SPECTROSCOPIC STUDY OF THE FREE RADICAL HCCN AND ITS PRECURSOR (DIAZOACETONITRILE) IN INERT MATRICES

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This is to certify that the

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ABSTRACT

SPECTROSCOPIC STUDY OF THE FREE RADICAL HCCN AND ITS PRECURSOR (DIAZOACETONITRILE) IN INERT MATRICES

By

Achille Dendramis

Two related projects were pursued in the course of this research effort. The first project involved the free radical, HCCN. The free radical was produced in a matrix via photolysis of diazoacetonitrile, NNCHCN, with radiation of wavelengths longer than 3,500 Å. IR spectra of HCCN and 3 of its isotopes (DCCN, $HC^{13}CN$, and $HCC^{15}N$) were studied. Since its equilibrium geometry is not known, two modified general valence force field (MGVFF) normal coordinate analyses based on two different geometries, bent and linear, were carried out. The results clearly favor the linear configuration and the values of the refined force constants allow some conclusions to be drawn regarding the electronic charge distribution of the molecule. The electronic spectrum of HCCN in an Ar matrix was also obtained. A tentative assignment of the observed progression in the UV part of the spectrum was made based on molecular orbital considerations and the previously published spectra of similar species such as NCN and NCO.

The second project involved the precursor of HCCN, diazoacetonitrile (DAN). DAN and 4 of its isotopes: NNCDCN, $NNCH^{13}CN$, $NNCHC^{15}N$,

and ^{15}NNCHCN were prepared and their IR and Raman spectra were studied in pure and matrix isolated forms. A MGVFF normal coordinate analysis was performed on the basis of C_s symmetry (structure known from microwave data). Fifteen force constants were used to fit 35 experimentally observed frequencies. The conclusions allowed to be drawn from the vibrational study correlate very well with the results of the microwave experiments.

SPECTROSCOPIC STUDY OF THE FREE RADICAL HCCN AND ITS PRECURSOR (DIAZOACETONITRILE) IN INERT MATRICES

By

Achille Dendramis

A THESIS

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To My Parents

Εις τους γονεις μου

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Coming from a different country with a different language and cultural background, I had to make many adjustments in my way of doing things including communication with people, attitude towards science, and assuming new responsibilities within the graduate framework. I am grateful to Dr. George E. Leroi for helping me make these adjustments and for his support and patience throughout the entire doctoral program.

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INTRODUCTION

Free radicals* in general are useful for the testing and further development of molecular orbital theory. The latter has been very successful in terms of understanding in considerable detail the behavior of simple free radical species.

An even wider implication of the study of free radicals has to do with the importance of excited states of ordinary molecules in various chemical processes, which is being increasingly recognized. A thorough understanding of relatively simple free radical species can provide considerable help in the understanding of the behavior of more complicated species with similar unfilled or partially-filled MOs.

HCCN, apart from being just another free radical, presents an interesting problem. Depending on the electronic charge distribution, it may have a carbene, nitrene or allene type structure. Determination of its equilibrium configuration may shed some light on the relative stability of these structures. In addition, determination of its vibrational potential function will provide a test of

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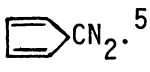
*The definition of a free radical most commonly employed by physical chemists and chemical physicists is the following:

> A diatomic or polyatomic molecule which in its ground state possesses one or more atoms (excepting, of course, hydrogen) with which less than eight valence electrons are associated. (Reference 17c)

the transferability of force constants among similar free radicals such as NCCCN, NCN, and HCCCH (the last two being isoelectronic to HCCN).

Finally, the properties of HCCN may be of interest to the astrophysicist since it is quite possible that this species exists in the interstellar medium. This speculation is supported by the presence, in the interstellar medium, of similar species such as HCN, HCCCN, HCC, and CN, which have all been detected spectroscopically.[1]

The most convenient source of HCCN is known to be NNCHCN (diazoacetonitrile, sometimes denoted DAN) which, upon photolysis with radiation of λ>3,500 Å, produces HCCN and N_2. Not much is known regarding the vibrational spectroscopy of diazo compounds in general. The only members of this class which have been studied in some detail to date are CH_2N_2[2], $HC{\equiv}CCHN_2$,[3] H_3CCCHN_2,[4] and  [5] Therefore, the study of the vibrational spectrum of DAN is of interest to the vibrational spectroscopist since apart from obtaining information regarding the chemical bonding in this species, the transferability of force constants among these molecules can also be tested. Furthermore, characterization of the precursor will help in the understanding of the vibrational spectrum of HCCN due to the presence of similar characteristic groups of atoms in these molecules.

The primary goal of this work is to obtain information regarding the geometry and nature of chemical bonding of the species HCCN through the study of its vibrational spectrum. A parallel interpretation of the vibrational spectrum of the precursor is also given. Comparison of its vibrational potential function with the ones of

similar species is critically discussed and the conclusions arrived at from the overall vibrational study are compared with the results of the microwave observations.

CHAPTER I

THE FREE RADICAL HCCN

Background Information on HCCN

The only spectroscopic study of HCCN which has been published to date is with regard to its ESR spectrum, which was reported by Skell, Bernheim et al. at Penn State in 1964.[6] HCCN was produced via photolysis of its precursor, diazoacetonitrile, isolated in a polychlorotrifluoroethylene (PCTFE) matrix at 77 K. This report was followed by two others by the same researchers, one in 1965[7] and the other in 1970.[8] Their results can be summarized as follows: HCCN possesses a triplet ground state and the g-factors of its electrons are considerably different from the g-factor of a free electron, indicating a significant amount of spin-orbit coupling. Linearity of the free radical was assumed because of the zero value of the E zero-field splitting parameter.

In 1970 it was realized that free rotation of a bent free radical along its long axis in a matrix results in a low E value, thus giving the false impression that the radical is linear. Since different matrices pose different barriers with regard to the rotation of the guest molecules, it was felt that taking ESR spectra of the same free radical in different matrices was necessary before any statements regarding its geometry could be made.[9]

A study of this kind was made on HCCN by Wasserman et al., and a brief note stating the results of that study was included in a paper they published on CH_2;[9] "The attempts we have made to examine HCCN in a variety of matrices at 4 K have only given spectra corresponding to E=0, thus supporting the linear form."

An attempt to study its UV spectrum in the gas phase via flash photolysis experiments was made by Merer and Travis in 1966.[10] However, their observations were complicated by the simultaneous production of other free radicals such as CNC and CCN, thus preventing a complete study of HCCN.

In 1968 an LCAO MO calculation of the extended Hückel type carried out on HCCN among other free radicals appeared in the literature.[11] The result was stated as follows: "There is no doubt that the ground state of these molecules will be a linear triplet." The molecules implied were HCCN and NCCCN in their carbene configurations.

Finally, in a paper published in 1973 by Skell et al.,[12] it was shown, based on the stereospecificity of the reaction between cis-2-butene and the photolysis product of diazoacetonitrile, that HCCN is produced in its singlet state. The triplet state population increased at the expense of the singlet with time, indicating that the triplet is the ground state of this molecule.

At this point it should be mentioned that despite the available information in the literature, the linearity and/or electronic charge distribution of HCCN is far from being conclusively proven either experimentally or theoretically. Experimentally, the argument is the lack of hyperfine structural data in the ESR spectra. Theoretically,

recent ab-initio calculations on C_3H_2[13] and C_3N_2[14] free radicals (which were also proclaimed as linear in their ground states based on LCAO MO calculations[11]) suggest that both of these molecules have bent structures. The results of preliminary ab-initio calculations on HCCN done in this department[15] make this even more clear. Two minima were found in the potential energy surface of HCCN, one corresponding to a carbene bent structure and the other to a nitrene linear one. The linear form was found to lie lower than the bent one by ~4 Kcal/mole. This energy difference however is within the uncertainty inherent in the calculations, leaving the question of linearity and electronic charge distribution still unanswered.

Approach to the Study of HCCN

In the gas phase HCCN is believed to have a half life of $\sim 10^{-6}$ seconds (deduced from flash photolysis UV experiments).[10] Contrary to their extensive use in the UV region of the spectrum, flash photolysis experiments in the IR are not possible. This is due to the absence of fast responce IR detectors. Therefore the only alternative left for obtaining the IR spectrum of HCCN was to use the matrix isolation technique.

Matrix isolation spectroscopy, as it is known today, was developed by Pimentel and his co-workers at Berkeley. Since their first report,[16] a multitude of papers have been published on the IR, UV and recently Raman observation of unstable species employing this technique. There are many excellent review articles and books which treat the subject. Some of these, the most informative in the author's opinion, are

included in the list of references.[17]

The method can be briefly described as follows: the molecule of interest or the precursor of the molecule of interest is mixed with at least a hundred fold excess of an inert gas (usually noble gases or N_2), and the mixture is rapidly condensed on to the cold substrate of a cryogenic cooler at a temperature sufficiently low that diffusion of the solute species is prevented. The matrix sample so obtained can then be subjected to spectroscopic investigation as it is or, if the species of interest is reactive, after photolysis of its precursor in the matrix.

This is of course a highly simplified presentation of the technique. Many variations have been incorporated over the years, establishing the matrix isolation method as a valuable tool for the spectroscopic examination of a variety of chemical species.[17j] One aspect of the technique that should be stressed specifically is the condition of the guest molecules in the matrix. The condition is very similar to the gas phase, something that is exemplified by the fact that absorption bands of matrix-isolated species are generally observed within 5 or 10 cm^{-1} of the gas phase band origins. This permits the theory of molecular vibrations[18] developed for molecules in the gas phase to be applied equally successfully to matrix-isolated species.

The absorption bands of the guest molecules are very sharp for several reasons. First because low temperatures in general result in small band widths, second because intermolecular interactions present in other condensed phases are almost completely absent in the matrix, and third because rotation is quenched for all but very small molecules.

This sharpening of the bands allows near-degenerate bands, which overlap completely even in the vapor phase or in dilute solution at room temperature, to be resolved in the matrix spectra. However, information provided by the band envelopes in the gas phase concerning the symmetry of the vibration is lost along with the possibility of deriving structural data from rotational analysis. Therefore, the preparation and observation of isotopically labelled species is even more important to the identification and band assignments of free radicals in matrices than it is in gas phase studies.

Finally, it should be mentioned that on occasion matrix spectra are complicated by the splitting of the absorption bands of the guest molecules due to their entrapment in different sites in the solid lattice. This problem however can be easily overcome by annealing the sample at a temperature where the matrix cage loosens enough to allow some movement of the molecules. All the peaks decrease somewhat in intensity, but the ones due to alternate sites decrease much more rapidly.

The only method by which HCCN has been positively identified is the ESR technique. Therefore, before the IR experiments were begun, a repeat of the ESR experiment done by Skell et al.[6] was thought necessary to ensure that the right track was followed. The photolysis light source available to the author was different than the one used by Skell et al., thus making this experiment even more necessary.

The matrix sample was prepared the same way as in Reference 6, the only difference being the solvent which was dioctyl phthalate instead of methylene chloride. The matrix sample was photolyzed for one

hour with a 150 Watt Xenon lamp. A pyrex filter and a water filter were also used. The ESR spectrum obtained is shown below in Figure 1.

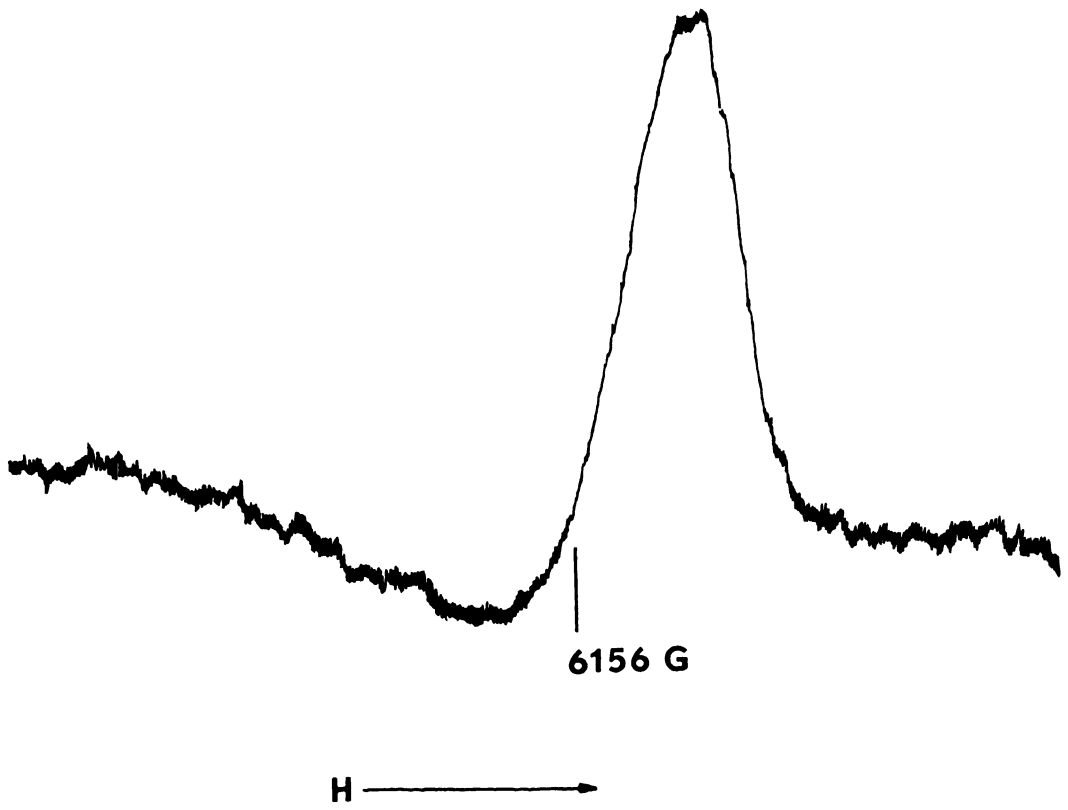


Figure 1. ESR Spectrum of HCCN in PCTFE (77 K)
(ν = 9.207 KMc/sec)

The observed band (whose shape is very similar to the one obtained by Skell et al.)[6] disappeared upon annealing of the matrix, indicating that its appearance was due to a reactive species. The field at which this band is observed (6,156 G) is slightly different than the one

reported by Skell et al.[6] (6,256 G). However, it was obtained at a slightly different frequency, and is considered to be well within experimental error.

It is quite possible that upon photolysis of a compound in a matrix several species are produced. Some of them may be stable, some unstable. It is up to the experimentalist to first minimize the possibility of simultaneous production of species other than the one of interest and second to identify the bands due to the latter. In the case of HCCN, restricting the photolyzing radiation to wavelengths longer than 3,500 Å ensured that no C-H bond breakage took place, therefore overcoming the problem that Merer and Travis had in the gas phase UV experiments.

For band identification and eventual species identification, the following method, generally accepted in the literature,[17i] was employed. The rate of growth of new bands as a function of photolysis time and the rate of disappearance of these bands upon controlled diffusion were recorded. One expects that bands due to the same species will have the same rate of growth, while those due to different species will differ appreciably. However, this is not adequate for proving that the new bands are due to reactive species. The proof comes with the results of the controlled diffusion technique. The latter consists of slowly raising the temperature of the matrix up to a certain point where the matrix is known to relax its rigidity (40 K for Ar and 35 K for N_2). At this point, some of the free radicals have the chance to escape from their cage and react with one another or other species, thus causing a decrease in intensity of their IR bands. This obviously does

not affect the bands of stable species. This way the groups of bands due to reactive species in the matrix are distinguished from those of stable species. Again, the rate of dissapearance of bands as a function of time spent at the controlled diffusion temperature is expected to be the same for bands due to the same species and different for bands of different species.

Finally, isotopic substitution and observation of the corresponding frequency shifts coupled with normal coordinate analysis allows verification of the band assignments and positive identification of the species responsible for them.

In the next section the methods followed to obtain the matrix samples and for the synthesis of all the isotopic precursors of HCCN are described, along with the instrumentation employed by the author in order to obtain the spectroscopic data.

Method of Obtaining the Matrix Sample

The precursor of HCCN, diazoacetonitrile, is explosive,[19] has a low vapor pressure (<1 Torr at 25°C) and decomposes rather quickly at room temperature regardless of whether it is in solution or in pure form, under vacuum or not. Because of its low vapor pressure and instability at room temperature, gas phase mixing of DAN with inert gases (in a vacuum line using standard manonmetric techniques) for matrix isolation experiments was not possible. (An attempt to do this resulted in the yellow-brown coloring of the vacuum line walls within minutes.)

