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Preface

The work described in this report was done by the author in collaboration with Drs. Milligan and Jacox. The latter performed the measurements and analysis of the infrared data. The author of this report carried out the ultraviolet measurements. A manuscript based upon this report will be submitted for publication in the Journal of Chemical Physics under the joint authorship of the three participants.

MATRIX ISOLATION STUDY OF THE PHOTOLYSIS OF CYANOGEN AZIDE. THE INFRARED AND ULTRAVIOLET SPECTRA OF THE FREE RADICAL NCN.

Dolphus E. Milligan, Marilyn E. Jacox, and Arnold M. Bass*

National Bureau of Standards, Washington, D. C.

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Abstract

The infrared and ultraviolet absorption spectra of the free radical NCN have been observed following photolysis at wavelengths longer than 2800 Å of cyanogen azide isolated in argon, nitrogen, carbon monoxide, and carbon dioxide matrices. The infrared-active vibrational fundamentals of NCN appear at 423 and at 1475 cm^{-1}. Isotopic studies are consistent with this identification. The force constants and thermodynamic properties of NCN have been estimated. Two ultraviolet absorption systems are associated with NCN. The first of these, previously reported, lies near 3290 Å. The second system is comprised of a progression of bands spaced at intervals of approximately 1045 cm^{-1}, lying between 3000 and 2400 Å. The nature of this second transition is discussed. At wavelengths longer than 2800 Å both cyanogen azide and NCN have been found to photolyze with the production of carbon atoms. The nature of the new features observed in the infrared and ultraviolet spectral regions after photolysis with short wavelength radiation is considered.

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* Work supported in part by NASA.

INTRODUCTION

Considerable attention has recently been focused upon the free radical NCN, which has been detected in independent studies of the emission and absorption spectra of rather complicated chemical systems. Jennings and Linnett(1) observed an emission spectrum near 3290 Å following the introduction of various hydrocarbons into a stream of active nitrogen. Among the possibilities which they suggested to account for this emission was the free radical NCN. However, since isotopic studies were not feasible in their experiments, this identification could not be confirmed. Studies by Herzberg on the flash photolysis of diazomethane have yielded a variety of spectral features in absorption, among them a system near 3290 Å which has been found to correspond to the emission observed by Jennings and Linnett. Herzberg and Travis(2) have confirmed the assignment of this system to NCN and have reported a detailed rotational analysis of the (0,0) band of this transition. They have found NCN to be a linear symmetric molecule with a $^3\Sigma_g^-$ ground state.

Despite these important contributions to our understanding of the geometric and electronic structure of NCN, much remains to be learned about this species. The molecular dimensions have been found to change very little during the observed electronic transition. Consequently, the vibrational fundamentals of NCN could not be deduced from the ultraviolet spectroscopic data, except for an estimate of 370 ± 50 cm^{-1} for the ground state bending frequency. Reflectivity losses in the multiple-reflection cell used for the absorption studies, together with the accumulation of carbon deposits during photolysis, prevented the search for other transitions at shorter wavelengths.

Application of the matrix isolation technique affords the possibility of stabilizing sufficient concentrations of NCN for direct infrared observation. However, a complicated sequence of chemical reactions is involved in the production of this species either by the reaction of a hydrocarbon with active nitrogen or by the photolysis of a mixture of cyanogen and diazomethane in an excess of nitrogen, the system in which Herzberg and Travis obtained their highest yields of NCN. Thus, neither of these processes is suitable for the production of NCN in a matrix. The recent report of Marsh and Hermes(3) of the synthesis of cyanogen azide, on the other hand, provides a very promising source of NCN for matrix observations. A variety of azides have been found to undergo photolysis either in the gas phase or in a matrix with the elimination of molecular N_2 as the primary process. By photolyzing HN_3 in an Ar or N_2 matrix, Milligan and Jacox(4) have produced the free radical NH in sufficient concentration for direct infrared spectroscopic observation. Milligan(5) has obtained the vibrational fundamentals of both $N^{35}Cl$ and $N^{37}Cl$ by photolyzing ClN_3 in an Ar or N_2 matrix, and Milligan and Jacox(6) have extended these observations, obtaining the infrared spectra of NBr and NF, as well.

The successful studies on the halimino radicals, together with the frequent parallels between the chemical behavior of the CN group and that of halogen atoms, suggested very strongly that NCN might be observed following the photolysis of cyanogen azide in a matrix.

Evidence confirming the production of NCN by this means, leading to the direct observation of the vibrational fundamentals of this species, has been presented by Milligan et al(7). The present discussion gives a more complete account of the infrared studies, including the consideration of other species produced upon prolonged photolysis. Ultraviolet observations over an extended spectral range are also reported.

EXPERIMENTAL DETAILS

A satisfactory and safe synthesis of cyanogen azide for these experiments involves the passage of a gaseous mixture of cyanogen bromide (Eastman Organic Chemicals)(8) or of cyanogen chloride, prepared by the method described by Coleman, Leeper, and Schulze(9), with the matrix material through a column packed with dry, finely-powdered sodium azide (Fisher Scientific Co.)(8) at room temperature. Reaction of the cyanogen halide is virtually complete if a freshly-packed azide column 12-15 cm. in length is used. Once the column has been "deactivated" by depletion of the azide concentration on the surface of the particles, the azide can be recovered and reactivated by crystallization from a saturated boiling aqueous solution to which a few milliliters of hydrazine hydrate have been added(10). Precipitation by pouring the hot solution into an excess of acetone gives a finely-divided crystalline material which, after filtration and drying, is very reactive with cyanogen bromide or with cyanogen chloride. The mixture of cyanogen azide with the matrix material is deposited directly, through a variable leak; gaseous mixtures containing cyanogen azide are not stored. Matrix materials used for the present experiments are argon, nitrogen, carbon monoxide, and carbon dioxide. Typical mole ratios are between 100 and 300.

Experiments involving matrix-isolated $N_3C^{15}N$ and $N_3{}^{13}CN$ have also been conducted. 95% $KC^{15}N$ and 50.5% $Na^{13}CN$ (Merck, Sharp, and Dohme of Canada, Ltd.)(8) have been coverted to cyanogen bromide by the procedure of Hartman and Dreger(11) and then to cyanogen azide by the gas phase preparation outlined above.

The cryostats used in these experiments are similar to that described by Milligan(12). Samples were condensed on a cesium iodide window for the infrared studies and on a lithium fluoride window for the ultraviolet observations.

Temperatures of 14° and 20°K, the triple point and normal boiling point of hydrogen, respectively, were used for the observations.

The photolysis source was a medium-pressure mercury arc. A Corning 0-53 (Pyrex 7740) filter(8) was used in many of the experiments to exclude radiation of wavelength shorter than 2800 Å. As is shown, the nature of the photolytic products is drastically altered if shorter wavelength radiation penetrates to the sample.

Infrared spectra were recorded on a double-beam, prism-grating spectrometer (Beckman IR-9)(8). Under the conditions of a typical experiment, the resolution and frequency accuracy are both approximately 1 cm^{-1} between 400 and 2000 cm^{-1} and 2 cm^{-1} between 2000 and 3000 cm^{-1}. The CsI interchange for this spectrometer was used to study the spectrum between 250 and 400 cm^{-1}. The resolution and frequency accuracy of this unit are approximately 3 cm^{-1}.

Studies of the infrared and ultraviolet spectra on the same sample were made by photographing the ultraviolet absorption spectrum on Eastman Kodak 103a-F plates(8), using a Hilger medium quartz spectrograph(8) placed above the infrared spectrophotometer. Both a tungsten lamp and a hydrogen discharge lamp have been used as background sources. More extensive ultraviolet observations were made using an evacuable scanning Ebert-Fastie monochromator(13), provided with a plane grating ruled with 1200 grooves per mm. With the slit widths used (100 microns), the spectral resolution was about 1 Å. The detector was an end-on photomultiplier tube with a sodium salicylate coating. Background continua were provided by a hydrogen discharge lamp with a "Suprasil"(8) window for the wavelength region 1600-3500 Å, and by a Sylvania "Sun-Gun" Lamp(8) for the wavelength region 3500-6000 Å.

