet Production of CN $B\,^2\Sigma$ and NCN $A\,^3\Pi$*

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The photodissociation of NCN_3 in the vacuum ultraviolet has yielded CN $B\,^2\Sigma$ and NCN $A\,^3\Pi$. No NCN $^1\Pi$ was detected. The fluorescence intensity of the CN violet emission, I_f/I_0, was measured as a function of incident wavelength, λ. The I_f/I_0-vs-λ curve shows structure, indicating that the process

$$NCN_3\xrightarrow{h\nu}CN\ B\,^2\Sigma+N_3,$$

is predissociative. The yield at 1216 Å is estimated to be approximately 2.5%. The threshold wavelength of incident photons to yield CN $B\,^2\Sigma$ is 1685±20 Å. The production of NCN $A\,^3\Pi$ is attributed to the formation of N_2 $A\,^3\Sigma$

$$NCN_3\xrightarrow{h\nu}NCN\ X\,^3\Sigma+N_2\ A\,^3\Sigma,$$

with the threshold wavelength of 1915±30 Å followed by the sensitized reaction, $N_2\ A\,^3\Sigma+NCN_3\rightarrow NCN\ A\,^3\Pi+2N_2$. Bond dissociation energies obtained from threshold energies are $D(\text{NC–N}_3)=4.2\pm0.1$ eV ($=96\pm2$ kcal mole^{-1}) and $D(\text{NCN–N}_2)=0.3\pm0.1$ eV ($=7\pm2$ kcal mole^{-1}) where the error limit indicates an experimental uncertainty of the threshold energy measurements. Estimated heats of formation are $\Delta H_f^\circ(\text{NCN}_3)=4.7\pm0.2$ eV ($=108\pm5$ kcal mole^{-1}) and $\Delta H_f^\circ(\text{NCN})=5.0\pm0.2$ eV ($=115\pm5$ kcal mole^{-1}) from which $D(\text{N–CN})$ of 4.3 ± 0.2 eV ($=99\pm5$ kcal mole^{-1}) is obtained. The absorption coefficient of NCN_3 in the region 1200 to 2000 Å has been measured. A comparison is made of bond energies of several azide compounds.

I. INTRODUCTION

The photochemical decomposition of NCN_3 has been studied by means of a matrix-isolation technique at low temperatures[1,2] and by flash kinetic spectroscopy in the gas phase.[3]

The product NCN in the metastable singlet and triplet ground states is identified in solid, as well as in gas phases from their absorption spectra. Kroto[3] found, in addition, CN and N_3 radicals together with a small amount of CNC radical. From these observations two primary reactions [(1) and (2)] may be predominant in the photolysis of NCN_3,

$$NCN_3\xrightarrow{h\nu}CN+N_3, \tag{1}$$

$$NCN_3\xrightarrow{h\nu}NCN+N_2. \tag{2}$$

In the vacuum ultraviolet, the energy of the incident photon is sufficiently large to produce CN, NCN, N_2, and N_3 in their electronically excited states, and the production of each can be seen from its emission spectrum. The formation of NH $c\,^1\Pi$ and $A\,^3\Pi$ was observed in the vacuum-ultraviolet photolysis of HN_3.[4,5] The photolysis of NCN_3 in the vacuum ultraviolet may yield electronically excited singlet as well as triplet NCN in analogous reactions. The emission of the triplet NCN at 3290 Å was observed by Jennings and Linnett[6] when various hydrocarbons were introduced into a stream of active nitrogen. However, no singlet system appears to have been seen in the emission. This work was initiated to obtain information on electronically excited species produced from the vacuum-ultraviolet photolysis of NCN_3, and to measure threshold energies for the production of these excited species from which various bond energies and heats of formation can be deduced.

II. EXPERIMENTAL

The apparatus to measure the fluorescence intensity as a function of incident wavelength has been described.[7] The light source was a hydrogen discharge lamp operated on a high-voltage ac power supply. The lamp was attached to the entrance slit of a 0.5-m Seya–Namioka vacuum-ultraviolet monochromator which provided monochromatic light of about 7 Å bandwidth. The fluorescence intensity was measured at right angles to the incident beam at the exit slit. An appropriate broad-band filter was used to isolate the fluorescence within a desired spectral region. A time constant of 5 sec was incorporated in the recorder and a scanning rate of 20 Å/min was used. The reaction cell, made of monel, was 4±0.05 cm in length. The pressure of a gas was measured by a calibrated diaphragm gauge. The same reaction cell was used for the measurement of the absorption coefficient of NCN_3 (with a resolution of