Usually when the species of interest (or its precursor) has such a low vapor pressure, one of two alternate routes can be followed in order to get the matrix sample. First, a molecular beam of the species of interest is formed by heating it up to a fairly high temperature. This beam is mixed with the inert gas (which forms another separate beam) just before condensation on the cold substrate. This method has the advantage of high reproducibility of the matrix-to-guest (M/G) ratio, and at the same time has a high flexibility in terms of varying the M/G ratio, since all one has to do is vary the temperature to which the species of interest is heated. Both these features, which are also inherent to the normal gas phase mixing procedure, are very important. Varying the M/G ratio is necessary for identifying peaks due to dimers, trimers, etc. of the species of interest and therefore avoiding band misassignments, and also for establishing the optimum M/G ratio. The latter is considered to be the lowest M/G ratio which still enables effective isolation, since this permits the highest sensitivity during spectroscopic observations. Reproducibility of the M/G ratio is important not merely in order to reproduce accurately previous experimental data, but also for being able to readily obtain good spectra once the optimum M/G ratio is established. That is vital when spectroscopic examination of isotopically substituted species is required.

Unfortunately this technique could not be used since DAN decomposes, and more often than not violently explodes, upon heating. Therefore, the second route was chosen. In this method, the species of interest is kept in a trap and inert gas is forced to pass through the

trap on its way to being deposited on the cold substrate.[20] This method offers very little flexibility in terms of varying the M/G ratio, and it is not very reproducible. In short, it is the worst possible compromise that one can make for matrix isolation experiments. It was however, the only way.

The trap containing DAN was kept between 0°C and -10°C and had to be as close to the cold substrate as possible to minimize decomposition while DAN was being carried by the matrix gas. Figure 2 below shows

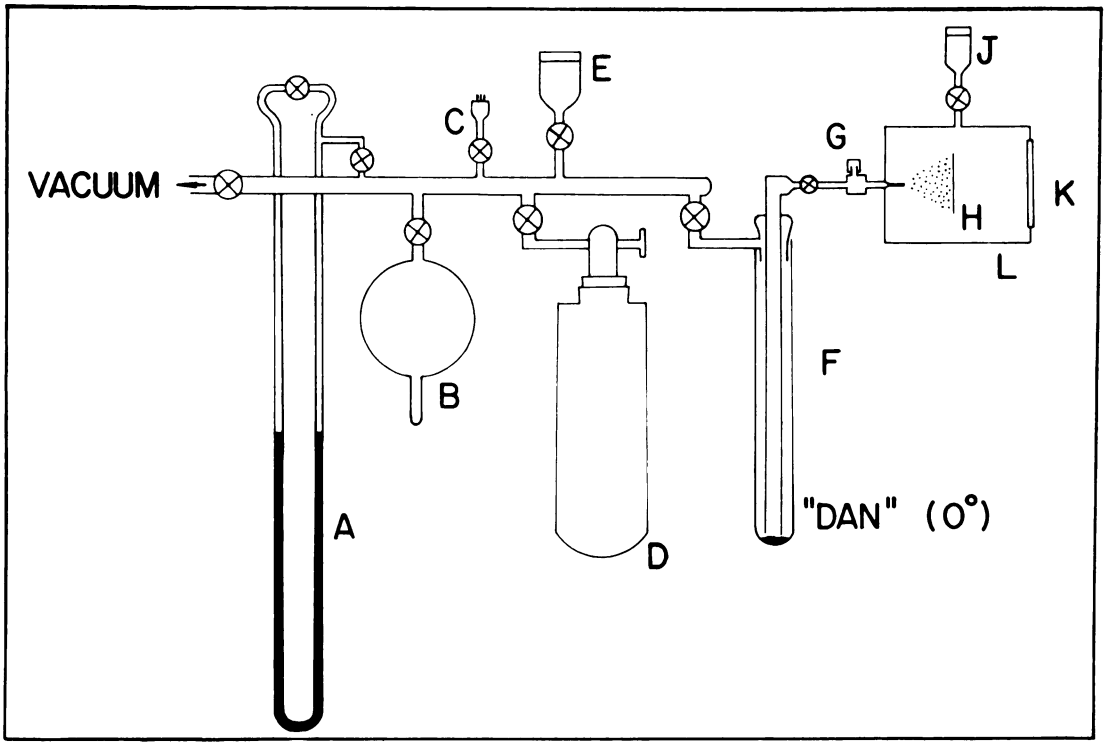


Figure 2. Experimental Arrangement for Matrix Deposition

the experimental arrangement used for this purpose: A- Mercury

manometer, B- two liter bulb, C- thermocouple pressure gauge, D- matrix gas tank, E- ion gauge, F- 0°C to -10°C trap containing pure DAN, G- calibrated needle valve, H- cold substrate, J- ion gauge, K- photolysis window, and L- rotatable shroud of cryogenic cooler.

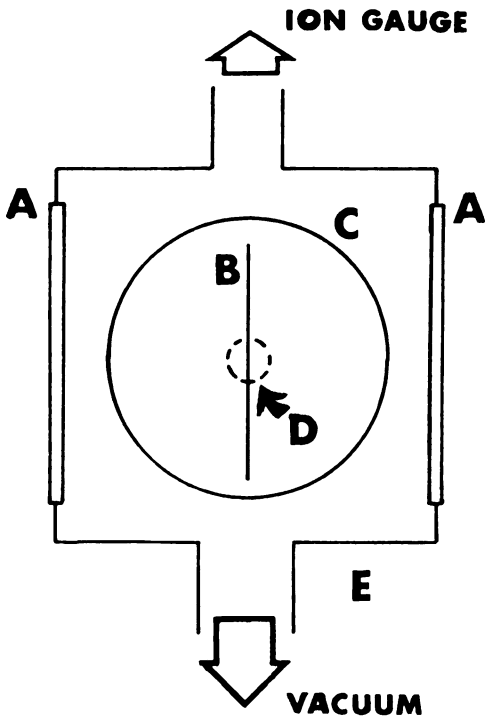


Figure 3. Cold Substrate Area

Figure 3 above shows the area around the cold substrate from a different angle and in more detail: A- outer windows (CsI for IR and quartz for UV and Raman), B- cold substrate (CsI for IR, sapphire for UV and copper for Raman), C- photolysis window (quartz), D- spray-on orifice, E- rotatable shroud of cryogenic cooler.

The matrices were deposited over a period of 5 to 26 hours with deposition rates of .1 to 10 mmol/hr. Due to the method of "mixing" the matrix gas with the precursor, the matrix-to-guest ratio is not precisely known but is believed to be around 700. This estimate is based on a value for the vapor pressure (at 0°C) of diazoacetonitrile obtained from an empirical equation. The values of its vapor pressure known at two other temperatures (35°C and 45°C) were used as input data for this calculation.

The spectra of the pure solid were obtained using the same arrangement, the trap being at room temperature. DAN was carried over and deposited on the cold substrate simply by means of the pressure and temperature differential which existed between the trap and the cold substrate.

Synthesis

Diazoacetonitrile was prepared by a modification of the procedure described by Dewar and Petit.[21] The major disadvantage of their method was the presence of chloroacetonitrile in the final product. Chloroacetonitrile, a by-product of the reaction, was easily identified by its IR spectrum[22] in the matrix. Repeated attempts to remove the latter from the final product through vacuum distillation using a variety of cold temperature baths failed. In matrix studies the presence of species other than the one of interest is not as detrimental as in other types of studies (e.g. spectral studies of pure solids) since all the molecules present are supposedly isolated from each other and no serious perturbations can take place. Chloroacetonitrile, however,

still posed a big problem since some of its peaks in the vibrational spectrum masked frequency regions of interest. Since it also contains a CN group, it would also cause considerable loss of ^{13}C and ^{15}N atoms used in the form of $K^{13}CN$ and $KC^{15}N$ respectively for the synthesis of the isotopes $NNCH^{13}CN$ and $NNCHC^{15}N$. ($K^{13}CN$ and $KC^{15}N$ were available in limited quantities due to the high cost of such compounds.)

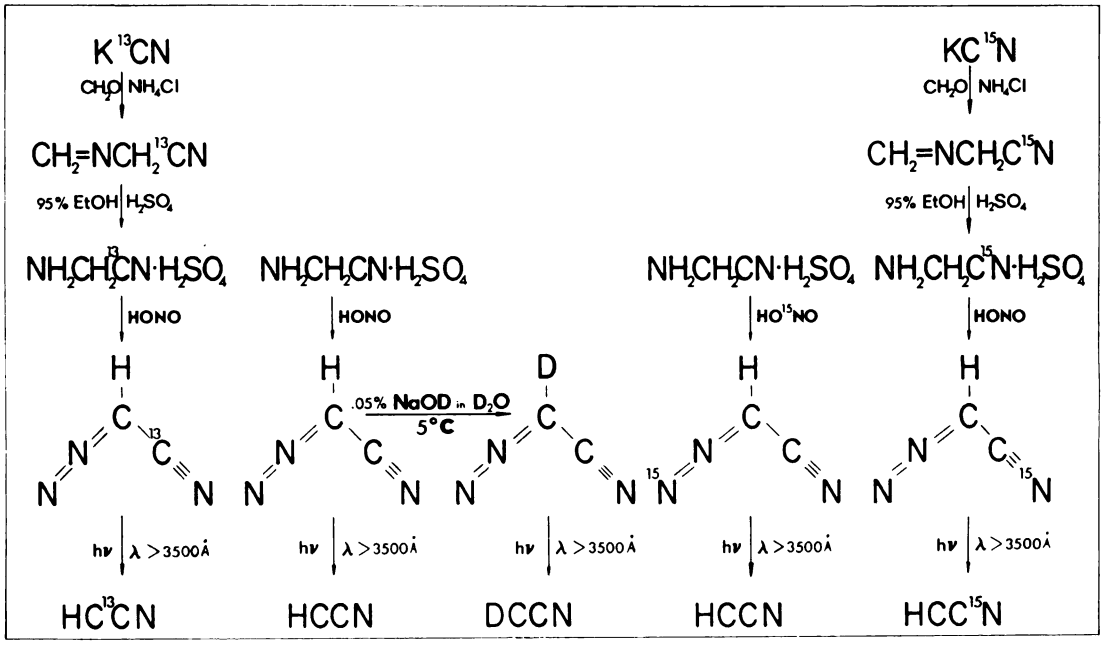


Figure 4. Scheme of Isotope Synthesis

The general synthetic route employed for the preparation of diazoacetonitrile and its isotopically labelled counterparts is shown schematically in Figure 4 above. Modifications of the procedure described in Reference 21 included a different starting material, $H_2NCH_2CN \cdot H_2SO_4$, instead of $H_2NCH_2CN \cdot HCl$ (the cause of the presence of chloroacetonitrile

in the final product) and adjustment of the pH of the aqueous solution of $H_2NCH_2CN \cdot H_2SO_4$ from pH 1 to pH 4 prior to addition of $NaNO_2$. It was found that very acidic solutions prevented diazotization from taking place. Furthermore, the time allowed for reaction prior to each extraction had to be considerably longer since the reaction rate is much slower for $H_2NCH_2CN \cdot H_2SO_4$ than for $H_2NCH_2CN \cdot HCl$.[23] The temperature was kept between 10°C and 12°C since lower temperatures resulted in very slow reaction rates.

A variety of solvents were used for the extraction of DAN from the aqueous solution; these included dipentyl ether, dichloromethane, dibutyl phthalate and dioctyl phthalate. A useful solvent had to meet the following requirements: immiscibility with H_2O, low freezing point (<5°C), and vapor pressure different enough from that of diazoacetonitrile to facilitate eventual retrieval of the latter in pure form through vacuum distillation. Dioctyl phthalate was the only solvent that met the requirements which allowed complete separation of diazoacetonitrile from the solvent.

Complete removal of water from the final solution of diazoacetonitrile in dioctyl phthalate turned out to be a difficult task, and a variety of drying procedures were tested. Anhydrous Na_2SO_4 and molecular sieves (type 4A) seemed to give the best results, although not without considerable loss of diazoacetonitrile due to its adsorbance by the drying agents. P_2O_5, $CaCl_2$, $CaSO_4$, and $Mg(ClO_4)_2$ did not prove to be successful drying agents. Vacuum distillation employing a variety of cold-temperature baths, attempted after drying the solution with Na_2SO_4 or molecular sieves, also did not lower the water content any

further. As a result, small quantities of water were always present in the spectra. However, that turned out to be an advantage rather than a disadvantage since, depending on the number of peaks observed for each vibration of H_2O, it was possible to assess the effectiveness of the isolation of the trapped species. When only one peak for each normal mode of H_2O was observed (water monomer) the quality of the spectra was the best for the species of interest.

NNCDCN was prepared by an exchange process. Eighteen mls of NNCHCN in dioctyl phthalate were cooled to 5°C using a cyclohexane-liquid N_2 slush bath[24] and 12 mls of a .05% solution of NaOD in D_2O were introduced dropwise over a period of one hour. The mixture was vigorously stirred throughout the entire reaction. After all the NaOD solution was added, the mixture was stirred one half hour longer. NaCl was used to facilitate the extraction of diazoacetonitrile from the aqueous layer. Separation of the two layers was more rapidly accomplished by the use of a centrifuge (as opposed to a separatory funnel) followed by removal of the upper layer with a hypodermic syringe. Speeding up the separation of the two layers is necessary since NNCDCN is converted back to NNCHCN upon standing in contact with the aqueous layer at room temperature. 60% - 80% deuteration could be achieved this way. Deuteration higher than 60% was achieved only when the reaction mixture was centrifuged immediately after the reaction was over. The NaOD solution was added dropwise since the reaction is highly exothermic. If the temperature rises above 15°C thermal decomposition of diazoacetonitrile occurs rapidly. Lowering the temperature below 5°C resulted in the solidification of D_2O (freezing point 3.82°C), so

a temperature of 5°C seemed to be the best compromise.

After completion of the reaction, the ratio of the amount of deuterated diazoacetonitrile to the amount of unlabelled diazoacetonitrile in the mixture was found to be independent of the concentration of NaOD in D_2O. At the same time, the higher this concentration the greater the decomposition of diazoacetonitrile (both labelled and unlabelled), and therefore the lower was the yield of the product.

^{15}NNCHCN (55% in ^{15}N) was prepared in the same way as unlabelled diazoacetonitrile by the use of $Na^{15}NO_2$ (55 atom % ^{15}N) instead of unlabelled $NaNO_2$. NNCH$\overset{*}{C}$N (60% in ^{13}C) and NNCHC$\overset{*}{N}$ (60% in ^{15}N) were prepared through a three-step process[25,26,21] as depicted in Figure 4. $K^{13}CN$ (60 atom % ^{13}C) and $KC^{15}N$ (50 atom % ^{15}N) were used as starting materials. The labelled potassium cyanide starting material was purchased from Merck, Sharp and Dohme of Canada, Ltd.

Before concluding this section, it should be mentioned that the synthesis, although seemingly trivial when written in terms of reactions, required a considerable amount of time and extra precautions. This was due to the explosive nature of diazoacetonitrile, the purity necessary in the final product, the absence in the literature of any established technique regarding the deuteration procedure, and the availability of only small amounts of ^{13}C and ^{15}N labelled starting materials.

Instrumentation

An Air Products model CS-202 Displex cryogenic helium refrigeration system was used for all the solid state experiments. Typical

temperatures were between 12 K and 21 K measured by a gold (.07% iron) vs. chromel thermocouple imbedded in the cold substrate. Thermal contact between the cold substrate and the thermocouple junction was achieved with Air Products Cry-Con grease or woods metal. The volume around the cold substrate was continuously evacuated by a vacuum line having an oil diffusion pump backed by a rotary mechanical pump. Liquid nitrogen-cooled traps were used between the cooler and the diffusion pump and between the diffusion pump and the mechanical pump. The pressure in the area around the cold substrate prior to deposition was measured by an ion gauge attached directly to the shroud of the cryogenic cooler (see Figures 2 and 3). It was normally better than 10^{-7} Torr. For controlled diffusion experiments, a Cryodial Model ML 1400 automatic temperature regulator was used, with the heater (40 Watt Zener diode) and temperature sensor (calibrated platinum resistor) mounted on a copper block next to the cold substrate. Temperature control capability was ±.02 K.

For IR experiments, CsI was used for the outer windows and the cold substrate. For UV-Vis experiments, quartz (UV-grade) was used for the outer windows and sapphire for the substrate. Quartz was used for the outer windows and copper for the substrate in the Raman work. Thin sheets of indium were placed between any two parts required to be in good thermal contact.

The following spectrometers were employed.

Perkin-Elmer Model 225 IR grating spectrophotometer (4000-200 cm^{-1}) with resolution better than 1 cm^{-1} above 500 cm^{-1} and between 1 and 2 cm^{-1} below 500 cm^{-1}. Reported frequencies should be

accurate to ±1 cm^{-1}.

Cary Model 17 UV-Vis spectrophotometer

Raman spectrometer comprised of a Jarrell-Ash 25-100 double Czerny-Turner monochromator coupled with a thermoelectrically-cooled RCA C31034 photomultiplier tube and a Spectra-Physics Model 165 Kr ion laser as exciting source. Baird-Atomic spike filters were used for the 6471 Å and 5682 Å laser lines to eliminate plasma lines.