OBSERVATIONS

The infrared spectra of a typical sample of Ar:N_3CN = 300 before photolysis, after photolysis using a Pyrex filter, and after unfiltered photolysis are shown in Figs. 1a and 1b. Between mole ratios Ar:N_3CN = 100 and 300, no mole ratio dependence of any of the features has been observed, either before or after photolysis. Table I summarizes the frequencies observed in such experiments, excluding the features known to be due to cyanogen bromide. For photolysis of matrix-isolated cyanogen azide to occur, ultraviolet radiation of wavelength shorter than about 3000 Å appears to be required; when a Corning 0-54 filter(8), having an absolute cutoff near 3000 Å, was placed in the photolysis beam, no photodecomposition of cyanogen azide was observed. After photolysis through a Corning O-53 (Pyrex 7740) filter(8), having an absolute cutoff near 2800 Å, features appear at 423 and at 1475 cm^{-1}. When unfiltered photolysis is conducted, these features and those of cyanogen azide are replaced by a number of other absorptions. The processes characteristic of unfiltered photolysis may occur at wavelengths as long as 2700-2800 Å; when a CCl_4 filter, with cutoff near 2700 Å, was used, features characteristic of the unfiltered photolysis were observed.

Although the infrared absorptions of cyanogen bromide appear to change very little if at all upon extended photolysis, certain features appearing after unfiltered photolysis have been found to undergo frequency shifts when cyanogen chloride is used instead of cyanogen bromide in the preparation of cyanogen azide. The frequencies of the features observed after unfiltered photolysis of mixtures prepared starting with cyanogen bromide and with cyanogen chloride are compared in Table II.

The features observed in N_2:N_3CN samples both before and after photolysis parallel completely those seen in the Ar matrix, as is shown by Figs. 2a and 2b, for which the absorption frequencies are summarized in Table III. Several of the features assigned to cyanogen azide are doubled, with typical splittings of 3 to 5 cm^{-1}.

The features observed in CO:N_3CN samples before photolysis and after photolysis using a Pyrex filter also parallel completely those seen in the Ar matrix, except for small matrix shifts. Of course, the 2100-2300 cm^{-1} region is obscured by the absorption of the CO matrix in these experiments. However, unfiltered photolysis of this system results in an almost entirely different pattern of absorption; only the 393 cm^{-1} feature appears to correlate with the Ar and N_2 matrix observations. Instead, features appear at 541, 550, 568, 576, 1562, 2280, and 2400 cm^{-1}. Observations on a sample of C_3O_2 in a CO matrix have confirmed the assignment of all of these features to C_3O_2. In addition, a transient absorption, with a half life at 14°K of approximately 3 minutes, appears at 1989 cm^{-1}. A detailed study of phenomena related to the observation of this transient species is to be the subject of a separate communication(14).

In studies of the system $CO_2:N_3CN = 100$, observed between 400 and 2400 cm^{-1}, features appear at 425 and at 1490 cm^{-1} upon photolysis through Pyrex. When the Pyrex filter **is** removed, an absorption readily identified as that of carbon monoxide appears at 2140 cm^{-1}. No other new features appear over the wavelength range studied. In this system, when the cyanogen azide has been completely photolyzed, an appreciable concentration of the species responsible for the 425 and 1490 cm^{-1} features remains. Further unfiltered photolysis leads to a marked growth in the carbon monoxide absorption.

The corresponding infrared observations on $Ar:N_3C^{15}N$ (95%) = 100 are presented in Table IV. It is noteworthy that the 423 cm^{-1} feature shifts only slightly and that the intense 1475 cm^{-1} feature, which shifts some 6.5 cm^{-1}, remains unsplit in the ^{15}N experiments. On the other hand, the 393 cm^{-1} feature appearing after unfiltered photolysis is replaced by absorptions at 385 and 391 cm^{-1} in the ^{15}N studies. Other features appearing after unfiltered photolysis in Ar and N_2 matrices are shifted slightly in frequency but remain unsplit.

The results of a study of the system Ar:CO:$N_3{}^{13}CN$ (50.5%) = 160:1:1 are summarized in Table V. The features characteristic of the presence of CO in the system, which are discussed elsewhere$^{(14)}$, have been omitted. The region between 2135 and 2155 cm^{-1} is obscured by the carbon monoxide absorption. The cyanogen azide features are, in general, found to be doubled, confirming that this species exists in the vapor phase as the monomer. Both of the features appearing upon photolysis through Pyrex become pairs of equally intense features in this experiment, confirming that the species responsible for their appearance also contains but one carbon atom. No splitting could be resolved in the 393 cm^{-1} absorption, but the 1241 cm^{-1} feature has associated with it an equally intense feature at 1222 cm^{-1}. In this experiment, very little residual cyanogen bromide was present, and the features which have been found to undergo a shift in frequency when cyanogen chloride is used in the synthesis of cyanogen azide were not observed.

The wavelengths of the features which have been observed in ultraviolet studies of the systems N_2:N_3CN, CO:N_3CN, and Ar:N_3CN are summarized in Tables VI and VII. No discrete ultraviolet absorptions attributable to cyanogen azide have been observed, but a weak, broad absorption band is observed between 2100 and 2300 Å. This substance photolyzes with great ease when subjected to shorter wavelength ultraviolet radiation. After photolysis through a Pyrex filter, an intense absorption appears near 3300 Å. As is shown in Fig. 3, a progression of absorption bands spaced at intervals of about 1045 cm^{-1} also appears between 3000 and 2400 Å. In the N_2 matrix observations, a second component appears about 50 cm^{-1} to the violet of each of the major peaks in this progression. Similar observations have been made in Ar matrix experiments, except that small matrix shifts occur and that the splittings in the 3000-2400 Å bands are somewhat smaller (about 35 cm^{-1}). On photolysis with unfiltered radiation, all of these features diminish in intensity and ultimately disappear, and, as shown in Fig. 4, in the N_2 matrix an intense feature appears near 4190 Å (near 4240 Å in the Ar matrix), together with weaker features at somewhat shorter wavelengths.

In CO matrix observations, the features appearing near 3300 Å and between 3000 and 2400 Å after photolysis through a Pyrex filter are very intense, unstructured, and markedly broadened. However, after photolysis using unfiltered radiation they are replaced by three absorptions near 4365, 4195, and 4005 Å, as shown in Fig. 4. The central feature exhibits somewhat different growth behavior from the other two. Upon prolonged photolysis its intensity levels off, whereas the intensities of the other two features continue to grow.

In addition to the long wavelength features (3700-4500 Å) that appear on prolonged unfiltered photolysis, a rather complex band system appears at shorter wavelengths (2400-1700 Å), as shown in Table VII and Fig. 5. The bands are generally similar in argon and nitrogen matrices, but are not observed at all in the CO matrix. In Fig. 5c the spectrum of cyanogen in argon at 14°K is reproduced to demonstrate that none of the observed structure in the photolysis products can be attributed to cyanogen.

The photographic observations of the ultraviolet spectrum on samples which were also studied in the infrared spectral region have established that the growth rates and photolytic behavior of the infrared and ultraviolet features are exactly parallel. Thus, for example, the intense ultraviolet absorption near 3300 Å, the progression beyond 3000 Å, and the 423 and 1475 cm^{-1} infrared features all undergo simultaneous changes in intensity as the duration of photolysis and the wavelength of the photolyzing radiation are varied.

When extended photolysis of the sample was conducted using the full light of the mercury arc, all of the features characteristic of photolysis with shorter wavelength radiation except the 1241 cm^{-1} feature, which diminishes slowly in intensity, remained unchanged in intensity after the cyanogen azide and the substance responsible for the 423 and 1475 cm^{-1} absorptions had been destroyed. It has not been possible to use such studies to sort out the precursors of the various features characteristic of short wavelength photolysis, since cyanogen azide and the other possible precursor of these absorptions photolyze at approximately the same rate. The possibility of complete initial destruction of the cyanogen azide by photolyzing through a Pyrex filter, followed by photolytic destruction of the intermediate and observation of the products, could not be realized; even after prolonged photolysis through Pyrex, an appreciable concentration of cyanogen azide remained. It is believed that the extensive ultraviolet absorption of the product species filters much of the radiation effective in photolyzing cyanogen azide. As previously mentioned, it is anticipated that N_2 and NCN will be the primary products of the photolysis of N_3CN. A check on the possibility of the reverse reaction to re-form cyanogen azide was made by photolyzing a $^{14}N_2:N_3C^{15}N = 100$ sample using a Pyrex filter. No formation of $N_3C^{14}N$ was detected after photolysis.

The features at 423 and 1475 cm^{-1} were found to disappear when the sample was warmed to a temperature of 35°K, permitting diffusion to occur in the matrix. The features appearing at 393 and 1241 cm^{-1} after photolysis with more energetic radiation also disappeared at this temperature. However, the features at 1236, 1923, and 2110 cm^{-1} could be observed at somewhat higher temperatures, and the remaining peaks were too weak before the warmup operation for significant studies of them to be made.