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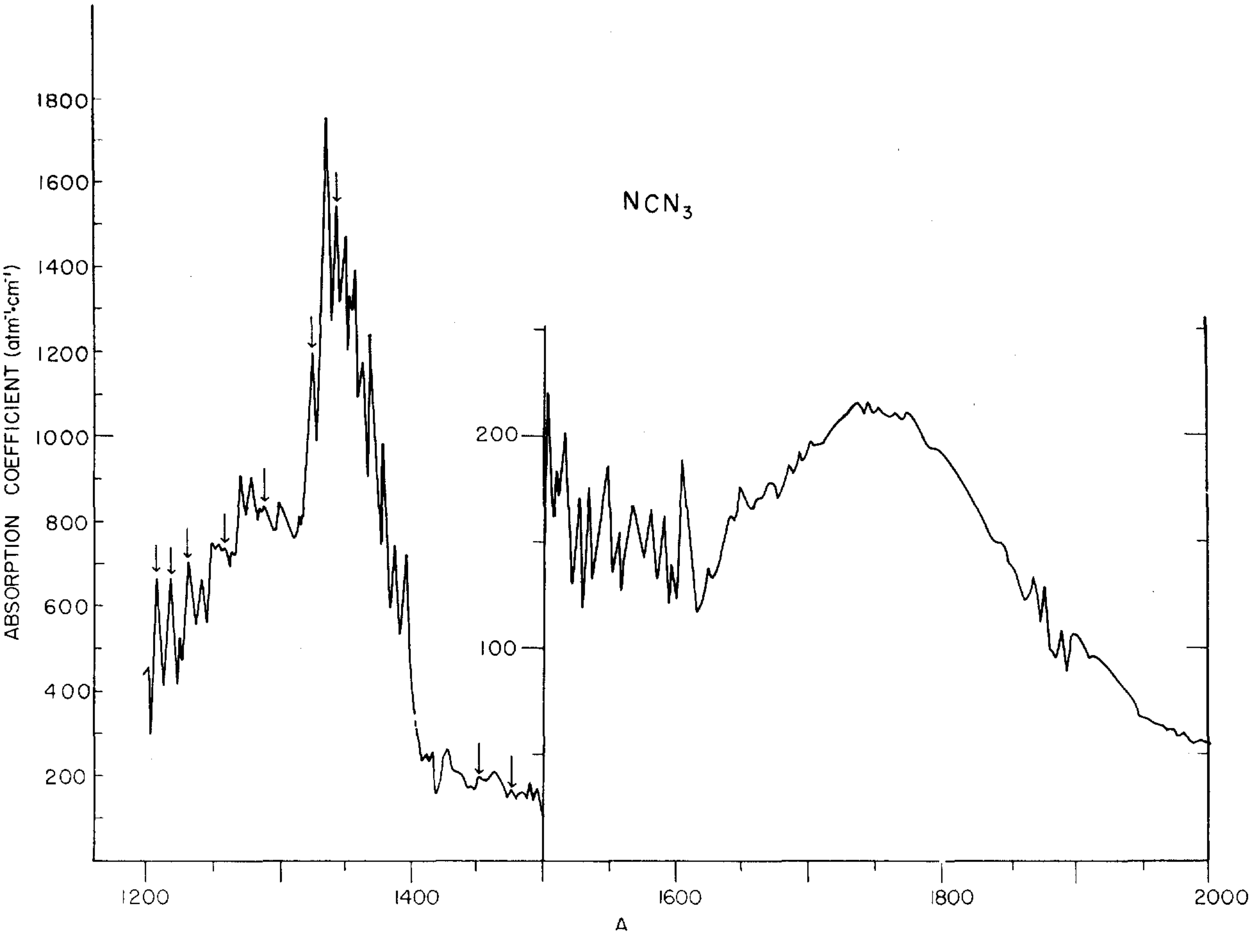

FIG. 1. Absorption coefficient of NCN_3 in the region 1200–2000 Å at 2-Å intervals, resolution ~3 Å, arrows indicate absorption bands responsible for the production of CN $B\ ^2\Sigma$.

about 3 Å). In order to identify an emission spectrum, the cell was attached to the entrance slit of the monochromator and the fluorescence, excited by various monochromatic light sources, was observed at right angles to the incident beam. The spectrum was monitored by means of a 13-stage photomultiplier placed behind the exit slit. Monochromatic light sources used were the Kr (1165, 1236 Å), Xe (1295, 1470 Å), Hg (1849 Å), and I (2062 Å) lamps excited by a 2450-MHz microwave generator. Since the window of the lamp lost its transmission very quickly during photolysis, it was necessary to use a fast scanning rate (50–100 Å/min) with a sacrifice of signal-to-noise ratio.