Varian E-4 EPR spectrometer system with 8.8-9.6 GHz operating frequency range, 100 KHz field modulation frequency and 250-10,000 G magnetic field strength.

For the photolysis of the precursor, a 150 Watt Xenon lamp (Bausch and Lomb) was employed. A 0-52 Corning filter was used to cut off radiation of $\lambda<3,500$ Å and a water filter was inserted between the light source and the cryostat to prevent heating of the matrix. A quartz lens was used to concentrate the photolyzing radiation over the area of the cold substrate.

Research grade Ar and N_2 (Matheson) were used for matrix gases without further purification. The majority of the experimental work was done with Ar. At this point the author would like to justify the use of Ar as a matrix gas as opposed to other inert gases such as Ne, Kr, Xe, and N_2 which are extensively used in matrix studies. Xe and Kr are inferior to Ar since they, in general, result in more light scattering due to the larger atomic size. Ne, which by the same token would have been preferred over Ar, could not be used in these

experiments because the low temperature limit of our cryogenic cooler is higher than the temperature at which Ne is known to relax its rigidity. Finally N_2, which was considered for some time the ideal matrix gas for isolating molecules of the size of NNCHCN and HCCN, was used in a few experiments but was finally discarded for two reasons. First, an extensive site splitting was observed in almost all bands in the spectrum which made the band assignment task extremely difficult. Second, there are some recent cases in the literature where complexes with N_2 and the species of interest are reported to exist.[27]

Vibrational Spectra of HCCN and Its Isotopes

Application of elementary group theory methods[28] shows that all vibrations for HCCN (5 for the linear structure, $C_{\infty v}$ symmetry or 6 for the non-linear, C_s symmetry) are both IR and Raman active. Therefore, theoretically either kind of spectroscopy employed should be adequate by itself in terms of furnishing the needed data (i.e. vibrational frequencies). It is well known however that the intensities of some of the vibrational frequencies change drastically in going from one technique to the other. Therefore peaks that are not observed in one case might be intense enough to be observed in the other. In addition, it is is always a way of double checking the validity of experimental frequencies, which although not necessary still remains desirable.

However, repeated attempts to obtain the Raman spectrum of matrix-isolated HCCN failed. This was of no surprise since no one has been able to obtain conventional Raman spectra of similar species to date. This is due to the fact that Raman spectroscopy in general is not as

sensitive as IR spectroscopy and also to the inherent weak Raman scattering properties of species of this nature. Two other techniques however have been successfully applied to the observation of vibrational frequencies of reactive species, laser induced fluorescence spectroscopy [29] and resonance Raman spectroscopy.[30] Either technique requires the use of a laser line with frequency near a strong absorption band of the species under investigation. Since the electronic absorption spectrum of HCCN was not known, the next step was to obtain this information in an Ar matrix. This was accomplished and is discussed in detail in a later section of this dissertation. The only absorption band which could be attributed to HCCN was a band in the UV part of the spectrum between 2400 Å and 3400 Å. Since no laser line is currently available in this frequency range in our laboratory, neither method could be employed.

Therefore infrared spectroscopy remained the only source by which information on vibrational frequencies of HCCN could be obtained. Figure 5 shows the IR spectrum of HCCN in an Ar matrix (B) and the same frequency ranges before photolysis (A) and after extensive annealing (C). Figures 6, 7, and 8 show the IR spectra of DCCN, $HC^{13}CN$, and $HCC^{15}N$ respectively in Ar matrices.

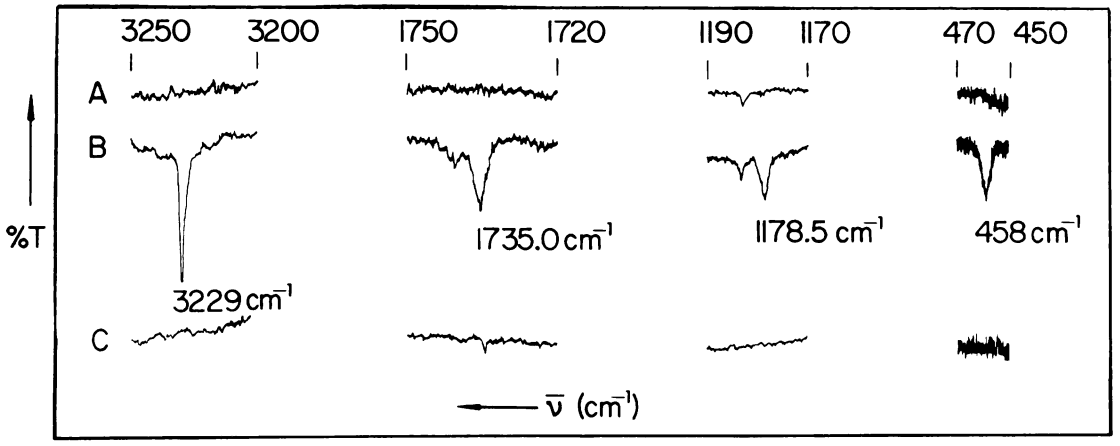


Figure 5. IR Spectrum of HCCN in an Ar Matrix

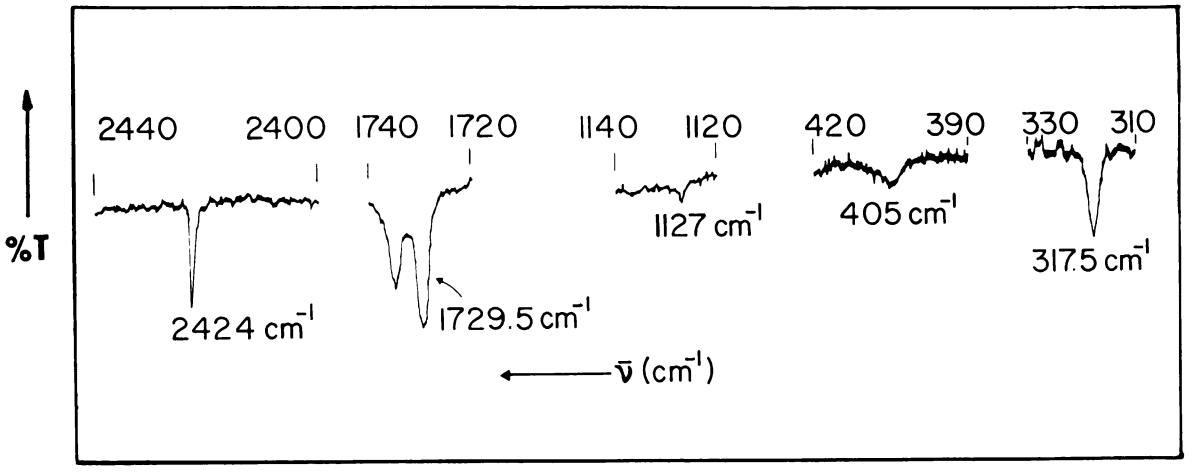


Figure 6. IR Spectrum of DCCN in an Ar Matrix

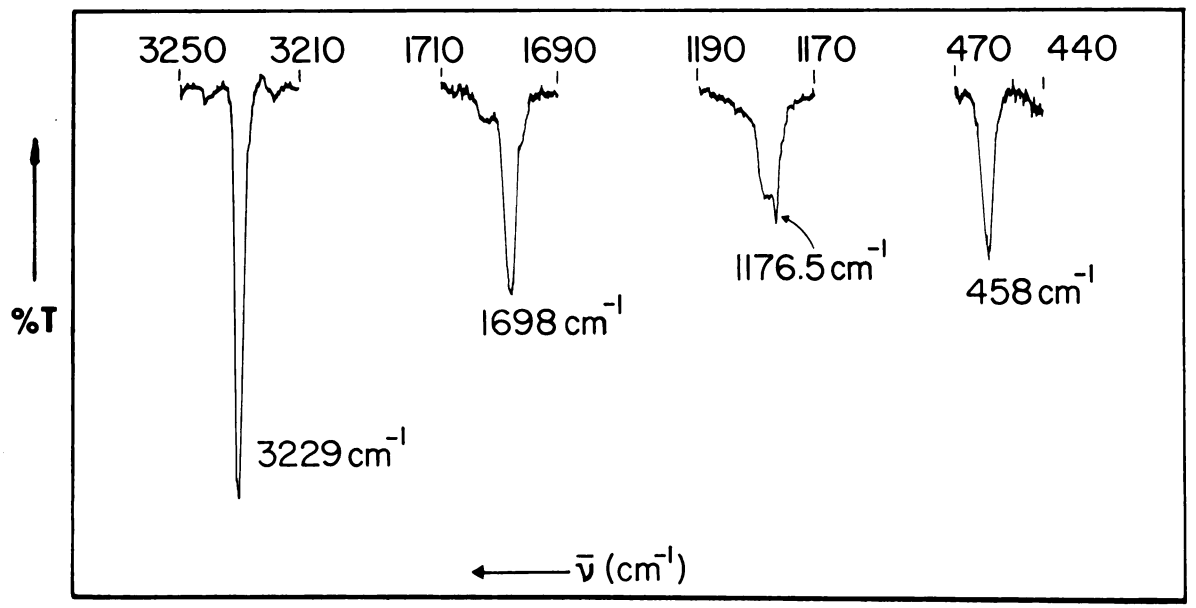


Figure 7. IR Spectrum of $HC^{13}CN$ in an Ar Matrix

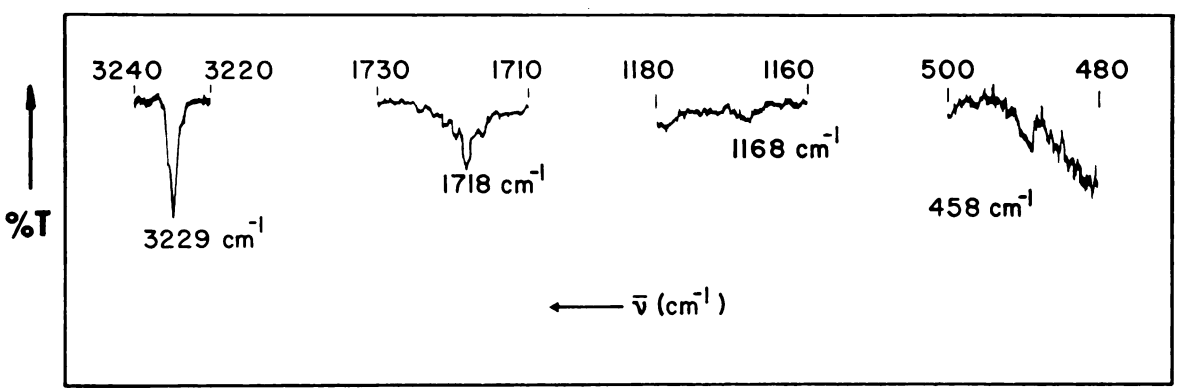


Figure 8. IR Spectrum of $HCC^{15}N$ in an Ar Matrix

Normal Coordinate Analysis

Each observed fundamental frequency corresponds to one normal mode of vibration. The latter is defined as a vibration during which all atoms in the molecule move with the same frequency in such a way that the Cartesian components of the displacements change according to sine curves.[31] The normal modes are completely independent of one another, whereas each normal mode may be a mixture of various internal modes such as bond stretching or angle deformations. Although it is easy to measure the normal frequencies, what is of interest in chemistry are the properties of individual chemical bonds. To relate these quantities, one must perform a normal coordinate analysis. Normal coordinate analysis involves computation of theoretical spectra from assumed structures and force constants; these are then brought into coincidence with the observed bands by adjustment of the assumed structure or force constants. Unfortunately, the set of force constants obtained this way is not unique. The reason for this is because there are always more force constants in a molecule than normal modes. Therefore, additional data are required to "constrain" the solution so that it fits the observed spectrum and the additional information. One important source of additional data is provided by the spectra of isotopically substituted molecules. Since the bonding should be essentially unaffected by isotopic substitution, the normal coordinate analysis can be repeated with only atomic masses changed; the computation should then reproduce the isotopic spectrum. The most serious defect of the method lies in the assumption of purely harmonic motion. As anharmonicity effects are often of the order of 1% of the observed frequencies, it is pointless

to try to reproduce the spectrum more precisely than this unless enough information on anharmonicity can be obtained to enable corrections to be made on the observed frequencies. In this work normal coordinate analysis was performed by using the Shimanouchi computer programs.[32] Two articles written also by Shimanouchi et al. were found pertinent for the understanding and more efficient use of the programs.[33,34] The calculations were carried out on a CDC 6500 computer located in the Computer Center at Michigan State University. A detailed description of normal coordinate analysis will not be presented here since it is not essential to the understanding of the text. Excellent accounts on normal coordinate analysis are abundant in the literature.[35] A brief discussion of force constants and their significance will however be given because of their importance in understanding other sections later in the thesis.

The potential energy of a molecule (V) as a function of its 3N-6 internal displacement coordinates, R_i (which specify completely the internal configuration of the molecule, where i=1 to 3N-6) may always be expanded in a Taylor series about the equilibrium configuration:[36]

$$(1) \qquad V = V_e + \sum_i \left[\frac{\partial V}{\partial R_i}\right]_e (R_i) + 1/2 \sum_i \sum_j \left[\frac{\partial^2 V}{\partial R_i \partial R_j}\right]_e (R_i)(R_j) + \cdots$$

In the harmonic approximation terms of cubic order and higher are discarded. The first term, V_e, simply defines the arbitrary zero of the energy scale while the second term is zero since the derivatives are taken in the equilibrium configuration, in which by definition V is a

minimum with respect to all the R_i. So, equation (1) becomes:

$$V = 1/2 \sum_i \sum_j \left[\frac{\partial^2 V}{\partial R_i \partial R_j}\right]_e (R_i)\cdot(R_j)$$

The terms in brackets represent the force constants, f_{ij}, of the molecule under consideration. These are the parameters a vibrational spectroscopist hopes to get from the observed vibrational frequencies. f_{ij} is the restoring force in coordinate i caused by a small unit displacement of coordinate j, keeping the other coordinates fixed.[37] If i=j= a bond length, then f_{ii} is a measure of this bond's strength (although not completely comparable to a diatomic molecular force constant since it includes effects arising from changes in other internal coordinates) which is determined by the electronic distribution when the nuclei are at their equilibrium positions. Caution should be exercised in the use of the term "bond strength" since the term used here is different than the energy required to break a bond. Rather the force constant is a measure of the bond strength at the minimum in the potential energy curve and is therefore directly related to the equilibrium configuration.

The dissociation energy (DE) is a different measure of strength since when a bond stretches enough to dissociate, its electronic structure (and apparent force constant) changes considerably. Therefore, the dissociation energy is not closely related to the binding forces at the equilibrium configuration.

The usefulness of force constants in general relies on:

1) the correlation of their values with bond nature, electron delocalization, and interatomic interaction.

2) the use of their values to calculate and estimate vibrational frequencies and the further use of the results for band assignments.

Perhaps the best way to close this brief presentation on force constants is by giving a definition of the latter from a different perspective:

> Near the equilibrium point the force constant associated with the repulsive energy is dominant over that associated with the attractive energy. When the binding force between two atoms forming a chemical bond is large, the distance between the two atoms becomes small, the repulsion between the two nuclei including surrounding inner-shell electrons is large, and, accordingly the force constants are also large. In this way the force constant is a measure of the binding force.[33]

Since for reasons stated earlier the linearity of HCCN could not be taken for granted, it seemed necessary to perform two parallel normal coordinate analyses assuming two different structures, one bent and one linear. Table I shows the molecular parameters used for the normal coordinate analyses of the two structures along with the molecular parameters corresponding to an allene-type structure transferred from the molecules C_3H_4[38] (allene) and NCN.[39] These molecular parameters were used for a third normal coordinate calculation to test the sensitivity of the frequency fitting and values of force constants as a function of the bond lengths of the molecule.