During warmup, a blue glow, shading into a deep rose color in the center of the sample, which was subjected to more intensive photolysis because of the characteristics of the quartz focusing lens, has been observed.

DISCUSSION

As is seen from the initial traces of Figs. 1 and 2 and from Tables I and III, the correspondence between the infrared features reported by Marsh and Hermes(3) for cyanogen azide and the most prominent features in the matrix observations is excellent. Thus, the reaction of the major portion of the cyanogen halide with the azide in the column to form cyanogen azide is firmly established. Weaker features at 444, 450, 865, and 923 cm^{-1}, not reported in the earlier work, may also be assigned to cyanogen azide, as may be a weak feature near 655 cm^{-1}, generally obscured by the absorption of traces of carbon dioxide in the sample.

Identification of NCN

The parallel growth and disappearance of the infrared absorptions at 423 and 1475 cm^{-1}, of the intense ultraviolet band near 3300 Å, and of the 3000-2400 Å progression suggest that all of these features are contributed by a single species. Warmup data indicate that this species is highly reactive. In an earlier communication,(7) this species has been identified as the free radical NCN. Factors of importance in its identification are:

(1) Photodecomposition of azides by the splitting off of molecular N_2 occurs quite commonly. Assuming that this is also the primary photolytic process for cyanogen azide, the free radical NCN should be the other product.

(2) The appearance of an intense ultraviolet absorption near 3290 Å provides strong indication that the free radical NCN is indeed produced in the present experiments. Since all of the other features observed after Pyrex-filtered photolysis appear and disappear simultaneously with this feature, it is suggested that they, too, may be identified with NCN. Moreover, the 423 cm^{-1} feature appears close to the value of the ground state bending frequency (370 ± 50 cm^{-1}) estimated for NCN by Herzberg and Travis(2).

(3) Recent electron spin resonance observations by Wasserman, Barash, and Yager(15) of the Pyrex-filtered photolysis

of cyanogen azide suspended in a fluorocarbon matrix have yielded a triplet species with a spin-spin coupling in excellent agreement with that found by Herzberg and Travis for NCN.

(4) The infrared observations employing ^{13}C substitution show that the product species contains one and only one carbon atom, while the observation that each of the infrared features undergoes a small frequency shift, without doubling, when $N_3C^{15}N$ is photolyzed requires that either the ^{15}N atom remains in a unique position after photolysis or all of the N atoms are equivalent. As shown by Table VIII, agreement between the observed frequencies and those calculated for isotopically-substituted NCN (assuming that the corresponding frequencies for $^{14}N^{12}C^{15}N$ are the mean of the values for $^{14}N^{12}C^{14}N$ and $^{15}N^{12}C^{15}N$) is excellent.

In summary, available evidence points strongly to the conclusion that all of the features observed after Pyrex-filtered photolysis of cyanogen azide arise from the species NCN. Using the frequencies observed in an argon matrix and a simple valence force potential, the force constants of NCN have been calculated to be $k_{CN} = 5.38$ mdyn/Å and $k_{bend} = 0.22$ mdyn/Å. Although Herzberg and Travis have obtained bond distances for ground state NCN comparable to those for carbon-nitrogen double bonds, the value of k_{CN} compares more closely to that of carbon-nitrogen stretching force constants of typical singly-bonded species. However, our generalizations regarding typical values of force constants have been made using relatively stable singlet species; little is known regarding force constants for triplet molecules.

Using the calculated value for k_{CN}, the infrared-inactive symmetric stretching fundamental of NCN is predicted to lie at 808 cm^{-1}. However, this estimate has neglected the role of the stretching interaction force constant, which has been found to be appreciable for a number of linear triatomic species, including CO_2(16), N_2O, and CCO(14). Subject to the assumption that the symmetric stretching fundamental of NCN is 808 cm^{-1}, the thermodynamic properties summarized in Table IX have been estimated for NCN ($^3\Sigma_g^-$). Values appropriate to a symmetric stretching fundamental as high as 1000 cm^{-1} for three different temperatures have been included.

Electronic Spectrum of NCN

The ground state electronic configuration of NCN has been found to be

$$\ldots 2\sigma_g^{\ 2}\ 2\sigma_u^{\ 2}\ 1\pi_u^{\ 4}\ 1\pi_g^{\ 2}\ ,$$

and the ground state has been observed to possess $^3\Sigma_g^-$ symmetry. Herzberg and Travis have related the upper state of the 3290 Å transition to the $^3\Pi_u$ state of the

$$\ldots 2\sigma_g^{\ 2}\ 2\sigma_u\ 1\pi_u^{\ 4}\ 1\pi_g^{\ 3}$$

electron configuration. Another relatively low electron configuration for NCN is expected to be

$$\ldots 2\sigma_g^{\ 2}\ 2\sigma_u^{\ 2}\ 1\pi_u^{\ 3}\ 1\pi_g^{\ 3}\ .$$

The transition between the ground state and the $^3\Sigma_u^-$ state within this configuration would be allowed. In accordance with the arguments of

Walsh(17), NCN would be expected to remain linear in this state, although it is likely that an appreciable change in the carbon-nitrogen bond distances would result, accompanied by a progression in the upper state symmetric stretching frequency. The analogous pair of transitions has been observed by Dixon(18, 19) for NCO, which has a ground state electronic configuration differing from that of NCN by the addition of one electron to the $1\pi_g$ orbital. As for NCN, the lowest allowed transition has been found to occur with very little change in the moment of inertia. Furthermore, the B ($^2\Pi$) - X ($^2\Pi$) system of NCO, lying between 2650 and 3200 Å, possesses a progression in the upper state symmetric stretching vibration, ν_1'. Dixon(19) reports some evidence for the predissociation of NCO in the B ($^2\Pi$) state. In view of these parallels, it appears reasonable to assign the 3000-2400 Å progression observed for NCN to the transition B ($^3\Sigma_u^-$) - X ($^3\Sigma_g^-$), involving excitation of the upper state symmetric stretching fundamental.

A third electronic configuration to which an allowed transition would be possible for NCN would involve the promotion of one of the $1\pi_g$ electrons, giving

$$\ldots 2\sigma_g^{\,2}\ 2\sigma_u^{\,2}\ 1\pi_u^{\,4}\ 1\pi_g\ 1\bar{\pi}_u \quad \text{or} \quad \ldots(a_1')^2(b_1'')^2(a_1')^2(b_2')^2(a_1's_C)(a_2''),$$

in the notation of Walsh(17). There is some uncertainty in the relative order of orbital energies appropriate to the bent configuration. In a state belonging to this configuration, the arguments of Walsh predict that NCN would be bent. Furthermore, since an electron is promoted from a bonding π-orbital to an antibonding π-orbital, the carbon-nitrogen bonds would be weakened. Thus, photodissociation from this state would be likely. An alternative assignment of the 3000-2400 Å progression to a transition having its upper state of this electronic configuration appears, however, to be relatively improbable. With such an assignment, the progression would be expected to involve separations representing twice the upper state bending frequency. The observed separation (about 1045 cm^{-1}) would thus correspond to a bending frequency of approximately 520 cm^{-1}, some 100 cm^{-1} higher than the value observed for the ground state. Although an increase in the bending frequency in going from a linear to a bent configuration cannot be excluded, it appears to be rather unlikely. Dixon$^{(20)}$ has concluded from an analysis of the carbon monoxide flame bands that the analogous Rydberg-type transition of CO_2 leads to a molecular angle of 122° in the upper state and has estimated that the bending frequency in this upper state is near 600 cm^{-1}, compared to 667 cm^{-1} in the linear ground state.

Mechanism of Reactions Occurring in the Matrix

The present studies and those of Wasserman, Barash, and Yager$^{(15)}$ indicate that, at wavelengths between 3000 and 2800 Å, the photodecomposition of cyanogen azide leads to the production of the free radical NCN:

$$N_3CN + h\nu\ (3000>\lambda>2800\ \text{Å}) \rightarrow NCN + N_2 \qquad (1)$$

By spin conservation, NCN should be formed in an excited singlet state, which is deactivated by the matrix to the observed ground triplet state.