The NCN_3 was prepared by the technique described by Milligan, Jacox, and Bass[2] with some modification. The BrCN (a solid with a vapor pressure of 86 torr at room temperature), obtained commercially, was placed at the bottom of a tube which was packed with a column of dry and finely powdered NaN_3. After the tube was evacuated and the stopcock closed, the mixture was left overnight until all solid BrCN disappeared. The NCN_3 thus obtained was analyzed mass spectrometrically. It was found that as soon as NCN_3 was introduced into a heated inlet system it decomposed completely into nitrogen and polymeric materials, since only $m/e=28$ was observed. The entire spectrum was therefore scanned in 20 sec after cooling the inlet system. The sample contained about 20% CO_2, 6% C_2N_2, and 1.5% BrCN. No further purification was attempted since it exploded when cooled by liquid nitrogen. The N_2O and NO, both obtained commercially, were purified by bulb-to-bulb distillation.

TABLE I. Mass spectrometric analysis of NCN_3; electron accelerating voltage is 70 V, scanning time is 20 sec.

m/e	Relative abundance[a]			Process
26	7.8	2.3	1.5	$CN^+ + N_3$
28[b]	100	100	100	$N_2^+ + NCN$
40	33.4	23	1.8	$NCN^+ + N_2$
42	1.4	1	0.3	$N_3^+ + CN$
68	11.3	5	0.6	NCN_3^+

[a] Three successive runs of the same sample.

[b] The instrumental resolution is sufficient to separate the N_2^+ peak from the CO^+ peak coming from CO_2.

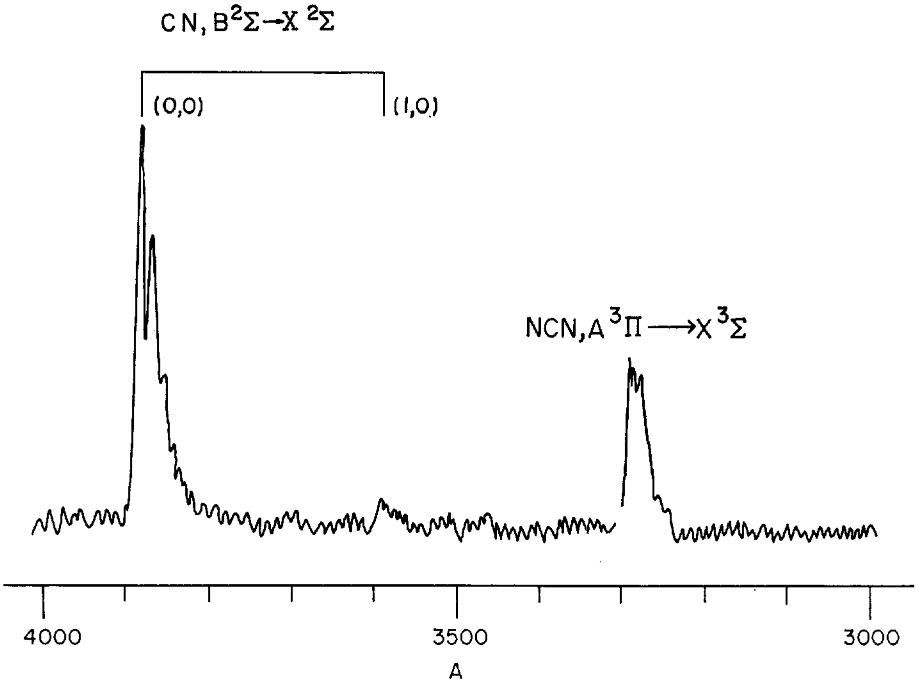

FIG. 2. Emission bands produced from 0.7 torr NCN_3 excited by the Xe lamp, resolution ~7 Å.

III. RESULTS

Table I shows a mass-spectrometric analysis of NCN_3. Main fragment peaks observed were N_2^+, NCN^+, CN^+, and N_3^+. Since the peak ratio of NCN_3^+ to N_2^+ decreased very rapidly with time along with other peak ratios, NCN^+/N_2^+, CN^+/N_2^+, it could not be determined with certainty. The decomposition of NCN_3 proceeded even at room temperature and at low pressure. However, it was found that the sample could be stored without much decomposition in a glass bulb for about 48 h after the sample was made, judging from the consistency of the fluorescence results.

Figure 1 shows the absorption coefficient of NCN_3 in the region 1200–2000 Å measured at 2-Å intervals. The absorption coefficient,[8] k, is defined as $I=I_0 \exp(-kpl)$ where I_0 and I are the intensities of the incident and transmitted light, p is the pressure in atmospheres at 25°C, and l is the path length in centimeters. The pressure used ranged from 0.37–5 torr depending on the extent of absorption. The absorption coefficient was calculated on the basis of 80% NCN_3 and 20% CO_2. Since the absorption coefficient of CO_2 is at most 30 $\text{atm}^{-1}\cdot\text{cm}^{-1}$ in the region above 1200 Å,[9] it does not contribute very much to the spectrum of NCN_3. Some bands in the 1200–1600-Å region may be due to the presence of C_2N_2 whose absorption spectrum shows several diffuse bands in this region.[10]

The absorption spectrum may be divided into four regions A, B, C, and D similar to that of HN_3.[5] Region A (1600–2000 Å) is composed of a broad continuum on which several very weak diffuse bands are superimposed. The maximum of the continuum lies at about 1750 Å with a value of k of about 210 $\text{atm}^{-1}\cdot\text{cm}^{-1}$. Region B (1400–1600 Å) consists of a broad continuum with a number of weak bands superimposed. In Region C (1300–1400 Å) there are many weak bands on an underlying strong and rather narrow continuum whose maximum k is about 1400 $\text{atm}^{-1}\cdot\text{cm}^{-1}$ at about 1340 Å. Region D (1200–1300 Å) contains many diffuse bands superimposed on a broad continuum whose maximum appears to lie at about 1280 Å.