Table I. Molecular Parameters Used for the Normal Coordinate Analysis of HCCN

HCCN (Carbene-like) Source: Preliminary Ab-initio Calculations[15]		HCCN (Nitrene-like) Source: Preliminary Ab-initio Calculations[15]		HCCN (Allene-like) Sources: Allene, NCN[38,39]	
C-C	1.385 Å	C≡C	1.19 Å	C=C	1.30 Å
C-H	1.08 Å	C-H	1.08 Å	C-H	1.07 Å
C≡N	1.170 Å	C-N	1.44 Å	C=N	1.23 Å
HCC	130°	HCC	180°	HCC	180°
CCN	180°	CCN	180°	CCN	180°

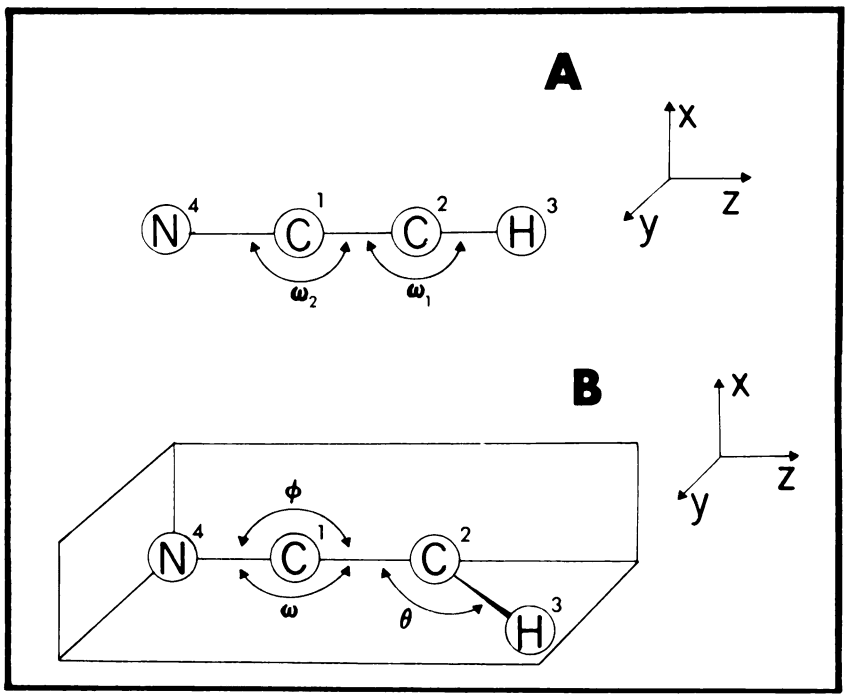


Figure 9. Internal Coordinates for the Free Radical HCCN (A- Linear, B- Bent)

Figure 9 and Table II give the internal and symmetry coordinates of HCCN for the bent structure and the linear. Symmetry coordinates are derived from internal coordinates (which are the bond lengths and angles of the molecule) by use of elementary Group Theory methods.[28] The reason behind their use is due to the great simplification of normal coordinate analysis which, in this way, can be performed on one symmetry species (of the symmetry point group the molecule belongs to) at a time. This is due to the simplification of the corresponding diagonalization of the kinetic energy and force constant matrices which are directly involved in the calculation of vibrational frequencies.

Table II. Symmetry Coordinates for the Free Radical HCCN

Linear Form $C_{\infty v}$ Symmetry Point Group		Bent Form C_s Symmetry Point Group
$S_1 = \Delta r_{23}$		$S_1 = \Delta r_{23}$
$S_2 = \Delta r_{14}$		$S_2 = \Delta r_{14}$
$S_3 = \Delta r_{12}$	A'	$S_3 = \Delta r_{12}$
		$S_4 = \Delta\theta$
$S_4 = \Delta\omega_1$		$S_5 = \Delta\omega$
$S_5 = \Delta\omega_2$		
	A"	$S_6 = \Delta\phi$

The initial force constants were transfered from the following free radicals: C_3H_2,[40] CCO[41] and NCN.[42,43] The results of the force constant calculations are shown in Tables III, IV, V, VI and VII. Since only five frequencies were observed at most, two normal coordinate analyses had to be performed on the bent structure depending on the assignment of the frequency observed at 405.0 cm^{-1} as an in-plane or or out-of-plane fundamental.

Note that on the following Tables (III, IV, V, VI and VII) the notation in the column under PED is as follows: AB= AB stretch
ABC= ABC bend

Table III. Normal Coordinate Analysis of HCCN: Linear Form*; Nitrene-like Molecular Parameters

			Frequencies (cm^{-1})			Primary Contributors
		ν	Obs.	Cal.	$\Delta\nu$	PED***
HCCN		ν_1	3229.0	3228.9	(-0.1)	CH(96)
	Σ^+	ν_2	1735.0	1737.3	(+2.3)	CN(103) CC(28)
		ν_3	1178.5	1178.7	(+0.2)	CC(80)
	Π	ν_4	458.0	458.5	(+0.5)	CCH(108) CCN(17)
		ν_5	(369.5)**	372.0	(+2.5)	CCN(92)
DCCN		ν_1	2424.0	2424.9	(+0.9)	CD(90)
	Σ^+	ν_2	1729.5	1730.8	(+1.3)	CN(104) CC(24)
		ν_3	1127.0	1128.8	(+1.8)	CC(79) CD(8)
	Π	ν_4	405.0	405.0	(0.0)	CCN(85) CCD(56)
		ν_5	317.5	317.5	(0.0)	CCD(53) CCN(24)
$HC^{13}CN$		ν_1	3229.0	3228.6	(-0.4)	CH(96)
	Σ^+	ν_2	1698.0	1695.7	(-2.3)	CN(104) CC(26)
		ν_3	1176.5	1175.1	(-1.4)	CC(82)
	Π	ν_4	458.0	457.1	(-0.9)	CCH(109) CCN(14)
		ν_5	(364.5)**	363.0	(-1.5)	CCN(95)
$HCC^{15}N$		ν_1	3229.0	3228.9	(-0.1)	CH(96)
	Σ^+	ν_2	1718.0	1716.5	(-1.5)	CN(102) CC(31)
		ν_3	1168.0	1167.3	(-0.7)	CC(77)
	Π	ν_4	458.0	458.4	(+0.4)	CCH(108) CCN(17)
		ν_5	-----	370.3	----	CCN(92)

*$C_{\infty v}$ symmetry point group

**uncertain band, not used in force constant calculations
***Potential Energy Distribution

Table IV. Normal Coordinate Analysis of HCCN: Bent Form*
(405 cm^{-1} band as in-plane)

		ν	Frequencies (cm^{-1}) Obs.	Cal.	Δν	Primary Contributors PED***
HCCN		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1735.0	1736.4	(+1.4)	CN(86) CC(38)
	A'	ν_3	1178.5	1170.6	(-7.9)	CC(65) CN(18)
		ν_4	458.0	458.6	(+0.6)	CCH(99) CCN(16)
		ν_5	(369.5)**	379.2	(+9.7)	CCN(87)
	A"	ν_6	-----	313.7	----	CCN(100)
DCCN		ν_1	2424.0	2391.4	(-32.6)	CD(97)
		ν_2	1729.5	1723.3	(-6.2)	CN(87) CC(36)
	A'	ν_3	1127.0	1155.3	(+28.3)	CC(65) CN(17)
		ν_4	405.0	404.8	(-0.2)	CCN(86) CCD(35)
		ν_5	317.5	317.7	(+0.2)	CCD(68) CCN(17)
	A"	ν_6	-----	313.7	----	CCN(100)
$HC^{13}CN$		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1698.0	1691.4	(-6.6)	CN(87) CC(37)
	A'	ν_3	1176.5	1169.5	(-7.0)	CC(66) CN(17)
		ν_4	458.0	456.6	(-1.4)	CCH(100) CCN(12)
		ν_5	(364.5)**	370.4	(+5.9)	CCN(91)
	A"	ν_6	-----	305.3	----	CCN(99)
$HCC^{15}N$		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1718.0	1720.7	(+2.7)	CN(84) CC(41)
	A'	ν_3	1168.0	1156.2	(-11.8)	CC(62) CN(20)
		ν_4	458.0	458.4	(+0.4)	CCH(99) CCN(16)
		ν_5	-----	376.8	----	CCN(87)
	A"	ν_6	-----	311.9	----	CCN(99)

*C_s symmetry point group, **uncertain band, ***Potential Energy Distrib.

Table V. Normal Coordinate Analysis of HCCN: Bent Form*; (405 cm^{-1} band as out-of-plane)

			Frequencies (cm^{-1})			Primary Contributors
		ν	Obs.	Cal.	$\Delta\nu$	PED***
HCCN		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1735.0	1736.4	(+1.4)	CN(86) CC(38)
	A'	ν_3	1178.5	1170.6	(-7.9)	CC(65) CN(18)
		ν_4	458.0	458.4	(+0.4)	CCH(102) CCN(10)
		ν_5	-----	367.9	----	CCN(93)
	A"	ν_6	(369.5)**	403.4	(+33.9)	CCN(100)
DCCN		ν_1	2424.0	2391.4	(-32.6)	CD(97)
		ν_2	1729.5	1732.3	(+2.8)	CN(87) CC(36)
	A'	ν_3	1127.0	1155.3	(+28.3)	CC(65) CN(17)
		ν_4	-----	392.7	----	CCN(81) CCD(43)
		ν_5	317.5	317.6	(+0.1)	CCD(60) CCN(23)
	A"	ν_6	405.0	403.4	(-1.6)	CCN(100)
$HC^{13}CN$		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1698.0	1691.4	(-6.6)	CN(87) CC(37)
	A'	ν_3	1176.5	1169.5	(-7.0)	CC(66) CN(17)
		ν_4	458.0	457.0	(-1.0)	CCH(103)
		ν_5	-----	358.9	----	CCN(95)
	A"	ν_6	(364.5)**	392.6	(+28.1)	CCN(99)
$HCC^{15}N$		ν_1	3229.0	3236.8	(+7.8)	CH(99)
		ν_2	1718.0	1720.7	(+2.7)	CN(84) CC(41)
	A'	ν_3	1168.0	1156.2	(-11.8)	CC(62) CN(20)
		ν_4	458.0	458.2	(+0.2)	CCH(102) CCN(10)
		ν_5	-----	365.5	----	CCN(93)
	A"	ν_6	-----	401.1	----	CCN(100)

*C_s symmetry point group

**uncertain band, not used in force constant calculations

***Potential Energy Distribution

Table VI. Normal Coordinate Analysis of HCCN Linear Form*
Allene-like Molecular Parameters

		ν	Frequencies (cm^{-1}) Obs.	Cal.	Δν	Primary Contributors PED***
HCCN		ν_1	3229.0	3228.9	(-0.1)	CH(96)
	$\sum^+$	ν_2	1735.0	1737.3	(+2.3)	CN(103) CC(28)
		ν_3	1178.5	1178.7	(+0.2)	CC(80)
	Π	ν_4	458.0	458.5	(+0.5)	CCH(103) CCN(17)
		ν_5	(369.5)**	371.0	(+1.5)	CCN(89)
DCCN		ν_1	2424.0	2424.9	(+0.9)	CD(90)
	$\sum^+$	ν_2	1729.5	1730.8	(+1.3)	CN(104) CC(24)
		ν_3	1127.0	1128.8	(+1.8)	CC(79) CD(8)
	Π	ν_4	405.0	405.0	(0.0)	CCN(81) CCD(49)
		ν_5	317.5	317.7	(+0.2)	CCD(56) CCN(24)
$HC^{13}CN$		ν_1	3229.0	3228.6	(-0.4)	CH(96)
	$\sum^+$	ν_2	1698.0	1695.7	(-2.3)	CN(104) CC(26)
		ν_3	1176.5	1175.1	(-1.4)	CC(82)
	Π	ν_4	458.0	456.9	(-1.1)	CCH(104) CCN(14)
		ν_5	(364.5)**	362.2	(-2.3)	CCN(92)
$HCC^{15}N$		ν_1	3229.0	3228.9	(-0.1)	CH(96)
	$\sum^+$	ν_2	1718.0	1716.5	(-1.5)	CN(102) CC(31)
		ν_3	1168.0	1167.3	(-0.7)	CC(77)
	Π	ν_4	458.0	458.5	(+0.5)	CCH(103) CCN(16)
		ν_5	-----	368.8	----	CCN(89)

*$C_{\infty v}$ symmetry point group

**uncertain band, not used in force constant calculations

***Potential Energy Distribution

Table VII. Force Constants for HCCN

Bent Form 405.0 cm^{-1} band as CCN ip		Bent Form 405.0 cm^{-1} band as CCN op	
K_{CC}=	7.480 (1.220)	K_{CC}=	7.480 (1.287)
K_{CH}=	5.716 (0.030)	K_{CH}=	5.716 (0.032)
K_{CN}=	10.922 (2.236)	K_{CN}=	10.921 (2.358)
H_{CCH}=	0.122 (0.007)	H_{CCH}=	0.124 (0.065)
H_{CCN}=	0.315 (0.038)	H_{CCN}=	0.294 (0.791)
H'_{CCN}=	0.192	H'_{CCN}=	0.317 (0.025)
$F_{CC,CN}$=	2.003 (0.899)	$F_{CC,CN}$=	2.002 (0.949)
$F''_{CCH,CCN}$=	0.040(0.015)	$F''_{CCH,CCN}$=	0.040 (0.079)
Linear Form Nitrene-like Bond Lengths		**Linear Form Allene-like Bond Lengths**	
K_{CC}=	7.533 (0.049)	K_{CC}=	7.533 (0.050)
K_{CH}=	5.566 (0.008)	K_{CH}=	5.567 (0.008)
K_{CN}=	12.241 (0.168)	K_{CN}=	12.241 (0.170)
H_{CCH}=	0.116 (0.001)	H_{CCH}=	0.113 (0.001)
H_{CCN}=	0.335 (0.004)	H_{CCN}=	0.307 (0.004)
$F_{CC,CN}$=	2.842 (0.111)	$F_{CC,CN}$=	2.842 (0.112)
$F_{CH,CC}$=	-0.456 (0.032)	$F_{CH,CC}$=	-0.456 (0.033)
$F''_{CCH,CCN}$=	0.060 (0.001)	$F''_{CCH,CCN}$=	0.046 (0.001)

Numbers in parentheses represent uncertainties; see Appendix A.

K- stretching force constant (mdyn/Å)

H- in-plane bending force constant (mdyn·Å)

H'- out-of-plane bending force constant (mdyn·Å)

F- stretching-stretching interaction force constant (mdyn/Å)

F"- bending-bending interaction force constant (mdyn·Å)

Assignment of the Observed Fundamentals* of HCCN

Since the normal coordinate analysis supports the linear geometry, the following discussion is based on the results shown in Tables III and IV.

ν_1

The band observed at 3,229 cm^{-1} in HCCN is shifted down to 2,424 cm^{-1} in DCCN. No detectable frequency shift in the other two isotopes could be observed and no resolvable shift is predicted by the normal coordinate analysis. The frequency range within which this band appears, the large shift upon deuteration and the normal coordinate analysis results all point towards assignment of this fundamental as the (ν_1) C-H stretch.

ν_2, ν_3

The two bands at 1,735 cm^{-1} and at 1,178 cm^{-1} will be examined together due to their behavior upon isotopic substitution which shows that a strong coupling exists between them. Their isotopic pattern is very similar to the one observed for ν_3 (anti-symmetric stretch) and ν_1 (symmetric stretch) of NCN[42,43] (which is isoelectronic to HCCN) as is shown on the following page.

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*The fundamentals are numbered in decreasing order of frequency by convention.[31]

	HCCN		NCN		
	$\nu_?$	$\nu_?$	ν_1	ν_3	
HCCN	1,735	1,178.5	1,197	1,475	NCN
$HC^{13}CN$	1,698	1,176.5	1,195	1,435	$N^{13}CN$
$HCC^{15}N$	1,718	1,168	1,178	1,468.5	$NC^{15}N$

(frequencies are given in cm^{-1})

Accordingly, the bands at 1,735 cm^{-1} and 1,178.5 cm^{-1} are assigned as the (ν_2) anti-symmetric and (ν_3) symmetric stretch of the CCN group respectively. The normal coordinate analysis results support this assignment.

ν_4

The band observed at 488 cm^{-1} in HCCN was shifted down to 317.5 cm^{-1} upon deuteration while it remained unshifted in the other two isotopes. This large isotopic shift alone implies that this band is due to a hydrogen motion of some kind. Since the CCH bending motion is the only other hydrogen motion left, it seems appropriate to assign this band to the (ν_4) CCH bend. Again this assignment is fully supported by the normal coordinate analysis results. It is interesting to note that the ratio of the two isotopic frequencies (458/317.5) is 1.44 which is higher than the theoretically predicted one (1.38). This is really surprising since the ratios of experimentally observed isotopic frequencies of similar motions in other molecules are found to be lower than 1.38

(e.g. cyanoacetylene,[44] H-C≡C-C≡N, for which the ratio is 663/552=1.27). Anharmonicity effects usually account for ratios smaller than the theoretically predicted ones. Therefore, this large shift is probably due to the fact that a rather drastic difference exists in terms of the primary contributors to this normal mode between HCCN and DCCN. This argument seems to be supported by the normal coordinate analysis results. (See Table III)

ν_5

A band observed at 405 cm^{-1} in the deuterated species is assigned as the deuterated analog of the (ν_5) CCN bend. This assignment is based solely on the results of the normal coordinate analysis, since this band's counterparts in HCCN and the other two isotopes have not been positively identified. Two weak bands, one at 369.5 cm^{-1} and one at 364.5 cm^{-1} were observed in HCCN and $HC^{13}CN$ respectively. These bands grew upon photolysis and disappeared upon annealing but their rate of growth and disappearance was hard to establish due to their weak intensities. Therefore they are tentatively assigned as the 405 cm^{-1} band counterparts in HCCN and $HC^{13}CN$. The normal coordinate analysis results are not incompatible with this assignment. An interesting feature of ν_5 is its shift towards higher frequency upon deuteration. (This situation although rarely encountered is reported in the literature for CH_2N_2[2] and $HC{\equiv}CCHN_2$.[3]) This again can be explained by invoking the difference in terms of potential energy contributors for ν_5 between HCCN and DCCN.