At wavelengths shorter than approximately 2800 Å, NCN undergoes photolysis. Since in the CO matrix experiments the major product of unfiltered photolysis has been found to be carbon suboxide, it is suggested that the photolysis of NCN is likely to proceed with the formation of N_2 and atomic carbon. Observations of the photolysis of NCN in the CO_2 matrix, in which appreciable NCN remained after all of the cyanogen azide had been photolyzed, support this conclusion; appreciable growth in the carbon monoxide absorption resulted as NCN was photolyzed. By spin conservation, the photolysis of NCN is likely to lead to the formation of $C(^3P)$

$$\mathrm{NCN}\ (^3\Sigma_g^-) + h\nu\ (\lambda < 2800\ \mathring{A}) \longrightarrow N_2 + C(^3P) \quad (2)$$

It is conceivable that the photolysis of NCN occurs by predissociation from the $^3\Sigma_u^-$ upper state. However, there does not appear to be an onset of appreciable broadening in the features observed beyond 2800 Å in Ar and N_2 matrices, although NCN has been found to photolyze efficiently at these wavelengths. Furthermore, it is difficult to envision dissociation of NCN $(^3\Sigma_u^-)$ to $C + N_2$; the most likely dissociative path from a linear excited state would probably involve atomization, a process for which a considerably greater energy than that corresponding to 2800 Å is expected to be required. On the other hand, the Rydberg-type transition to a bent configuration involves the promotion of an electron to an antibonding π-orbital, which correlates with the localization of this electron on the C atom as the valence angle approaches 90°. It is easy to envision the production of N_2 and C atoms from this configuration. Thus, although a definitive assignment cannot be made, it appears quite possible that the photodissociation of NCN involves a Rydberg-type transition, with a continuum underlying the discrete features observed beyond about 2800 Å.

Marsh and Hermes(3) have reported two regions of ultraviolet absorption for cyanogen azide--one centered near 2750 Å, which apparently accounts for the observed production of NCN, and another, twenty times as intense, near 2200 Å. It appears unlikely that NCN is produced in this higher energy transition, since in the unfiltered photolysis of cyanogen azide no large initial surge in the concentration of NCN has been observed. A possible mechanism for this higher energy photolysis involves the photoisomerization of cyanogen azide and subsequent decomposition or photodissociation of the species N_3NC:

$$N_3CN + h\nu\ (\lambda<2800\ \text{Å}) \rightarrow N_3 + CN \qquad (3).$$

The free radicals N_3 and CN would be expected to undergo rapid reaction, since they are trapped in the same cavity in the matrix. Such reaction could lead to the regeneration of some of the cyanogen azide. However, an appreciable fraction of the molecular fragments might be expected to recombine by Reaction (4):

$$N_3 + CN \rightarrow N_3NC \qquad (4).$$

Considerable precedent exists for the postulation of this process; Milligan and Jacox(21) have found that the vacuum ultraviolet photolysis of matrix-isolated HCN, ClCN, and BrCN leads principally to the corresponding isocyanides. The species N_3NC would be expected to be highly unstable and to decompose spontaneously or photolytically.

$$N_3NC \rightarrow 2N_2 + C \qquad (5).$$

The details of Reaction (5) are, of course, unknown. Such a process could be envisioned as involving the production of CN_2 as an intermediate. It is noteworthy that the photodecomposition of cyanogen azide by this higher energy process could easily lead to the appearance of C (^{1}D), as well as of C (^{3}P).

There is some suggestion that at least a small amount of CNN may be stabilized following the unfiltered photolysis of cyanogen azide. Wasserman, Barash, and Yager(15) have reported the appearance of a second triplet species which they believe to be CNN following the removal of the Pyrex filter from the photolyzing beam to which their fluorocarbon:cyanogen azide samples were subjected. The ultraviolet features appearing in nitrogen matrix experiments at 4189 and 3964 Å correspond very well with features observed by Goldfarb and Pimentel(22) at 4182 and 3968 Å following the photolysis of diazomethane with ultraviolet radiation shorter than 3400 Å. Robinson and McCarty(23) have observed a feature at 4240 Å following the photolysis of diazomethane in a krypton matrix. These workers have suggested that this feature, which has its counterpart in a strong band appearing at 4238 Å following the unfiltered photolysis of cyanogen azide in an argon matrix, may be assigned to CN_2 or to HCN_2.

It has not been possible to obtain a definitive assignment to CNN of any of the infrared features appearing after unfiltered photolysis. Both the 393 and the 1241 cm^{-1} features disappear readily on warmup, suggesting that they are contributed by a highly reactive species. However, the appearance of the 393 cm^{-1} feature but not of the 1241 cm^{-1} feature in the CO matrix experiments precludes the assignment of these two features to the same species. The ^{13}C matrix experiments suggest that the 1241 cm^{-1} feature is contributed by a species containing only one carbon atom. No splitting in the 393 cm^{-1} feature has been observed on ^{13}C substitution. However, the anticipated shift for the bending mode of ^{13}CNN would be expected to be small, and could easily not have been observed. Herzberg and Travis(2) have noted a correlation between the number of valence electrons and the bending frequency of various linear triatomic species, from which a value near 400 cm^{-1} would be predicted for CNN. Assuming that the skeletal bond distances determined for diazomethane by Cox, Thomas, and Sheridan(24,25) are appropriate also for CNN and that the 393 cm^{-1} feature may be assigned to $^{12}C^{14}N^{14}N$, the calculated bending frequencies for $^{12}C^{15}N^{14}N$ and $^{12}C^{14}N^{15}N$ are, respectively, 384 and 390.6 cm^{-1}. These values are seen to agree well within experimental error with the observed absorptions at 385 and 391 cm^{-1} in the system $Ar:N_3C^{15}N$.

Little can be said regarding the nature of the remaining absorptions appearing in the near ultraviolet following unfiltered photolysis of cyanogen azide. The correlation of the features observed in the CO matrix with those appearing in Ar and N_2 matrices is rather indefinite, although relatively large matrix shifts may conceivably occur in CO, the spacings differ appreciably, and the growth characteristics of the 4194 Å band differ from those of the other features.

The nature of the species contributing to the far ultraviolet absorptions is not known with certainty. As shown in Fig. [illegible], cyanogen can be excluded as a contributor to the observed spectra. The availability of C atoms for chemical reaction suggests the possibility that C_2 may be formed in sufficient concentration for observation of some of its spectral features. Ballik and Ramsay(26,27) have concluded from a detailed analysis of the spectrum of C_2 that the ground state of this species is of $^1\Sigma_g^+$ symmetry, with the $^3\Pi_u$ state of C_2, formerly thought to be the ground state of this species, some 610 cm^{-1} higher. Their summary of the known electronic states of C_2 indicates that the d $^1\Sigma_u^+$ - x $^1\Sigma_g^+$ transition occurs near 43240 cm^{-1}, or 2313 Å. Conceivably this transition may account for some of the features observed in the 2200-2300 Å region in the argon and nitrogen matrix observations. The failure of these features to appear in the carbon monoxide matrix experiments would be consistent with this possibility, since C atoms have been found to react with carbon monoxide.

CONCLUSIONS

The photolysis of cyanogen azide in argon, nitrogen, carbon monoxide, and carbon dioxide matrices with radiation of longer wavelength than 2800 Å yields primarily molecular N_2 and the triplet species NCN. The infrared-active vibrational fundamentals of NCN have been observed at 423 and at 1475 cm^{-1} in an argon matrix, with small shifts when the other matrices are employed. In addition to the $^3\Pi_u$ - $^3\Sigma_g^-$ transition at 3290 Å previously reported for NCN, a progression has been observed in the 3000-2400 Å region. It appears reasonable to assign this progression to a $^3\Sigma_u^-$ - $^3\Sigma_g^-$ transition, with excitation of the upper-state symmetric stretching vibration, with an approximate value of 1045 cm^{-1}. When NCN is subjected to radiation of wavelengths shorter than 2800 Å, it has been observed to photolyze. Studies in carbon monoxide and carbon dioxide matrices indicate that both cyanogen azide and NCN undergo photodecomposition with the production of C atoms.