IV. EMISSION SPECTRUM FROM THE PHOTOLYSIS OF NCN_3

The emission spectrum produced from NCN_3 excited by the Xe lamp was scanned in the spectral region 2000–5000 Å. Emissions observed in this region were the CN violet at 3890 Å [11] and the NCN triplet at 3290 Å.[12] No singlet system of NCN was found at 3327 Å.[3]

Figure 2 shows the emission spectra obtained from irradiation of 0.7 torr NCN_3 with the Xe lamp. In addition, the following observations were made.

(1) At the Kr lines, both the CN violet and NCN triplet systems were obtained. The intensity ratio of the CN to NCN emissions was approximately 6 to 1 both at the Kr and Xe lines.

(2) No emission was found when NCN_3 was photolyzed by the I lamp at 2062 Å.

(3) Only the triplet NCN emission was observed at 1849 Å. No CN violet system was seen.

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[8] 1 $\text{atm}^{-1}\cdot\text{cm}^{-1}=2.45\times10^4\ \text{cm}^3\ \text{mole}^{-1}\cdot\text{cm}^{-1}=4.06\times10^{-20}\ \text{cm}^2$.

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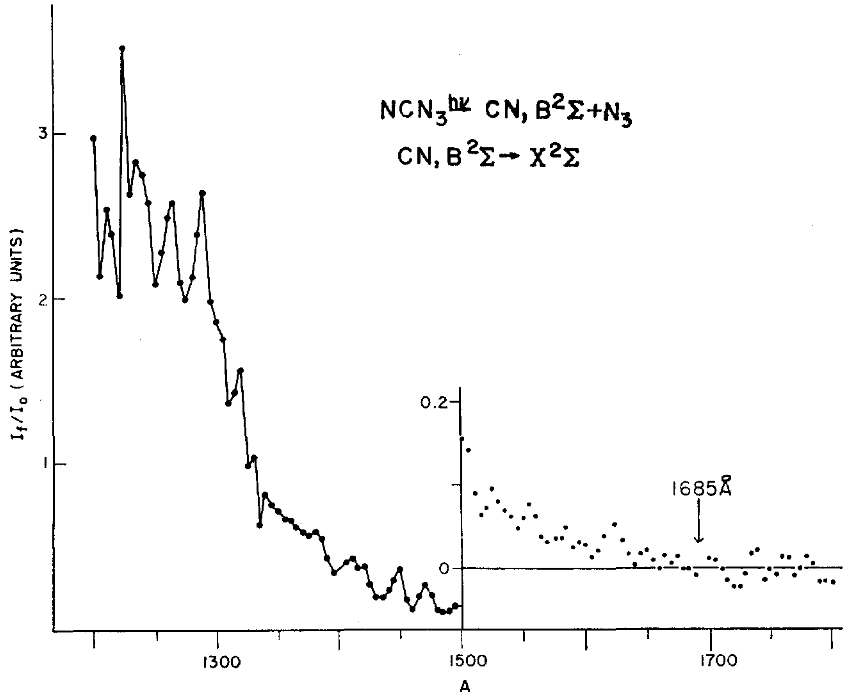

FIG. 3. Fluorescence intensity of the CN violet system as a function of incident wavelength produced from 0.95 torr NCN$_3$; threshold wavelength may be uncertain within 20 Å.

(4) When a mixture of 0.3 torr NCN$_3$ and 0.6 torr NO was irradiated at 1849 Å, NO γ bands were observed. No γ bands appeared in pure NO photolysis.

(5) When increasing amounts of N_2O were added to NCN$_3$ and the mixture was photolyzed by the Xe lines the intensity of the NCN emission increased, whereas that of the CN emission decreased. At 1.5 torr N_2O and 0.3 torr NCN$_3$ the intensity of the NCN emission increased by 20%, whereas that of the CN emission decreased by 70% in comparison with those of pure NCN$_3$.