Finally, if HCCN is not linear, the band at 405 cm^{-1} would have two possible assignments, one as a CCN in-plane bend (ν_5) and another

as a CCN out-of-plane bend (ν_6). Results of the corresponding normal coordinate analysis treatments are shown in Tables IV and V. These possibilities will be discussed in the following section.

Other Bands

Upon photolysis of diazoacetonitrile several bands grow in addition to the ones assigned to fundamentals of HCCN. None of these however showed behavior attributable to a reactive species. These bands are obviously due to stable molecules which are formed in the matrix through reactions between two or more HCCN molecules, diazoacetonitrile and impurities due to the synthesis methods employed. Their appearance in the matrices was not reproducible, which indicates that impurities are largely responsible for these bands since impurities are expected to differ in the different synthetic routes employed.

The Vibrational Potential Function of HCCN

The force constants obtained from the normal coordinate analysis performed on the linear configuration will be used here in this discussion, the reason being the considerably better frequency fit for this structure as compared to the bent. These force constants are shown in Table VII on page 37.

The following force constants[45] may be used as a guideline for an easier understanding of the discussion centered around the force constants of HCCN. Their values are considered typical for the bonds written next to them.

C-H	sp^3	4.8	C-C	sp^3-sp^3	4.5	C-N		~4.8
C-H	sp^2	5.3	C=C	sp^2-sp^2	9.7	C=N	(sp^2-C)	10.5
C-H	sp	5.9	C≡C	sp-sp	15.6	C≡N	(sp-C)	17.73

The stretching force constant for the CH bond is calculated at 5.567 mdyn/Å which lies between the one for cyanoacetylene[44] (5.86 mdyn/Å) and that of methyl cyanide[46] (5.0 mdyn/Å) and is similar to that of ketene[47] (5.439 mdyn/Å, taken as an average between the two force constants corresponding to the symmetric and anti-symmetric stretch of the CH_2 group). Therefore the value for HCCN seems to be compatible with a structure of the CCH group more like H-C=C (which is the case in ketene) rather than H-C≡C or H-C-C which are the cases in cyanoacetylene and methyl cyanide respectively.

The CC stretching force constant is calculated at 7.533 mdyn/Å and is much higher than that of methyl cyanide (5.161 mdyn/Å), somewhat lower than that of ketene (8.387 mdyn/Å) but very close to one of the two CC stretches of cyanoacetylene (7.83 mdyn/Å, corresponding to the CC bond adjacent to the CN bond), a molecule in which resonance is quite extensive. From the above comparison, it seems that the CC stretching force constant is compatible with a CC bond lying somewhere between a single and a double bond but closer to the latter.

The CN stretching force constant is calculated at 12.241 mdyn/Å which is lower than those of methyl cyanide (17,982 mdyn/Å) and cyanoacetylene (15.7 mdyn/Å) but higher than that of diazomethane[2]

(8.34 mdyn/Å) therefore implying a CN bond lying somewhere between a double and a triple bond, but closer to the former.

Now that the CC and CN bonds have been discussed individually, it seems appropriate in view of their strong coupling to examine them as a group and compare the latter with those of similar isoelectronic free radicals. The Table below makes such a comparison much easier.

	K_{CC} or K_{CN} (mdyn/Å)	K_{CO} or K_{CC} or K_{CN} (mdyn/Å)
CCO	7.97	14.06
HCCN	7.53	12.24
HCCCH[40]	12.05	12.05
NCN	8.60	8.60

An interesting pattern emerges. If the values of the force constants can be taken as rough measures of the electron densities between these atoms (which is not unreasonable, since they are measures of the binding forces between these atoms and these forces are presumably created by a strong electron overlap between the atoms) then the variation of the force constant values can be explained by simply invoking the difference in electronegativities between the atoms C, N, and O. Using HCCCH as a starting point, one would expect that in going from this molecule to NCN a considerable decrease in electron density around the carbon atom would take place with a simultaneous increase around the nitrogen atoms. This would cause some weakening of the CN bonds and therefore lowering of their force constants. On the other hand going from HCCCH to HCCN one would expect the electrons to shift towards the

nitrogen end of the molecule which would tend to break the equal strength balance of the two CC bonds in favor of the CN bond; this effect is expected to be even more pronounced as one moves to the CCO molecule. Indeed the argument, simple as it is, seems to qualitatively explain the force constant pattern in these simple isoelectronic free radicals.

The force constant of the CCH bend is calculated at 0.124 mdyn·Å. This value is lower than that of cyanoacetylene (0.150 mdyn·Å) and those of propargyl halides (0.14 mdyn·Å).[48] This can be explained by the fact that the unpaired spin density on the carbon atom next to the hydrogen would tend to more easily allow the rehybridization which accompanies the CCH bending and thus lead to a lower bending force constant.[40]

The force constant of the CCN bend is calculated at 0.307 mdyn·Å for the allene-type linear configuration, but at 0.335 mdyn·Å for the nitrene-type linear configuration. This is actually the only force constant where a significant value difference appears between these two configurations. Both values are considerably higher than that of cyanoacetylene (0.210 mdyn·Å), but very close to those of aliphatic nitriles (~0.310 mdyn·Å).[49]

Finally three interaction force constants were found to be important for a good agreement between the observed and calculated frequencies, namely those of the interaction between CCH and CCN bends (+0.046 mdyn·Å), between CH and CC stretches (-0.456 mdyn/Å), and especially between CC and CN stretches (2.842 mdyn/Å). The high value of the latter is typical of similar free radicals such as NCN (3.22 mdyn/Å),

CCO (2.37 mdyn/Å) and HCCCH (0.87 mdyn/Å). The high value of the CC,CN stretching interaction force constant is the reason why it is inappropriate to assign ν_2 and ν_3 as "primarily CN and CC stretches, respectively." Rather, they are designated as the anti-symmetric and symmetric stretches of the CCN group.

Conclusion

Although only five frequencies were observed for HCCN, this does not prove that the molecule is linear since one can always argue that the sixth frequency was too weak to be observed. This is indeed the case for HOCN which is expected to be non-linear[50] (based on elementary considerations of the molecular orbitals involved in the bonding between an O-H group and a C≡N group) and for which only five frequencies were observed in the IR spectrum.[50] Therefore the observation of only five frequencies can be considered as evidence towards the linearity of the molecule, but certainly not proof. However, a mere comparison of the normal coordinate analysis results for the two structures shows a much better frequency fir for the linear rather than the bent structure. (The frequency fit for the latter does not show any improvement when the 405 cm^{-1} band is assigned to ν_6 rather than to ν_5 as a comparison between Tables IV and V reveals.) This is considered strong evidence that HCCN is linear. Another fact that points towards the linearity of the molecule is the very low frequency of the HCC bending motion (458 cm^{-1}). CCH bending frequencies in non-linear molecules usually lie above 750 cm^{-1}.[51]

Although more than 8 force constants were initially used for both

structures, it was found that the fit was equally good with only 8 force constants, indicating that the rest of the interaction force constants were of little importance to the vibrational potential function. It is interesting to note that for the linear configuration the total number of force constants comprising the general valence force field is 9 and therefore calculation of the 9th force constant results in the complete determination of the force constant matrix. The value of this force constant which, is a measure of the interaction between the CH and CN bonds, was found to be 0.022 mdyn/Å with an uncertainty of 0.175. Unfortunately the large uncertainty associated with this force constant makes its value meaningless.

Finally attention is called to the large interaction force constant between the CC and CN bonds. According to a discussion of the physical significance of interaction force constants by Linnett and Hoare,[43,52] the relatively large positive value of the interaction constant for HCCN implies the presence of delocalized electrons in the groud state of this species. This is supported by the isotopic frequency shift pattern which implies that the CC and CN bonds are of similar strength.

The above may be interpreted to suggest that the structure of HCCN lies somewhere between a carbene and a nitrene form, i.e. H-$\dot{C}$=C=$\dot{N}$, which is an allene type structure. This structure is also favored by the arguments used in the discussion of the vibrational potential function of HCCN in the previous section.

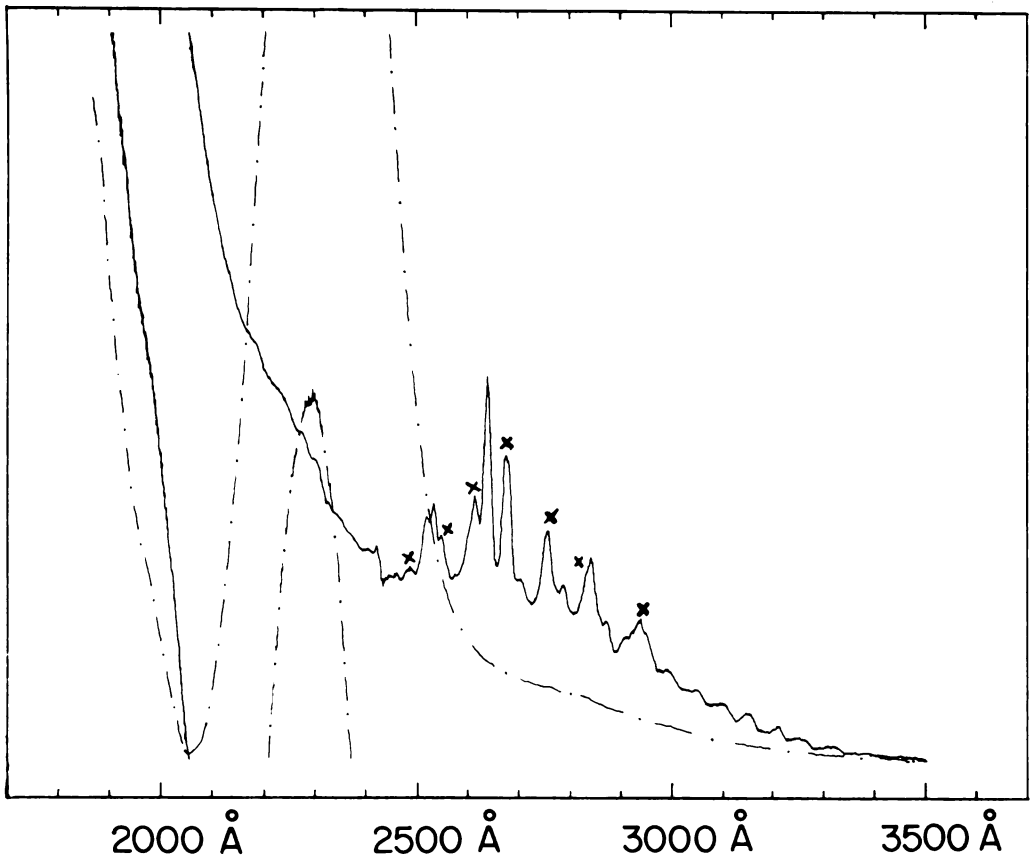


Figure 10. UV Spectrum of Diazoacetonitrile Before Photolysis (dotted line) and After Photolysis (solid line)

The Electronic Absorption Spectrum of the Free Radical HCCN

The electronic absorption spectrum of diazoacetonitrile isolated in an Ar matrix, before and after photolysis, was scanned between 185 nm and 800 nm. Only the UV part of the spectrum however is shown in Figure 10, since no bands were observed in the wavelength region between 350 nm and 800 nm.

The multiplet structure which appeared between 2400 Å and 3400 Å after the precursor was photolyzed showed similar behavior upon annealing as the bands of HCCN in the IR and therefore is attributed to the free radical HCCN. The multiplet structure is rather complicated but at least one progression can be singled out (members of the progression are marked with an ×) with a spacing of 1052 wavenumbers which may be associated with the upper symmetric stretch of the CCN group (the ground state symmetric stretch appears at 1178.5 cm^{-1}).

It is interesting to compare the observed spectrum with spectra of other free radicals such as NCN[42] (which is isoelectronic with HCCN) and NCO[53,54] (which has one more electron than NCN and HCCN). NCN shows a progression between 3500 Å and 2400 Å involving excitation of the upper state symmetric stretching fundamental, while NCO shows a progression between 3200 Å and 2650 Å which also involves excitation of the upper state symmetric stretching frequency. These two progressions have been assigned to $\pi \rightarrow \pi$ transitions, more specifically:

$B(^3\Sigma_u^-) - X(^3\Sigma_g^-)$ for NCN and $B^2(\Pi) - X(^2\Pi)$ for NCO.

However both of these free radicals show another intense absorption band ($\sigma \rightarrow \pi$ transition) without any vibrational structure,

$A(^3\Pi_u) - X(^3\Sigma_g^-)$ for NCN and $A(^2\Sigma_u^+) - X(^2\Pi)$ for NCO,

at longer wavelengths which is missing in the HCCN spectrum. It is conceivable that the analogous band in HCCN is also observed but is not as intense, since weak peaks are observed in the spectrum of HCCN around the wavelength range where the band is observed for NCN (3290 Å). If this is the case, though, it is not clear why the relative intensities of the two bands should be so different in the two molecules. The most

obvious explanation is that the band is missing because the electron in the molecular orbital responsible for this transition in NCN is not available in HCCN due to its participation in the CH bond, since this is the part of the molecule that differs from NCN.

Regardless of what the reason for this apparent discrepancy is, it does not seem unreasonable-- based on the strong similarities of the two molecules shown by their vibrational spectra, the apparent similarity of the progressions in the electronic spectrum and their being isoelectronic-- to tentatively assign the progression observed in the UV spectrum of HCCN to a $^3\sum - {}^3\sum$ transition involving excitation of an electron from a π orbital of lower energy to a π orbital of higher energy, in view of a similar assignment made for the analogous progression in NCN.

The complicated structure of this band as opposed to the simple progression observed for NCN is not unexpected[55] since HCCN is not a simple triatomic molecule with a center of symmetry like NCN.

The electronic absorption spectrum of a (50%-50%) mixture of HCCN and DCCN was also taken, but no change in the vibrational spacing was observed despite the large shift that the symmetric stretch was found to experience in the IR spectra upon deuteration (1178.5 cm^{-1} to 1127 cm^{-1}). This is probably due to the resolution under which the UV spectra could best be taken (1 Å, which corresponds to $\sim$40 cm^{-1} in this part of the spectrum).

Discussion of the Compatibility of the ESR Data with the Proposed Allene-Type Structure of HCCN

Only the problem of the electron distribution will be dealt with here, since the linearity of the molecule, strongly indicated by the vibrational spectrum, is in agreement with the ESR data available to date (see section on background information on HCCN). Therefore, the linearity of HCCN will be assumed throughout this section. Neglecting hyperfine interactions, the spin Hamiltonian for a linear triplet molecule is written as[56]

$$\hat{H} = \beta H \cdot g \cdot S + D(S_z^2 - 2/3)$$

where $\hat{H}$= the spin Hamiltonian, β= Bohr magneton, H= the magnetic field, g= g-factor, D= zero-field splitting parameter, and S= the total spin angular momentum (S_z is the z component of S). The value of D is roughly inversely proportional to the cube of the separation of the two unpaired spins and is a measure of electron delocalization. Therefore, the discussion will be based on the D values of HCCN and other free radicals available to date.

The D value for "fixed" (i.e. non-rotating in the matrix) methylene ranges from 0.74 cm^{-1} to 0.93 cm^{-1} depending on the matrix,[57] while that of NH is 1.86 cm^{-1}.[58] Having established the D value for the two extreme cases, i.e. methylene (both unpaired electrons localized at the carbon atom) and nitrene (both unpaired electrons localized at the nitrogen atom) we proceed to examine what happens when the opportunity for delocalization is offered to the unpaired electrons. HCCCH and NCN provide good examples of such a case. Both of these free radicals are known to have largely delocalized electrons.[13,40,42,59] The D value of

HCCCH is 0.628 cm^{-1} which is significantly lower than that of CH_2.* The two unpaired electrons in this molecule are, due to delocalization, further apart than they were in CH_2, thus resulting in a lower D value. A similar situation exists between NCN and NH. The D value of NCN is 1.544 cm^{-1} [60] which is much lower than that of NH.

If HCCN had a carbene-type configuration, its D value would be very similar to that of CH_2 although somewhat larger because of the additional muclear charge due to the presence of the nitrogen atom in the molecule.[6] If HCCN had a nitrene configuration, its D value would be very similar to that of NH.