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Table I

INFRARED ABSORPTIONS (cm^{-1}) APPEARING IN OBSERVATIONS ON $Ar:N_3CN$ SAMPLES

14°K

Initial	After Photolysis ($\lambda > 2800$ Å)	After Photolysis ($\lambda < 2800$ Å)
444	423 m	393 m
450	1475 s	984 vs
655 ?		1035 vw
865		1236 w
923		1241 m
1247 w		1923 m-s
1263 vs		2058 w
2101 vs		2102 m
2151 s		2108 sh
2163 m-s		
2208 vvs		
2249 vs		

Table II

FREQUENCIES (cm^{-1}) OF HALOGEN-DEPENDENT FEATURES APPEARING AFTER UNFILTERED PHOTOLYSIS OF Ar:N_3CN SAMPLES PREPARED USING BrCN and ClCN

BrCN	ClCN
984	996
1035	1025
1923	1945
2102	2113
2108	2118

Table III

ABSORPTIONS (cm^{-1}) APPEARING IN $N_2:N_3CN = 100$

14°K

Initial	After Photolysis ($\lambda > 2800$ Å)	After Photolysis ($\lambda < 2800$ Å)
450	423	394
454	1476 sh	984
871	1478	1038
874		1225 w
923		1249 sh
931		1252
1258		1926
1261		2060 w
2104		2112
2106		
2116 w		
2160		
2175		
2213		
2216		
2222 sh		
2226 sh		
2245		
2247		
2253		
2258		

Table IV

INFRARED ABSORPTIONS (cm^{-1}) APPEARING IN OBSERVATIONS

ON Ar:$N_3C^{15}N$ (95%) = 100

14°K

Initial	After Photolysis (λ > 2800 Å)	After Photolysis (λ < 2800 Å)
441	421	385
448	1468.5	391
852		1218
860		1238
918		1892
936		2030 w
1243 w		2092 (approx)
1259		
2092		
2140		
2149		
2154		
2202		
2208 sh		
2214 w		
2224		
2231		

Table V

ABSORPTIONS (cm^{-1}) OBSERVED FOR Ar:CO:N$_3$^{13}CN (50.5%) = 160:1:1

(excepting CO-dependent features)

Initial	$\lambda > 2800$ Å	$\lambda < 2800$ Å
436	412	392
444 sh	423	
447	1435	1222
451 sh	1475	1241
516 w		2028 vw
		2050 w
655 w		2056 w
856		
859 sh		
865 sh		
868		
871 sh		
914		
916 sh		
922 sh		
925		
928 sh		
1190 w		
1198 w		
1247		
1259 vs		
1263 vs		
2093 sh		
2096		
2100 sh		
2104		
(2135-2155 obscured by CO)		
2194		
2208		
2213		
2220 sh		
2245		
2250		

Table VI

ULTRAVIOLET ABSORPTION BANDS APPEARING AFTER SHORT-TIME PHOTOLYSIS OF H_3CN

	Nitrogen				Carbon Monoxide				Argon			
Int.	λ (Å)	ν (cm^{-1})	$\Delta_{\frac{1}{2}}\nu$	Δν	λ (Å)	ν (cm^{-1})	$\Delta_{\frac{1}{2}}\nu$	Δν	λ (Å)	ν (cm^{-1})	$\Delta_{\frac{1}{2}}\nu$	Δν
42	3303.6	30236	330		3314.3	30164	465		3343.5	29900	349	
3					3193.3	31306	313		3221.1	31036		
18	3009.8	33215	130		3023.4	33066	312		3020.3	33100	132	
11	3004.8	33270							3007.8	33237		
				1054				1048				1052
36	2917.2	34269	129		2930.5	34114	303		2915.5	34289	135	
25	2914.0	34307							2909.0	34366		
				1044				1047				1043
43	2831.0	35313	134		2843.2	35161	297		2829.5	35332	131	
29	2827.0	35363							2826.5	35369		
				1045				1061				1046
38	2749.6	36358	126		2759.9	36222	263		2748.1	36378	106	
25	2746.1	36404							2746.1	36404		
				1050				1033				1033
27	2672.4	37408	101		2683.4	37255	278		2672.2	37411	112	
16	2669.2	37453							2669.7	37446		
				1023				1040				1027
16	2601.3	38431	106		2610.5	38295	375		2600.8	38438	89	
10	2598.5	38472							2598.8	38468		
				1027				1031				1015
8	2533.6	39458			2542.1	39326	402		2533.9	39453		
5	2530.4	39508	140						2531.4	39492	78	
3	2526.9	39562										
				1016				1054				1029
2	2470.0	40474	139		2475.7	40380	245		2469.5	40482	74	
	2466.7	40528							2464.0	40572		
				1074				1060				1040
	2406.1	41548			2412.4	41440	310		2407.6	41522	112	

Table VII

ULTRAVIOLET ABSORPTION BANDS APPEARING AFTER PROLONGED PHOTOLYSIS OF N_3CN

Nitrogen			Argon			Carbon Monoxide		
Int.	λ(Å)	ν(cm^{-1})	Int.	λ(Å)	ν(cm^{-1})	Int.	λ(Å)	ν(cm^{-1})
5	4341	23030				24	4363	22914
7	4309	23201	2	4312	23179	1	4324	23120
75	4189	23865	80	4238	23589	(15)	4194	23837
1	4076	24527	4	4125	24236			
21	3964	25220	27	4011	24924	10	4005	24962
			25	3825	26136			
. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
			5	2500	39988			
11	2446	40871	9	2443	40921			
16	2384	41934	33	2383	41951			
11	2364	42288						
21	2327	42960	27	2333	42850			
5	2302	43427	10	2314	43202			
18	2271	44020	15	2276	43923			
6	2246	44510	10	2253	44371			
8	2216	45122	8	2227	44889			
5	2201	45420	10	2207	45296			
2	2181	45836						
9	2150	46497	10	2154	46411			
			4	2134	46846			
4	2099	47626	10	2105	47491			
			80	2055	48646			

Table VII—Continued

Nitrogen			Argon			Carbon Monoxide		
Int.	λ(Å)	ν(cm^{-1})	Int.	λ(Å)	ν(cm^{-1})	Int.	λ(Å)	ν(cm^{-1})
50	2033	49172	75	2037	49076		2000	49984
6	1968	50799	10	1976	50593		1948	51321
12	1957	51084						
5	1945	51400						
							1876	53290
10	1790	55850	20	1796	55664		1798	55600
			10	1735	57621		1758	56835

Table VIII

FREQUENCIES (cm^{-1}) OF ISOTOPICALLY-SUBSTITUTED NCN

Species	Observed	Calculated
$^{14}N^{12}C^{14}N$	423	....
	1475	....
$^{14}N^{12}C^{15}N$	421	421
	1468.5	1467.6
$^{14}N^{13}C^{14}N$	412	411.4
	1435	1434.8

Table IX

THERMODYNAMIC PROPERTIES (cal/mole-°K) OF NCN

(assuming ν_1 = 808 cm^{-1})

T(°K)	C_p^o	$\frac{H^o - H_o^o}{T}$	$\frac{-(F^o - H_o^o)}{T}$	S^o
273.16	10.22	8.16	45.12	53.28
298.16	10.53	8.35	45.85	54.19
300	10.55	8.36	45.90	54.26
400	11.56	9.04	48.40	57.44
500	12.30	9.62	50.48	60.10
600	12.85	10.12	52.28	62.40
700	13.27	10.55	53.88	64.42
800	13.56	10.90	55.30	66.20
900	13.79	11.21	56.61	67.81
1000	13.97	11.47	57.80	69.28
1100	14.11	11.71	58.90	70.61
1200	14.22	11.91	59.93	71.85
1300	14.31	12.09	60.89	72.99
1400	14.39	12.26	61.80	74.06
1500	14.45	12.40	62.65	75.05
2000	14.64	12.94	66.30	79.24
3000	14.78	13.53	71.66	85.20

……

(assuming ν_1 = 1000 cm^{-1})

300	10.29	8.28	45.88	54.15
1000	13.87	11.31	57.59	68.91
3000	14.77	13.45	71.32	84.78