V. FLUORESCENCE INTENSITIES AS A FUNCTION OF INCIDENT WAVELENGTH

The intensity of the fluorescence of the CN violet system was measured with a filter transmitting light of wavelength above 3400 Å to eliminate the NCN emission. Figure 3 shows that CN fluorescence intensity, I_f, normalized to that of the incident light, I_0, as a function of incident wavelength, λ, when 0.95 torr of NCN$_3$ was irradiated. The I_f/I_0-vs-λ curve shows a number of diffuse bands superimposed on continua. These peaks correspond to some of the absorption bands in Fig. 1 in which corresponding absorption bands are shown by arrows. It is apparent that not all absorption bands match with the emission peaks. The contour of the I_f/I_0-vs-λ curve does not follow the absorption spectrum. The I_f/I_0 is strongest in the absorption region D (1200–1300 Å) and decreases gradually in the region of longer wavelength with a long tail. The fluorescence yield at 1216 Å was estimated to be 2.5% on the basis that the yield of OH $^2\Sigma$ production from H_2O at 1216 Å is 5%.[13] The curve shows a gradual increase with decrease of incident wavelength near threshold. Therefore, it is not possible to determine precisely the threshold wavelength of the CN $B\,^2\Sigma$ production. The value obtained is 1685 Å with an estimated experimental uncertainty of ±20 Å. Since it was shown by mass-spectrometric analysis that NCN$_3$ contained several percent of C_2N_2 and 1.5% of BrCN, it is necessary to examine the effect of these impurities on the threshold determination. The threshold wavelength of the CN $B\,^2\Sigma$ formation from C_2N_2 is 1410 Å,[14] and therefore the presence of C_2N_2 does not affect the value of 1685 Å, although it might contribute to the fluorescence caused by absorption of light in Region D. The I_f/I_0-vs-λ curve of pure BrCN yielded strong peaks at 1470 and 1320 Å corresponding to C and D_0 absorption bands of BrCN.[15] The fluorescence intensity curve of NCN$_3$ does not show corresponding strong peaks at these wavelengths. By comparing the I_f/I_0 of known amounts of pure BrCN with that of NCN$_3$ at 1470 Å, it was estimated that NCN$_3$ contained no more than 1% of BrCN. Contribution of 1% BrCN to the I_f/I_0 at 1685 Å is so small that its presence does not alter the threshold value.

In order to construct I_f/I_0-vs-λ curve for the NCN triplet system it was necessary to isolate this spectrum. However, a filter combination to isolate the spectrum reduced the intensity so much that it was not possible to measure the threshold. Therefore, it was necessary

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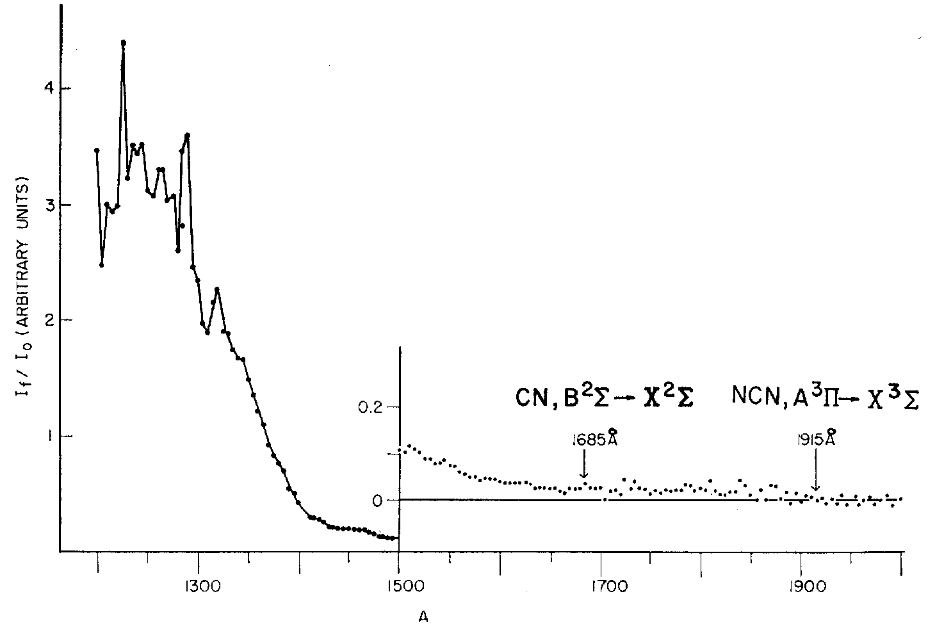

FIG. 4. Total fluorescence intensity of the CN violet and NCN triplet systems as a function of incident wavelength; threshold wavelength of the NCN production may be uncertain within 30 Å.

to employ a broad-band filter (transmission range 2300–4200 Å) which passed through both the CN and NCN bands. However, since it was shown that the emission at the exciting wavelength of 1849 Å consisted of the NCN bands only, the threshold should correspond to that of the NCN triplet bands. The I_f/I_0-vs-λ curve for the CN and NCN emissions is shown in Fig. 4. The contour of the curve is much the same as that of the CN emission in Fig. 3. The threshold wavelength obtained is 1915±30 Å.