The D value of HCCN has been found to be 0.836 cm^{-1} [7] which is significantly larger than that of CH_2. The difference between the two values is too large to be explained as being due only to the presence of the nitrogen atom in HCCN. Thus, at first glance it seems that the nitrene-type configuration contributes significantly (in terms of valence bond theory) to the overall D value, something that has already been speculated in the literature.[7] However a closer look at the factors which contribute to the D value shows otherwise.

Along with the spin dipole-dipole interaction that provides a first order contribution to the overall D value, there is a second order contribution which is due to the spin-orbit coupling. This contribution although small for CH_2[57] (10%) and HCCCH[61] (16%) is expected to be much larger for small free radicals containing nitrogen atoms. Therefore, for our purposes a more meaningful comparison between the D values of these free radicals can be made only after the spin-orbit contributions are taken out of the D values. Unfortunately the spin-orbit

*Assume D= 0.74.

contribution to the D value of HCCN is not known. However, one can get some idea of the magnitude of this contribution by citing the results obtained for a very similar free radical, namely isoelectronic NCN.

According to ab-initio calculations employing minimal STO-4G and extended 4-31G basis sets,[62] the spin-orbit contribution to the total D value for NCN is 60%!!! Even if the spin-orbit contribution for HCCN is only 20% (which is not unreasonable in view of the 16% contribution in HCCCN), its D value comes down to .690 cm^{-1}. This is lower than that of CH_2, which becomes .722 cm^{-1} after the spin-orbit contribution to the D value of the latter is taken out. Electron delocalization must now be assumed to account for the difference between the D value of HCCN and that of CH_2. It should be noted that the lowest experimental D value for CH_2 (.74 cm^{-1}) has been used throughout this discussion. Therefore, the value .722 cm^{-1} represents roughly the lower limit of the D value of CH_2. If the D value of CH_2 is taken to be larger than .74 cm^{-1} and the spin-orbit contribution in HCCN larger than 20%, the difference between the two values will increase further, thus favoring even more the allene-type configuration where delocalization of the unpaired electrons is quite extensive.

In view of the above it can be concluded that the ESR data available to date are compatible with the proposed allene-type structure for HCCN. However positive proof of this and the linearity may come only with hyperfine structure data obtained from the isotopic modifications of HCCN.

CHAPTER II

A STUDY OF THE VIBRATIONAL SPECTRUM OF DIAZOACETONITRILE

Background Information on Diazoacetonitrile

Diazoacetonitrile (DAN) was first prepared in 1898 by Curtius[63] who found it to be an orange-yellow oily liquid boiling at 46.5°C (15mm Hg). He also found that when isolated it is liable to explode violently. Some IR and UV data on diazoacetonitrile have been reported in the literature. Specifically three UV bands (2050 Å, 2480 Å, and 3280 Å) and three IR bands (3110 cm^{-1}, 2220 cm^{-1}, 2100 cm^{-1}) are mentioned. Both the UV work and IR work have been done in solution (EtOH and chloroform respectively). From a spectroscopist's point of view these results are rather meager. This is probably due to the different perspective associated with that work.[64] Diazoacetonitrile was also found to exhibit a strong absorption in NMR at 5.50 τ ($CDCl_3$ was used as a solvent).[64] The most complete spectroscopic work to date has been done in the MW by C.C. Costain and J. Yarwood.[65] Their observations were consistent with a planar structure and the molecular parameters they obtained for diazoacetonitrile are shown in Table VIII on page 62. The dipole moment of the molecule was found to be 3.45 ±0.07 D with the vector having a direction almost parallel to the CCN chain (see Figure 18).

Approach to the Study of Diazoacetonitrile

Due to diazoacetonitrile's low vapor pressure and high instability (half-life ~ 5 minutes when in the IR beam), it was impossible to obtain its IR spectrum in the gas phase. (The thought of using a long path cell was discarded since diazoacetonitrile leaves brown stains, on everything it contacts, which are hard to remove.) This was a serious drawback since the information regarding the symmetry of the vibrations which could be obtained fron the band envelopes in the gas phase spectra was lost. Consequently, the spectra of diazoacetonitrile in its matrix-isolated form were the main source of information available for the band assignment task. A helpful supplement regarding the latter were the spectra in the pure solid form. Spectra of diazoacetonitrile in solution (solvents employed were dichloromethane and dioctyl phthalate) were useful for quickly checking the success of the synthesis before engaging in the long and frustrating matrix isolation experiments.

Bands due to diazoacetonitrile were easily identified in the spectra by the decrease in their intensity upon phtolysis. Peaks due to impurities in general did not show any appeciable change in their intensities. Finally, it should be mentioned that careful handling of diazoacetonitrile coupled with the available information in the literature made it possible to avoid violent explosions, although a couple of minor ones did take place unexpectedly.

Vibrational Spectra of Diazoacetonitrile and Its Isotopes

Application of elementary Group Theory methods[28] shows that all 12 vibrations of diazoacetonitrile (C_s symmetry) are IR and Raman active.

Of those 12 vibrations, 9 belong to the A' symmetry species representing the in-plane vibrations and 3 belong to the A" symmetry species representing the out-of-plane vibrations.

IR survey spectra of diazoacetonitrile in N_2 (A) and Ar (B) are shown in Figure 11. A general comparison of the two shows clearly the extensive amount of site splitting caused by the N_2 matrix. This is particularly obvious in the region between 300 and 400 cm^{-1}. The single peak at 362 cm^{-1} in Ar is due to the CH wag out-of-plane vibration. The same peak is multiply split in the N_2 matrix. (The shifting towards higher frequency and the broadening with consequent loss of intensity of this peak is due to hydrogen bonding between diazoacetonitrile and the N_2 matrix. This is not unusual for compounds of this nature when isolated in N_2 matrices.)[50] Peaks marked with an × are due to chloroacetonitrile (see page 16), those with a check are due to H_2O and those with a circle are due to CO_2. Figure 12 shows the IR survey spectrum of diazoacetonitrile in N_2 before and after photolysis. Peaks marked with an arrow are due to HCCN. Peaks due to diazoacetonitrile are easily identified due to the decrease in their intensities upon photolysis.

Figures 13, 14, 15, and 16 show IR survey spectra in Ar of NNC$\overset{*}{H}$CN (50% D), NNCHC$\overset{*}{N}$ (60% ^{13}C), NNCHC$\overset{*}{N}$ (50% ^{15}N), and $\overset{*}{N}$NCHCN (55% ^{15}N) respectively. The peaks which were marked with an × in Figure 11 are missing in Figures 14 and 15. This is due to the modification of the synthesis method for diazoacetonitrile as mentioned on page 16, which overcame the problem of simultaneous production of chloroacetonitrile.

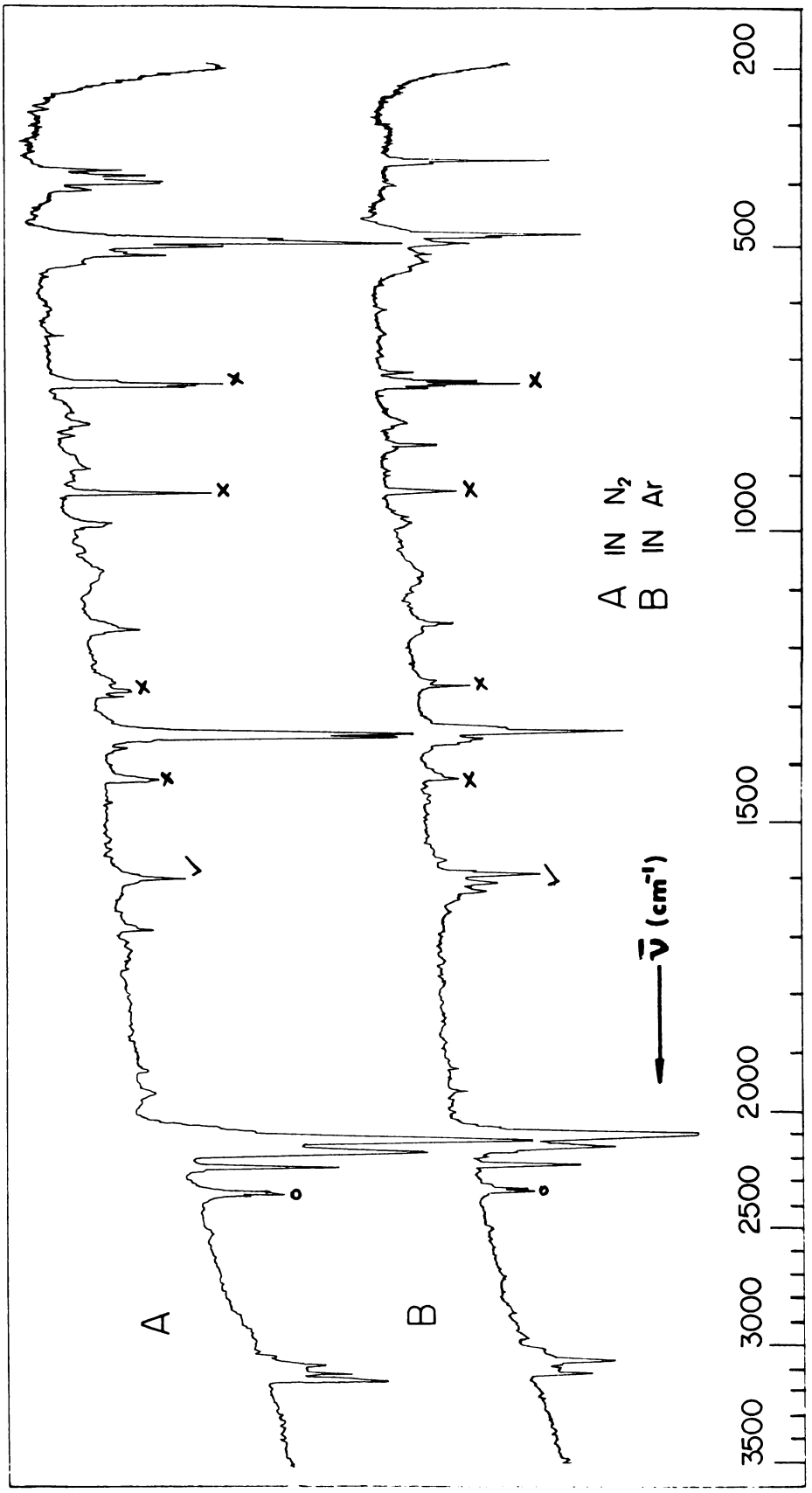


Figure 11. IR Spectra of Diazoacetonitrile in Inert Matrices

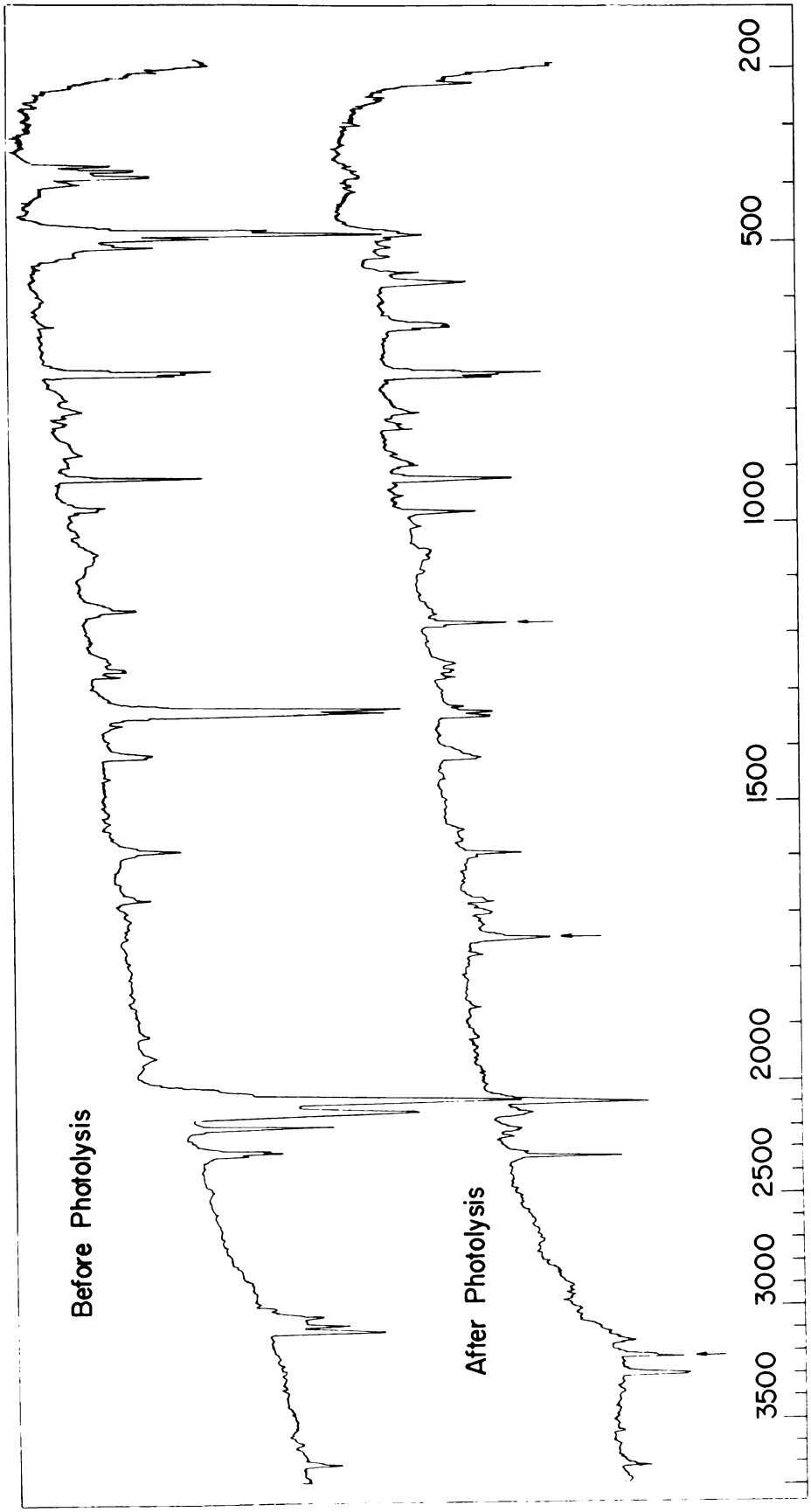


Figure 12. IR Spectrum of Diazoacetonitrile in a N_2 Matrix Before and After Photolysis

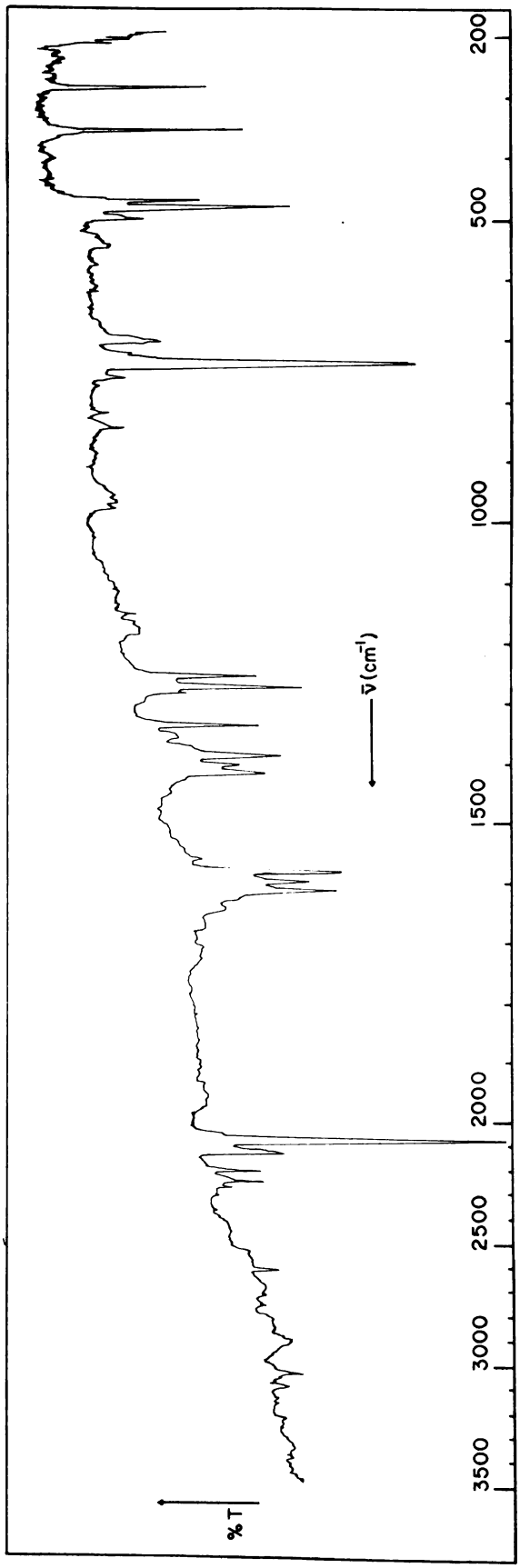


Figure 13. IR Spectrum of Diazoacetonitrile (NNC$\overset{*}{H}$CN-50% D) in an Ar Matrix