Figures 1a, b

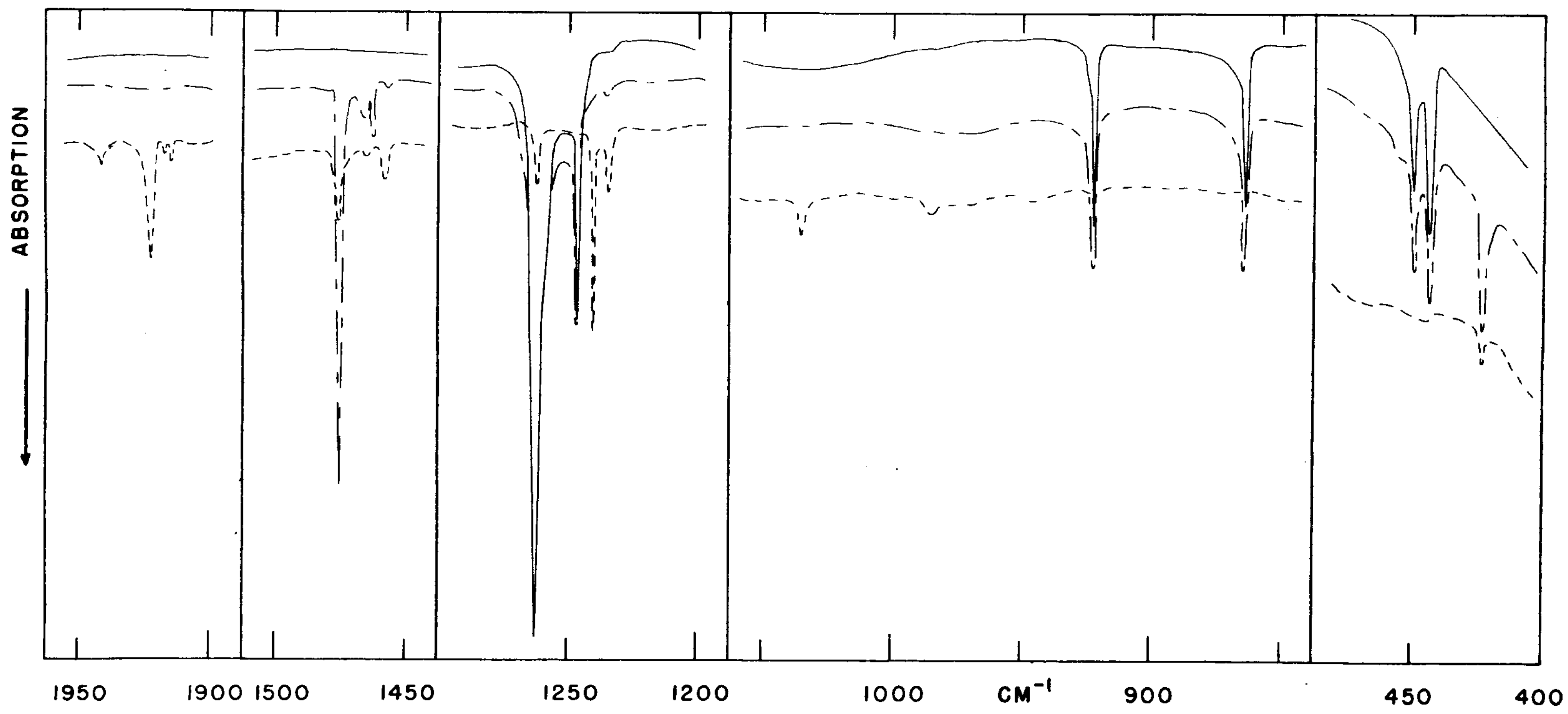
$Ar:N_3CN = 300$. 14°K

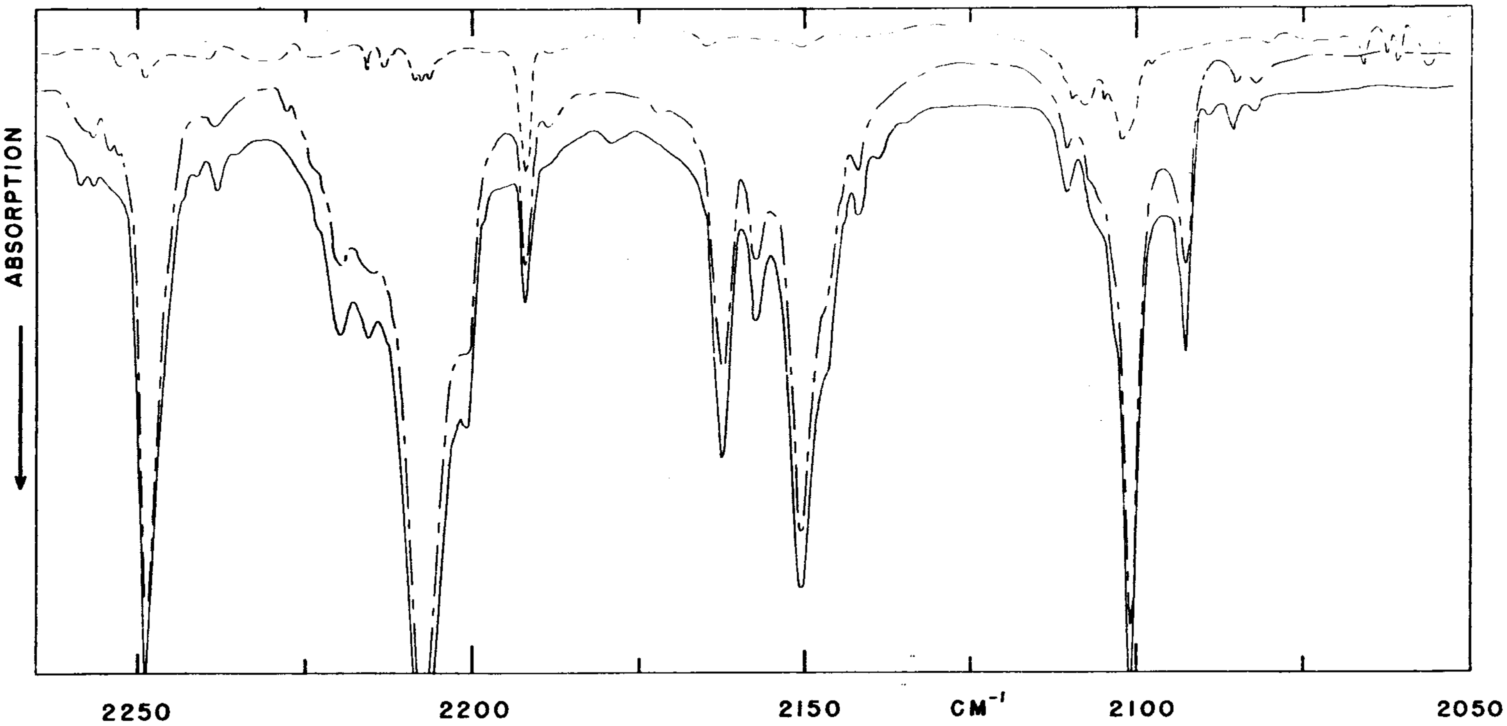
91 μ moles N_3CN

——— before photolysis

— — — 90 min. photolysis through Pyrex

- - - - 15 min. photolysis through CsI, plus 30 min. photolysis through LiF


ABSORPTION
1950
1900
1500
1450
1250
1200
1000
CM⁻¹
900
450
400


ABSORPTION
2250
2200
2150
CM⁻¹
2100
2050

Figures 2a, b

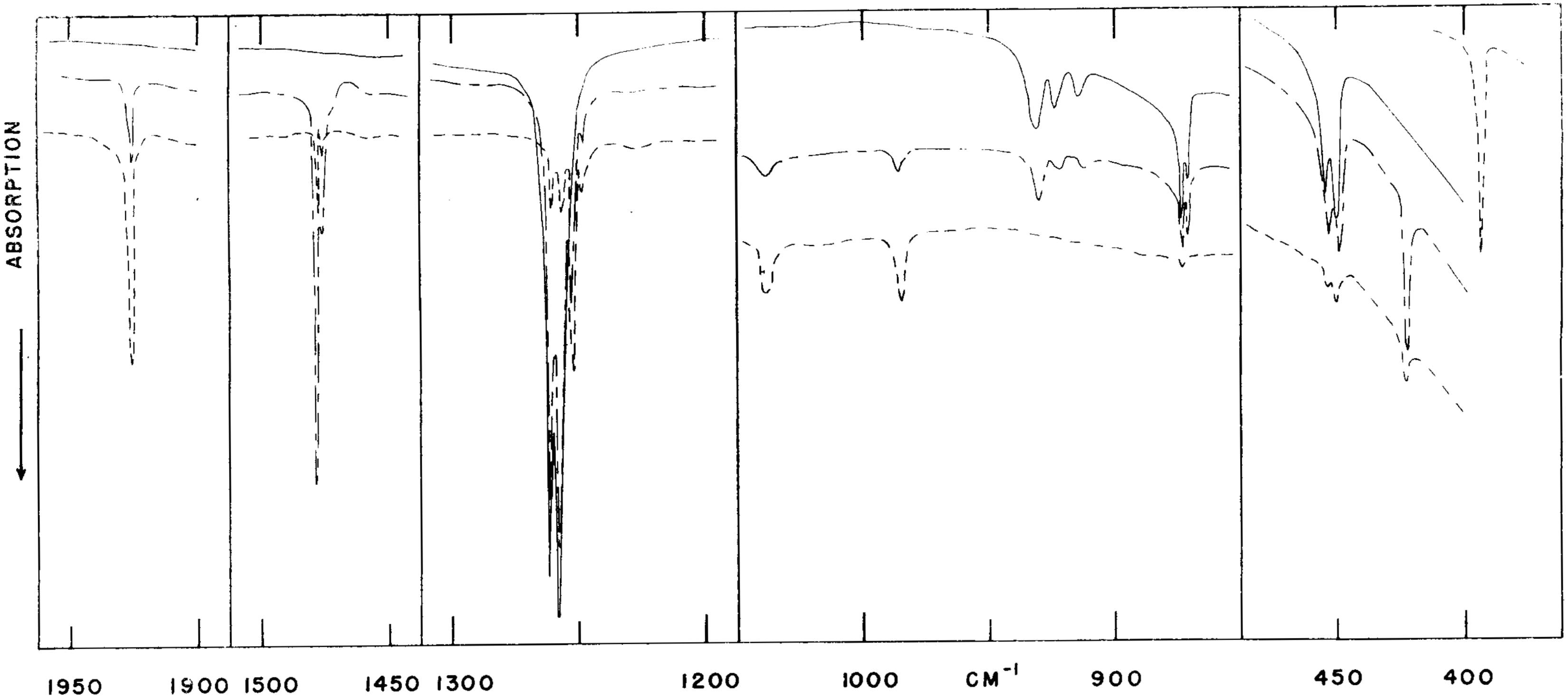
$N_2:N_3CN = 100.$ 14°K.