VI. DISCUSSION

A. Production of CN $B\,^2\Sigma$

The formation of CN $B\,^2\Sigma$ from NCN_3 must be due to

$$NCN_3 \xrightarrow{h\nu} CN\,B\,^2\Sigma + N_3. \qquad (1)$$

The I_f/I_0-vs-λ curve in Fig. 3 contains many diffuse peaks, indicating that CN $B\,^2\Sigma$ is formed by predissociation of an electronically excited NCN_3, which is formed predominantly by an absorption in Region D (1200–1300 Å). Since not all absorption bands in this region correspond to the emission peaks there must be another state dissociating to products other than CN $B\,^2\Sigma$ and N_3. Process (1), amounting to almost 2.5% of the total yield, is relatively minor. From the threshold value of 1685±20 Å corresponding to $h\nu = 7.36 \pm 0.1$ eV it is possible to compute an upper limit of the bond dissociation energy $D(NC\text{–}N_3)$,

$$D(NC\text{–}N_3) = h\nu - E_0 = 4.16 \pm 0.1 \text{ eV},$$

where E_0, the electronic energy of CN $B\,^2\Sigma$ ($=3.20$ eV).[16] Using the heats of formation $\Delta H^\circ_f(CN) = 4.38 \pm 0.05$ eV[14,17] and $\Delta H^\circ_f(N_3) = 4.5 \pm 0.2$ eV,[18] estimated by Evans, Yoffe, and Gray, ΔH_f^0 of NCN_3 is estimated to be 4.7 eV with an over-all uncertainty of ±0.2 eV. Uncertainty in $\Delta H^\circ_f(NCN_3)$ comes mainly from that of $\Delta H^\circ_f(N_3)$ which is estimated from a calculated $\Delta H^\circ_f(N_3^-)$ using a Born cycle and measured values of electron affinity E of N_3. $E(N_3) = 3.0$ eV appears to be uncertain within 0.2 eV. Since ΔH°_f of solid NCN_3 is 4.02 eV,[19] the heat of sublimation is 0.7 eV ($=16$ kcal mole^{-1}). This value is not very far from that of CNI which is 0.62 eV ($=15$ kcal mole^{-1}).[19] Since the electronegativity of N_3 is close to that of I[20] this may be a reasonable agreement.

B. Formation of NCN $A\,^3\Pi$

In flash photolysis of NCN_3, Kroto[3] followed the time dependence of the NCN radical by absorption spectroscopy. It was shown that at the shortest time delay after flash, the singlet NCN was predominant. Subsequently the singlet started to decay and the triplet to grow. This is a clear demonstration that the spin is conserved in Reaction (2), since NCN_3 is almost certainly in a singlet state

$$NCN_3 \xrightarrow{h\nu} NCN\,^1\Delta + N_2\,X\,^1\Sigma, \qquad (2)$$

and that Reaction (3), a spin-forbidden process, does not take place;

$$NCN_3 \xrightarrow{h\nu} NCN\,X\,^3\Sigma + N_2\,X\,^1\Sigma. \qquad (3)$$

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It was then expected that an electronically-excited NCN $^1\Pi$ should be produced in the vacuum ultraviolet photolysis;

$$NCN_3 \xrightarrow{h\nu} NCN\ ^1\Pi + N_2\ X\ ^1\Sigma. \qquad (4)$$

However, no emission was detected at 3327 Å due to the transition NCN $^1\Pi$–$^1\Delta$. Therefore, although Reaction (4) is spin allowed and is energetically possible in the vacuum-ultraviolet photolysis, it must be a very minor process. Besides the CN violet system, another system was found in the region 3260–3290 Å which can be ascribed to a transition NCN $A\ ^3\Pi$–$X\ ^3\Sigma$. Since Reaction (5) is a spin-forbidden process,

$$NCN_3 \xrightarrow{h\nu} NCN\ A\ ^3\Pi + N_2\ A\ ^1\Sigma, \qquad (5)$$

and the spin-allowed reaction (6) requires photon energy of at least 10 eV,

$$NCN_3 \xrightarrow{h\nu} NCN\ A\ ^3\Pi + N_2\ A\ ^3\Sigma. \qquad (6)$$

NCN $A\ ^3\Pi$ must be formed by a secondary process. The only energetically feasible process below the threshold wavelength of 1915 Å appears to be Reaction (7), which is spin allowed,

$$NCN_3 \xrightarrow{h\nu} NCN\ X\ ^3\Sigma + N_2\ A\ ^3\Sigma \qquad (7)$$

followed by Reaction (8),

$$N_2\ A\ ^3\Sigma + NCN_3 \rightarrow NCN\ A\ ^3\Pi + 2N_2, \quad \Delta H = -2.1\ \text{eV}. \qquad (8)$$

An alternative mechanism, namely, Reaction (9),

$$NCN_3 \xrightarrow{h\nu} N\ ^2P + CN\ X\ ^2\Sigma + N_2\ X\ ^1\Sigma, \qquad (9)$$

followed by Reaction (10), which is an almost thermoneutral process,

$$N\ ^2P + NCN_3 \rightarrow NCN\ A\ ^3\Pi + N_3, \qquad (10)$$

requires incident photon energy of more than 8 eV. The following observations are consistent with the mechanism (7) followed by (8) for the formation of NCN A $^3\Pi$.