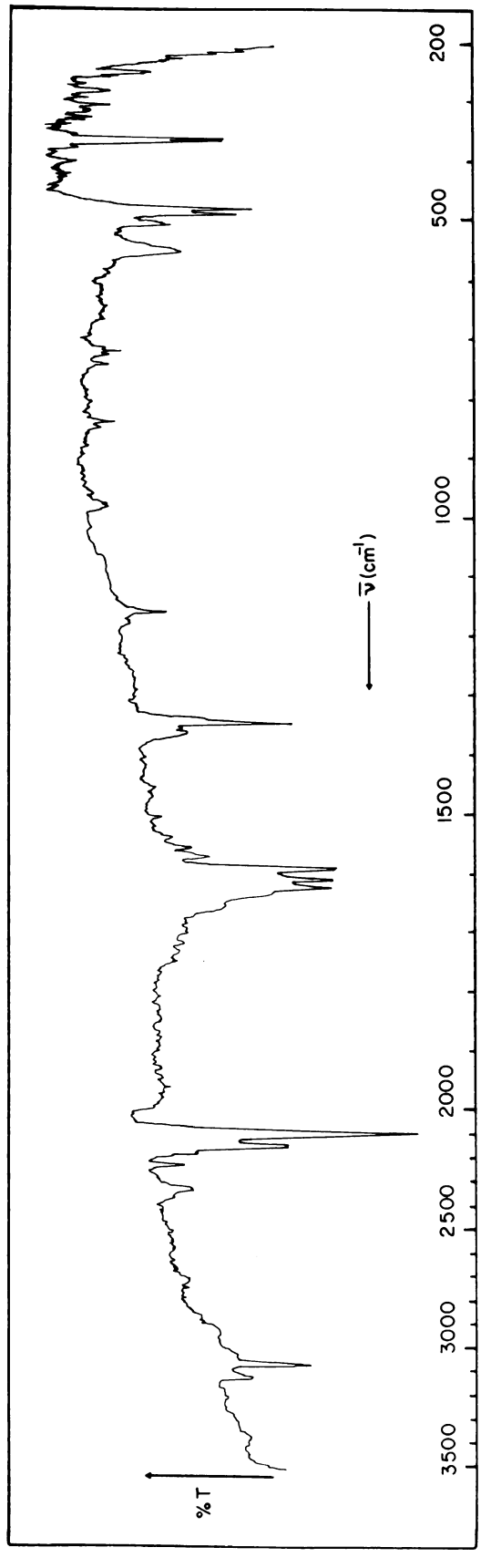


Figure 14. IR Spectrum of Diazoacetonitrile (NNCH$\overset{*}{C}$N-60% ^{13}C) in an Ar Matrix

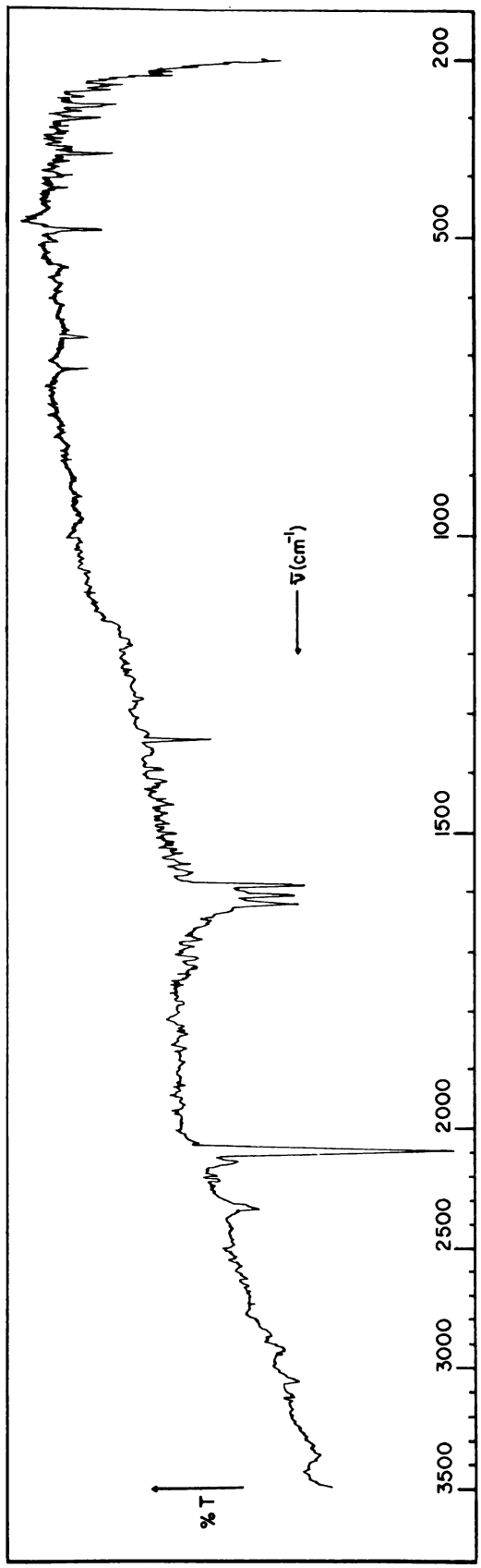


Figure 15. IR Spectrum of Diazoacetonitrile (NNCHC$\overset{*}{N}$-50% ^{15}N) in an Ar matrix

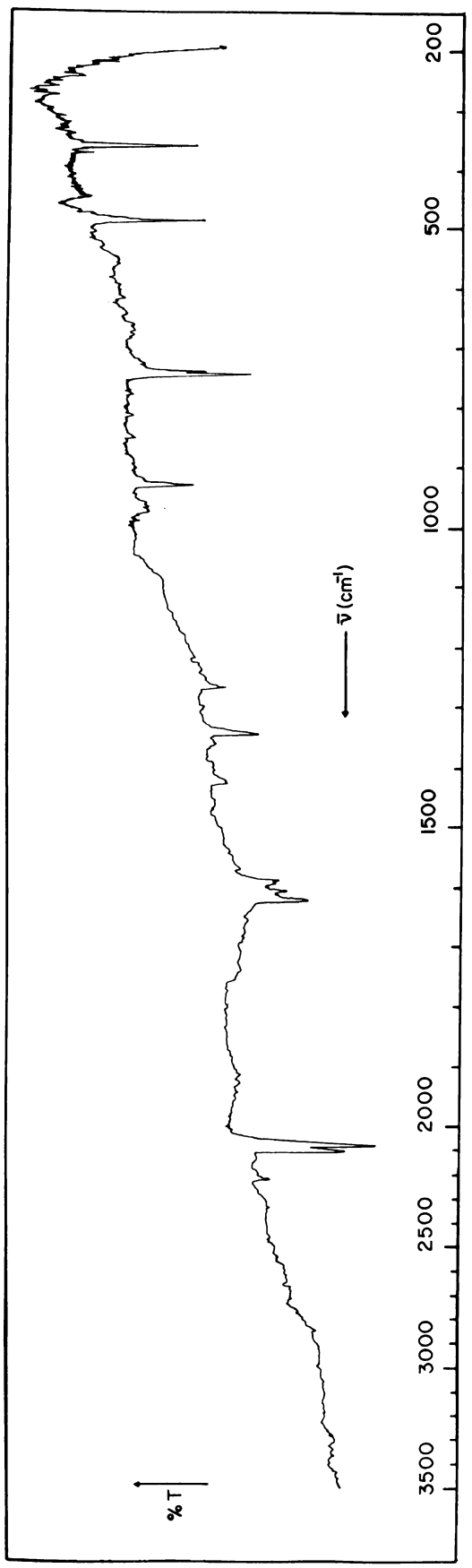


Figure 16. IR Spectrum of Diazoacetonitrile ($\overset{*}{N}NCHCN$-55% ^{15}N) in an Ar Matrix

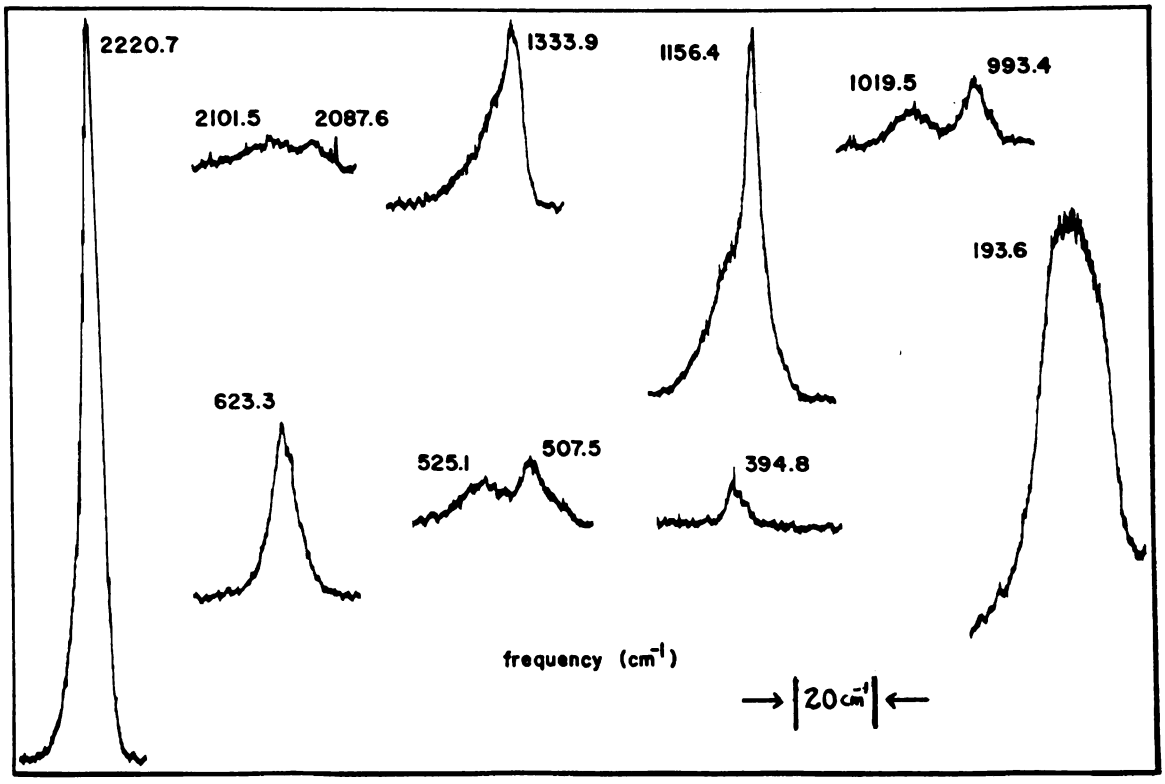


Figure 17. Raman Spectrum of Diazoacetonitrile (Pure Solid)

Finally in Figure 17 the Raman spectrum of diazoacetonitrile in pure solid form is shown. The observed frequencies from the IR spectra and the Raman spectrum used in the normal coordinate analysis are listed in Tables IX, X, XI, XII, and XIII where they are compared with the results of the normal coordinate analyses.

Table VIII. Molecular Parameters and Symmetry Coordinates for Diazoacetonitrile

Bond Lengths (Å)	Bond Angles
r_{12} = 1.424	θ_1 = 117°
r_{23} = 1.082	θ_2 = 119.534°
r_{14} = 1.165	θ_3 = 123.466°
r_{26} = 1.280	
r_{56} = 1.132	

A'	A"
$S_1 = \Delta r_{12}$	$S_{11} = \Delta\phi_1$
$S_2 = \Delta r_{23}$	$S_{12} = \Delta\phi_2$
$S_3 = \Delta r_{14}$	$S_{13} = \Delta\gamma$
$S_4 = \Delta r_{26}$	
$S_5 = \Delta r_{56}$	
S_6* $= (1/\sqrt{3})(\Delta\theta_1+\Delta\theta_2+\Delta\theta_3)$	
$S_7 = (1/\sqrt{6})(2\Delta\theta_2 - \Delta\theta_1 - \Delta\theta_3)$	
$S_8 = (1/\sqrt{2})(\Delta\theta_1 - \Delta\theta_3)$	
$S_9 = \Delta\omega$	
$S_{10} = \Delta\omega$	

*redundant symmetry coordinate

Normal Coordinate Analysis of Diazoacetonitrile

The molecular parameters and symmetry coordinates used for the force constant calculations are given in Table VIII. The internal coordinates, in-plane and out-of-plane, are shown in Figure 18 .

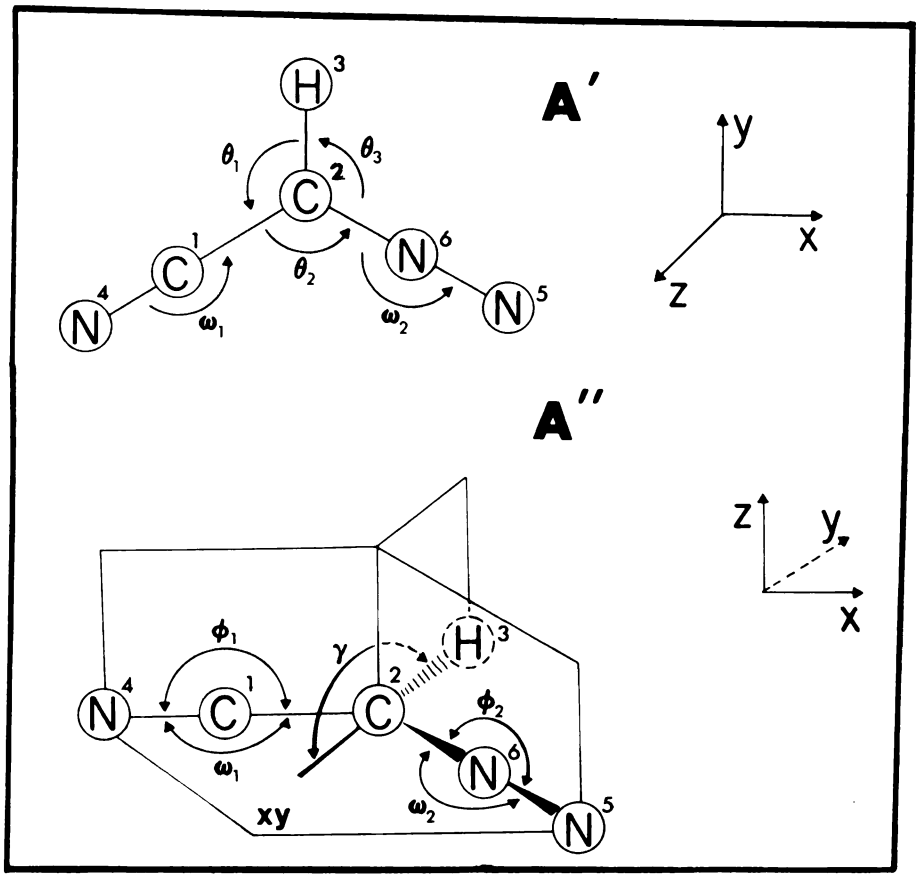


Figure 18. Internal Coordinates of Diazoacetonitrile (A' in-plane and A" out-of-plane)

Initial force constants were transferred from the molecules CH_2N_2[2] and $HC{\equiv}CCHN_2$.[3] The results of the calculations are shown in Tables IX, X, XI, XII, XIII and XIV. Fifteen force constants were used to fit 35 experimentally observed frequencies.

Table IX. Normal Coordinate Analysis of Diazoacetonitrile (NNCHCN)

	Frequency (cm^{-1})			Primary Contributors
ν	Obs.	Cal.	$\Delta\nu$	PED*
A'				
ν_1	3118.0	3114.9	(-3.1)	CH(99)
ν_2	2228.0	2229.2	(+1.2)	C≡N(86) CC(12)
ν_3	2102.0	2102.2	(+0.2)	NN(94) C=N(15) CN,NN(-10)
ν_4	1349.0	1349.0	(0.0)	CHwag(64) C=N(26) CN,CHwag(-18)
ν_5	1162.0	1162.0	(0.0)	C=N(43) CHwag(25) C=N,CHwag(14) NN(6)
ν_6	-----	907.9	----	CC(41) CNN(15) CC=N(15) CHwag(13)
ν_7	620.0	615.4	(-4.6)	CNN(60) CC(22)
ν_8	-----	433.1	----	CC≡N(68) CC=N(15) CNN(12)
ν_9	164.0**	163.8	(-0.2)	CC=N(60) CC≡N(27) CNN(9)
A"				
ν_{10}	-----	719.1	----	CNN(79) CHwag(16)
ν_{11}	488.0	488.4	(+0.4)	CC≡N(58) CHwag(22) CNN(17)
ν_{12}	362.0	362.3	(+0.3)	CHwag(60) CC≡N(35)

*Potential Energy Distribution

**Raman frequency, N_2 matrix

Note that on this and the following Tables the notation in the column under PED is as follows: AB= AB stretch
ABC= ABC bend
AB,BC= interaction between AB and BC.