170 μ mole N_3CN

——— before photolysis

— — — 15 min. photolysis through CsI

- - - - 85 min. photolysis through CsI


ABSORPTION
1950
1900
1500
1450
1300
1200
1000
CM^{-1}
900
450
400

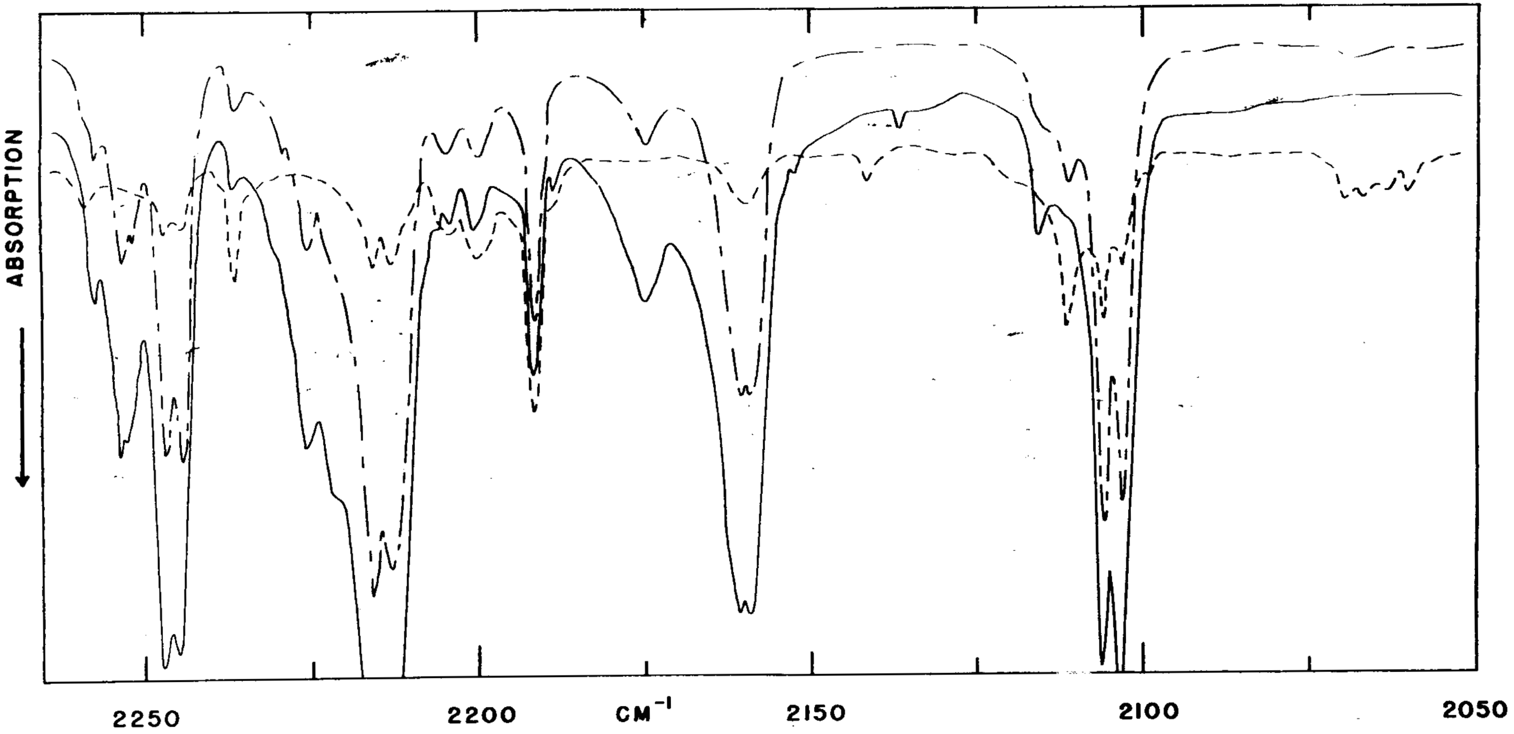

ABSORPTION
2250
2200
CM^{-1}
2150
2100
2050

Figure 3

Ultraviolet Absorption of N_3CN After Brief Period of Photolysis

(a) N_2 matrix

(b) CO matrix

(c) Ar matrix

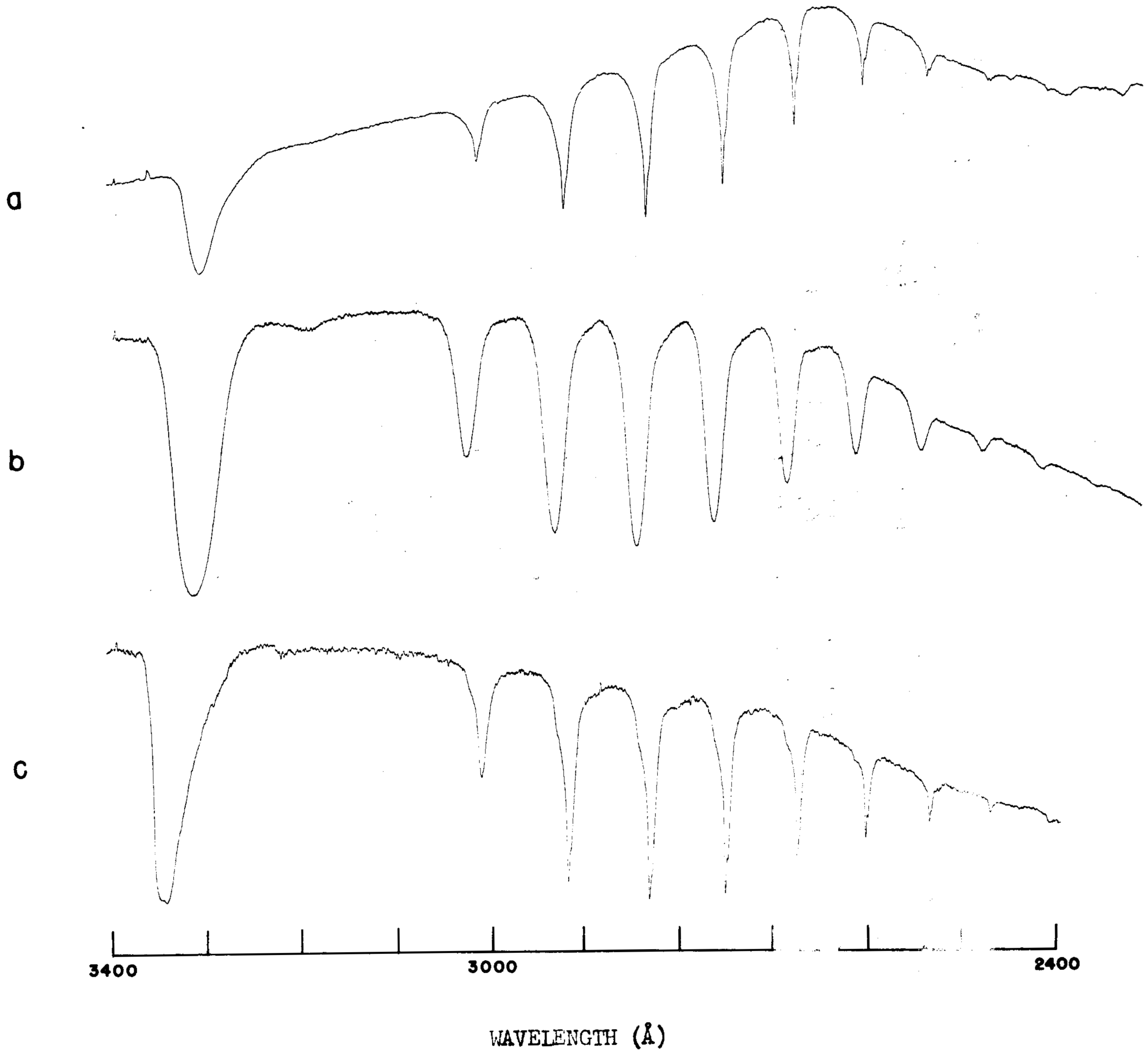

a
b
c
3400
3000
2400
WAVELENGTH (Å)