TABLE II. Bond dissociation energies and heats of formation obtained from photodissociation of NCN_3.

	eV[a]	kcal mole^{-1}
$D(NC–N_3)$	4.2 ± 0.1[b]	96 ± 2
$D(NCN–N_2)$	0.3 ± 0.1[b]	7 ± 2
$D(N–CN)$	4.3 ± 0.2[c]	99 ± 5
$\Delta H^\circ_f(NCN_3)$	4.7 ± 0.2[c]	108 ± 5
$\Delta H^\circ_f(NCN)$	5.0 ± 0.2[c]	115 ± 5

[a] 1 eV molecule^{-1} = 23.06 kcal mole^{-1} = 96.48 kJ mole^{-1}.

[b] Error limits indicate estimated experimental uncertainties of the threshold wavelength measurements.

[c] Error limits indicate the estimated over-all uncertainties.

TABLE III. Bond dissociation energies of some azides.

Compound	$D(R–N_3)$ eV	$D(R–N_3)$ kcal mole^{-1}	Reference
HN_3	4.1 ± 0.3[a]	95 ± 7	25
	3.9 ± 0.3[a]	90 ± 8	26
	3.7 ± 0.2[b]	85 ± 5	18
CH_3N_3	4.1 ± 0.3[a]	95 ± 7	25
	3.8 ± 0.3[a]	88 ± 8	26
NCN_3	4.2 ± 0.1[c]	96 ± 2	this work
$C_6H_5N_3$	3.7 ± 0.2[b]	84 ± 5	see text
cyclo-$C_5H_9N_3$	3.3 ± 0.3[a]	74 ± 7	see text
cyclo-$C_6H_{11}N_3$	3.5 ± 0.3[a]	80 ± 7	see text
	$D(R–N_2)$		
HN_3	0.4 ± 0.1	9 ± 2	25
	0.4 ± 0.1	9 ± 2	18
NCN_3	0.3 ± 0.1	7 ± 2	this work

[a] Error limits indicate the estimated over-all uncertainties [experimental, $\Delta H^\circ_f(R)$ and $\Delta H^\circ_f(N_3)$].

[b] Error limits indicate mainly the estimated uncertainty of $\Delta H^\circ_f(N_3)$.

[c] The error limit is the estimated uncertainty of the threshold wavelength measurement.

(1) A mixture of NCN_3 and NO, when irradiated at 1849 Å, produced emission bands of NO, indicating the formation of $N_2\ A\ ^3\Sigma$ from NCN_3, and the subsequent sensitized emission of NO by $N_2\ A\ ^3\Sigma$,[21]

$$N_2\ A\ ^3\Sigma + NO\ X\ ^2\Pi \rightarrow N_2\ X\ ^1\Sigma + NO\ A\ ^2\Sigma. \qquad (11)$$

(2) The photolysis of a mixture NCN_3 and N_2O at 1470 Å yielded a higher intensity of the NCN triplet emission but a substantially lower intensity of the CN violet than that from the pure NCN_3. Since the photolysis of N_2O at 1470 Å produces $N_2\ A\ ^3\Sigma$,[21,22] which is also produced from NCN_3, the relative concentration of $N_2\ A\ ^3\Sigma$ to that of CN $B\ ^2\Sigma$ formed from the mixture should be higher than that from the pure NCN_3. The NCN $A\ ^3\Pi$ is then produced from $N_2\ A\ ^3\Sigma$ according to Reaction (8), while CN $B\ ^2\Sigma$ is formed only from the direct photolysis of NCN_3, since Reaction (12) is endothermic by 1.1 eV,

$$N_2\ A\ ^3\Sigma + NCN_3 \rightarrow CN\ B\ ^2\Sigma + N_3 + N_2. \qquad (12)$$

Therefore the concentration of NCN $A\ ^3\Pi$ relative to that of CN $B\ ^2\Sigma$ produced in the mixture is larger than that formed in the pure NCN_3. A similar mechanism

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[22] K. H. Welge, J. Chem. Phys. **45**, 166 (1966).

was proposed by Welge[23] for the formation of NH $A\,^3\Pi$ from HN_3,

$$N_2\,A\,^3\Sigma+HN_3\rightarrow NH\,A\,^3\Pi+2N_2. \qquad (13)$$

The occurrence of Reaction (13) was directly demonstrated by Stedman and Setser[24] in the flow discharge of mixtures of Ar and N_2 to form $N_2\,A\,^3\Sigma$. When HN_3 was added downstream, the NH triplet emission was observed as a result of Reaction (13). The excited state of NCN_3 from which $N_2\,A\,^3\Sigma$ is produced must be the same as that yielding the CN $B\,^2\Sigma$ since the fluorescence intensity curve for the CN violet and the NCN triplet (Fig. 4) shows almost the same contour as that for the CN violet (Fig. 3). Once the mechanism of the NCN $A\,^3\Pi$ production is established, it is possible to compute an upper limit of the bond dissociation energy $D(NCN-N_2)$ from the threshold wavelength of Reaction (7), namely, 1915±30 Å ($h\nu=6.47\pm0.1$ eV), and the electronic energy E_0 of $N_2\,A\,^3\Sigma$ ($=6.17$ eV),[16]

$$D(NCN-N_2)=h\nu-E_0=0.3\pm0.1 \text{ eV}.$$

Combining with the previously obtained $\Delta H°_f(NCN_3)$ of 4.7±0.2 eV, $\Delta H°_f(NCN)$ is estimated to be 5.0±0.2 eV. Bond energies and heats of formation obtained by the photodissociation of NCN_3 are summarized in Table II.

C. Bond Dissociation Energies of Some Azide Compounds

Bond dissociation energies, $D(H-N_3)$ and $D(CH_3-N_3)$ may be obtained from appearance potentials (A.P.) of N_3^- produced from electron impact of HN_3 and CH_3N_3, using an estimated value of $E(N_3)$ of 3.0±0.2 eV.[18] Franklin *et al.*[25] obtained A.P. of N_3^- of 1.1±0.2 eV and 1.1±0.3 eV from HN_3 and CH_3N_3, respectively. Bond energies, $D(H-N_3)$ and $D(CH_3-N_3)$, obtained are, respectively, 4.1±0.2 eV and 4.1±0.3 eV. From the A.P. of N_2^+ they also obtained $D(HN-N_2)$ of 0.4±0.1 eV. Recently, Chiang and Wheeler[26] have studied desorption of N_3^- from a heated filament operating in gases of HN_3 and CH_3N_3. From the temperature variation of this current, $D(H-N_3)$ and $D(CH_3-N_3)$ of 3.9±0.3 eV and 3.8±0.3 eV are obtained. For the derivation of bond energies, however, they had to use binding energies of H and CH_3 adsorbed on a tungsten surface and an estimated value of $E(N_3)$. Another set of data may be derived from $\Delta H°_f(HN_3)$ of 3.11±0.01 eV,[18] $\Delta H°_f(N_3)$ of 4.6±0.2 eV,[18] $\Delta H°_f(H)$ of 2.26 eV[19] and $\Delta H°_f(NH)$ of 3.5±0.1 eV.[27] Bond energies derived are $D(H-N_3)=3.7\pm0.2$ eV and $D(HN-N_2)=0.4\pm0.1$ eV. Bond energies $D(R-N_3)$ of phenyl azide, cyclopentyl azide, and cyclohexyl axide may be computed from the following heats of formation:

$\Delta H°_f(C_6H_5N_3)=4.05$ eV (calculated from the heat of combustion obtained by Roth and Mueller),[28]

$\Delta H°_f(\text{cyclo-}C_5H_9N_3)=2.29$ eV,[29]

$\Delta H°_f(\text{cyclo-}C_6H_{10}N_3)=1.60$ eV,[29]

$\Delta H°_f(C_6H_5)=3.1\pm0.1$ eV,[30]

$\Delta H°_f(\text{cyclo-}C_5H_9)=0.95\pm0.2$ eV,[30]

$\Delta H°_f(\text{cyclo-}C_6H_{11})=0.52\pm0.2$ eV.[30]

Values computed are:

$$D(C_6H_5-N_3)=3.7\pm0.2 \text{ eV},$$

$$D(\text{cyclo-}C_5H_9-N_3)=3.3\pm0.3 \text{ eV},$$

$$D(\text{cyclo-}C_6H_{11}-N_3)=3.5\pm0.3 \text{ eV}.$$

Bond energies of some azides are given in Table III.

It is apparent that $D(R-N_3)$ is much stronger than $D(R-N_2)$, which is unusually weak, both in HN_3 and NCN_3. $D(NC-N_3)$ appears somewhat higher than $D(H-N_3)$ and $D(CH_3-N_3)$. Since bond energies $D(R-N_3)$ are based on an estimated value of $E(N_3)$ by Gray[20] ($=3.0\pm0.2$ eV), except that of NCN_3, values are at least uncertain within 0.2 eV. The data can therefore be improved by the more accurate determination of $E(N_3)$.

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