Figure 4

Near Ultraviolet Absorption Spectrum

After Prolonged Photolysis of N_3CN

(a) CO matrix

(b) Ar matrix

(c) N_2 matrix

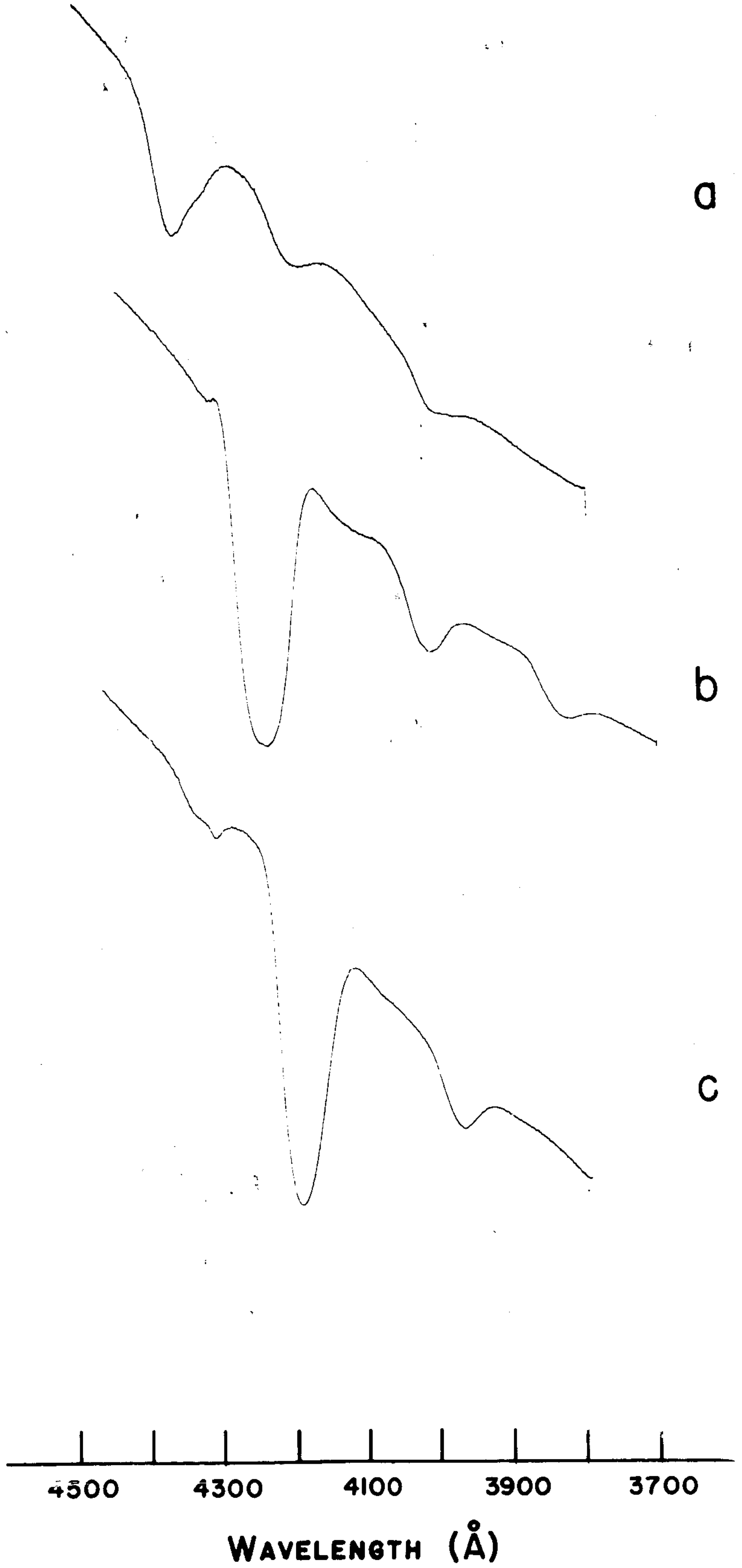

a
b
c
4500
4300
4100
3900
3700
WAVELENGTH (Å)

Figure 5

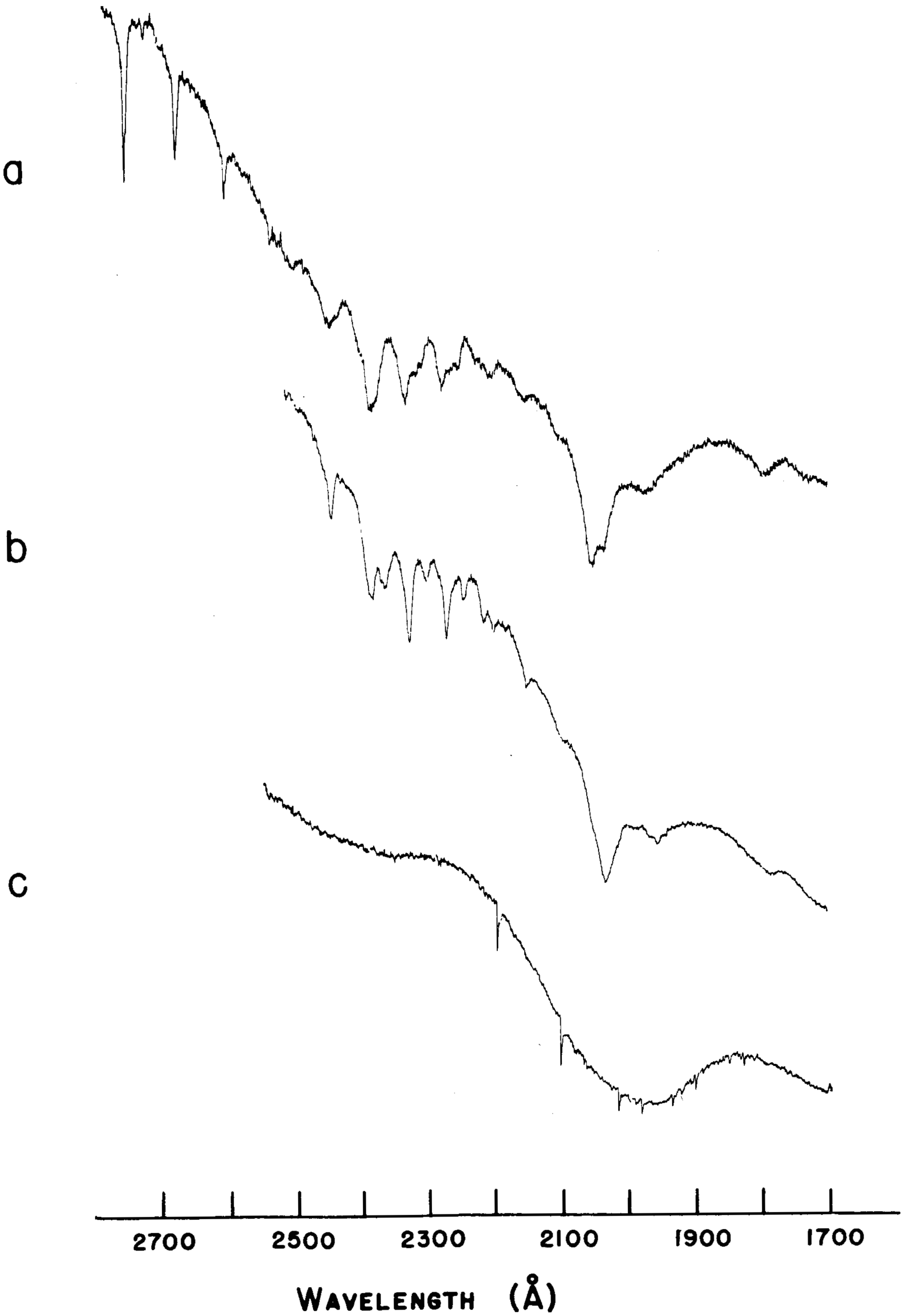
Far Ultraviolet Absorption Spectrum

After Prolonged Photolysis of N_3CN

(a) Ar matrix

(b) N_2 matrix

(c) Ar:C_2N_2


a
b
c
2700
2500
2300
2100
1900
1700
WAVELENGTH (Å)