Table X. Normal Coordinate Analysis of Diazoacetonitrile (NNCDCN)

	Frequency (cm^{-1})			Primary Contributors
	ν	Obs.	Cal.	$\Delta\nu$	PED*
A'					
	ν_1	2295.5	2314.1	(+18.6)	CD(89) C≡N(5)
	ν_2	2224.0	2223.7	(-0.3)	C≡N(81) CC(10) CD(6)
	ν_3	2100.5	2097.4	(-3.1)	NN(93) C=N(13) C=N,NN(-9)
	ν_4	1286.0	1285.4	(-0.6)	C=N(51) CC(26) CDwag(21) CN,CDwag(-14)
	ν_5	-----	989.2	----	C=N(26) CDwag(22)
	ν_6	-----	793.3	----	CDwag(57) CC(25)
	ν_7	-----	615.0	----	CNN(60) CC(21)
	ν_8	-----	426.9	----	CC≡N(66) CC=N(14) CNN(12)
	ν_9	-----	162.7	----	CC=N(61) CC≡N(27)
A"					
	ν_{10}	-----	713.2	----	CNN(83) CDwag(12)
	ν_{11}	477.0	476.8	(-0.2)	CC≡N(75) CNN(12) CDwag(11)
	ν_{12}	292.0	291.6	(-0.4)	CDwag(76) CC≡N(18)

*Potential Energy Distribution

Table XI. Normal Coordinate Anaysis of Diazoacetonitrile ($NNCH^{13}CN$)

	Frequency (cm^{-1})			Primary Contributors
ν	Obs.	Cal.	$\Delta\nu$	PED*
A'				
1	3118.0	3114.9	(-3.1)	CH(99)
2	2178.0	2176.0	(-2.0)	C≡N(86) CC(12)
3	2097.0	2102.0	(+5.0)	NN(93) C=N(14) CN,NN(-10)
4	1349.0	1348.7	(-0.3)	CHwag(64) C=N(26) CHwag,CN(-18)
5	1162.0	1161.9	(-0.1)	C=N(43) CHwag(25) CHwag,CN(14)
6	-----	905.1	----	CC(41) CNN(15)
7	612.0	613.2	(+1.2)	CNN(61) CC(22)
8	-----	421.4	----	CC≡N(68) CC=N(15) CNN(10)
9	-----	163.4	----	CC=N(60) CC≡N(28) CNN(10)
A"				
10	-----	718.4	----	CNN(79) CHwag(16)
11	479.0	479.7	(+0.7)	CC≡N(55) CHwag(26) CNN(17)
12	359.0	359.0	(0.0)	CHwag(57) CC≡N(39)

*Potential Energy Distribution

Table XII. Normal Coordinate Analysis of Diazoacetonitrile ($NNCHC^{15}N$)

	Frequency (cm^{-1})			Primary Contributors
ν	Obs.	Cal.	$\Delta\nu$	PED*
A'				
ν_1	3118.0	3114.9	(-3.1)	CH(99)
ν_2	2204.0	2202.7	(-1.3)	C≡N(85) CC(13)
ν_3	2099.0	2102.1	(+3.0)	NN(94) C=N(14) CN,NN(-10)
ν_4	1347.0	1346.7	(-0.3)	CHwag(65) C=N(26) CN,CHwag(-18)
ν_5	1162.0	1161.7	(-0.3)	C=N(43) CHwag(25) CN,CHwag(14)
ν_6	-----	903.6	----	CC(41) CNN(15) CC=N(15)
ν_7	-----	612.7	----	CNN(60) CC(22)
ν_8	-----	431.3	----	CC≡N(67) CC=N(15) CNN(12)
ν_9	-----	161.7	----	CC=N(60) CC≡N(28) CNN(10)
A"				
ν_{10}	-----	719.0	----	CNN(79) CHwag(16)
ν_{11}	488.0	486.9	(-1.1)	CC≡N(58) CHwag(23) CNN(17)
ν_{12}	362.0	361.0	(-1.0)	CHwag(59) CC≡N(36)

*Potential Energy Distribution

Table XIII. Normal Coordinate Analysis of Diazoacetonitrile (^{15}NNCHCN)

	Frequencies (cm^{-1})			Primary Contributors
	ν	Obs.	Cal.	$\Delta\nu$	PED*
A'					
	ν_1	3118.0	3114.9	(-3.1)	CH(99)
	ν_2	2228.0	2229.2	(+1.2)	C≡N(86) CC(12)
	ν_3	2079.0	2073.6	(-5.4)	NN(93) C=N(16) CN,NN(-10)
	ν_4	1347.0	1346.8	(-0.2)	CHwag(65) C=N(25) CC(18) CN,CHwag(-17)
	ν_5	-----	1154.9	----	C=N(42) CHwag(24) CN,CHwag(14)
	ν_6	-----	906.8	----	CC(41) CNN(15) CC=N(15)
	ν_7	-----	612.0	----	CNN(60) CC(22)
	ν_8	-----	431.9	----	CC≡N(68) CC=N(14) CNN(12)
	ν_9	-----	162.0	----	CC=N(60) CC≡N(27) CNN(10)
A"					
	ν_{10}	------	716.1	----	CNN(78) CHwag(17)
	ν_{11}	488.0	487.3	(-0.7)	CC≡N(59) CHwag(22) CNN(18)
	ν_{12}	362.0	362.0	(0.0)	CHwag(60) CC≡N(34)

*Potential Energy Distribution

Table XIV. Force Constants for Diazoacetonitrile

A'					
K_{CC}	= 5.130 (0.161)	K_{CH}	= 5.281 (0.007)	$K_{C\equiv N}$	= 16.990 (0.085)
$K_{C=N}$	= 7.260 (0.097)	K_{NN}	= 17.642 (0.051)	H_{CHwag}	= 0.480 (0.005)
$H_{CC=N}$	= 0.408 (0.066)	$H_{CC\equiv N}$	= 0.341 (0.139)	H_{CNN}	= 0.836 (0.012)
$F'_{C=N,CHwag}$	= -0.396 (0.005)	$F_{C=N,NN}$	= 1.502 (0.024)		
A"					
H'_{CNN}	= 0.882 (0.136)	$H'_{CC\equiv N}$	= 0.430 (0.02)	H'_{CHwag}	= 0.121 (0.003)
$F''_{CNN,CHwag}$	= 0.008 (0.005)				

K- stretching force constant (mdyn/Å)

H- in-plane bending force constant (mdyn·Å)

H'- out-of-plane bending force constant (mdyn·Å)

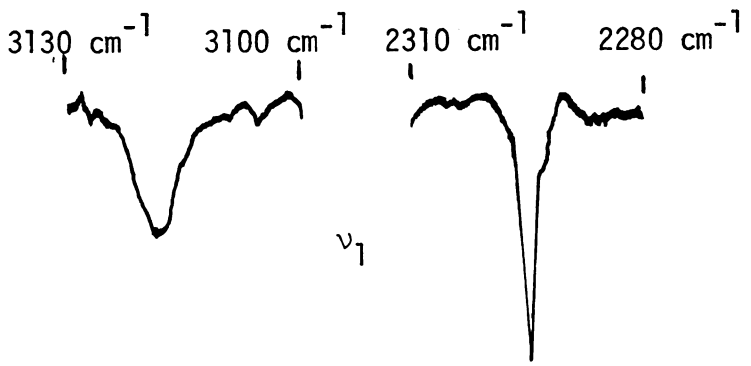
F- stretching-stretching interaction force constant (mdyn/Å)

F'- stretching-bending interaction force constant (mdyn)

F"- bending-bending interaction force constant (mdyn·Å)

Numbers in parentheses are uncertainties, see Appendix A.

Band Assignment of the Observed Fundamentals of Diazoacetonitrile

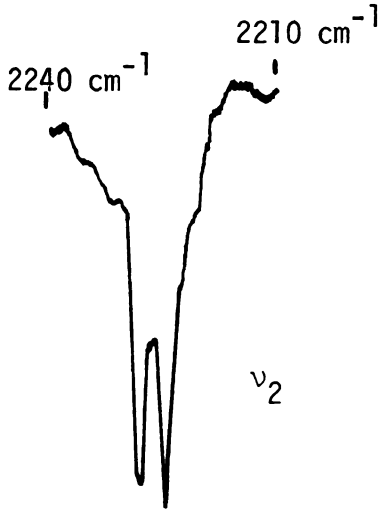


A' Class

ν_1

The band observed at 3118 cm^{-1} in NNCHCN shifts to 2295.5 cm^{-1} in NNCDCN. (Both of these bands are shown above.) No detectable shift could be observed in the other isotopes and indeed, none is predicted by the normal coordinate analysis. The frequency range within which this band is observed, coupled with the large deuterium shift and the results of the normal coordinate analysis leave no doubt that this band is the (ν_1) CH stretching fundamental. This frequency is very close to that of $HC{\equiv}CCHN_2$ (3100 cm^{-1})[3] and that of CH_2N_2 (3132 cm^{-1}, taken as an average of the symmetric and anti-symmetric stretches of the CH_2 group).[2] The large difference between the predicted and observed frequency in NNCDCN is not unusual for molecules of this nature.[2,3]

ν_1 is very weak in the Raman where it is observed at 3100 cm^{-1} (pure solid).



ν_2

The band observed at 2228 cm^{-1} in NNCHCN, based on its isotopic frequency pattern and the normal coordiante analysis results, is assigned to the (ν_2) C≡N stretching fundamental. Group frequency considerations[51] support this assignment. The band and its deuterated analog are shown above.

ν_2 is observed at 2220.7 cm^{-1} in the Raman spectrum of the pure solid and at 2230 cm^{-1} in the Raman spectrum of diazoacetonitrile in a N_2 matrix. Contrary to the IR (where it is of medium intensity) it is the strongest band in Raman!!

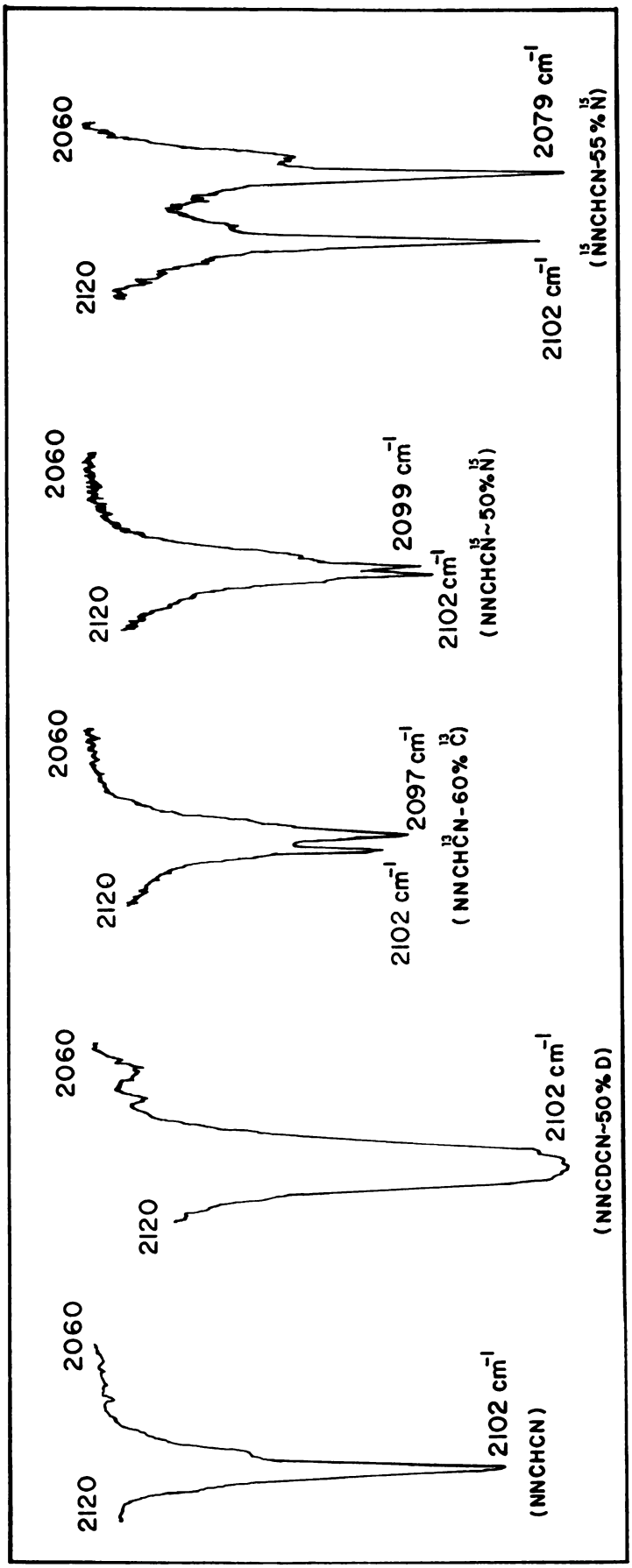
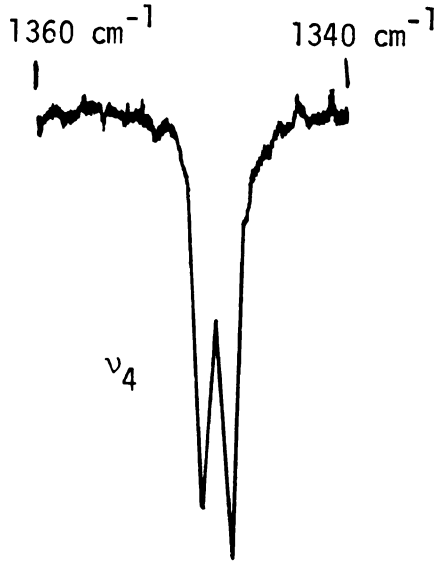


Figure 19. NN Stretching Fundamental (ν_3) of Diazoacetonitrile

ν_3

The band observed at 2102 cm^{-1} in NNCHCN, for the same reasons stated above, is assigned to the (ν_3) N≡N stretching fundamental. This value is close to that of $HC{\equiv}CCHN_2$ (2069 cm^{-1}) and almost identical to that of CH_2N_2 (2102 cm^{-1}). Perhaps the most interesting aspect of this band is the fact that it is split in the spectra of diazoacetonitrile with 60% ^{13}C and 55% ^{15}N in the C≡N group. The splitting may be interpreted as the result of a rather strong interaction between the C≡N and NN bonds, something that is implied by the MW experiment.[65] If this was the case one would expect that the band due to the C≡N stretch would appear split in the spectrum of diazoacetonitrile with 55% ^{15}N in the NN group. No such splitting was observed however! This band and its counterparts are shown in Figure 19.

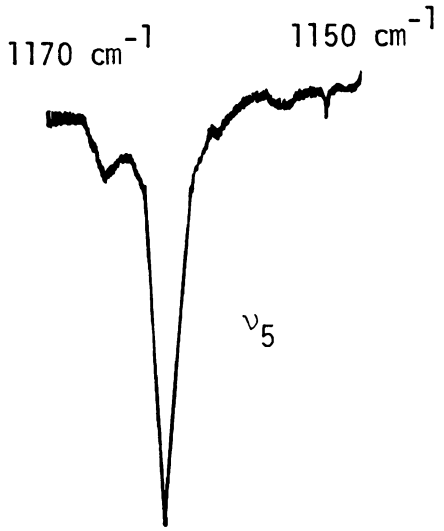
ν_3 although the strongest peak in the IR is very weak in the Raman. It is observed at 2109.5 cm^{-1} in the Raman spectrum of the pure solid.



ν_4

The band observed at 1349 cm^{-1} in NNCHCN is assigned to the (ν_4)

CH in plane wag vibration. This assignment is based mainly on the normal coordinate analysis results, which also show that it is very strongly coupled with the C=N stretching fundamental. It is interesting to note that this band shifts by an equal amount (2 cm^{-1}) in both $NNCHC^{15}N$ and $^{15}NNCHCN$ isotopes, something that may be explained by the symmetry of the molecule. (The two terminal nitrogen atoms are almost equally far away from the hydrogen atom.) This assignment is also supported by the assignment of the 1358 cm^{-1} band observed in the spectrum of $HC{\equiv}CCHN_2$. ν_4 and its counterpart in the spectrum of diazoacetonitrile (55% ^{15}N in the NN group) are shown on the previous page. This band is strong in both IR and Raman. In the latter it is observed at 1333.9 cm^{-1} (pure solid).



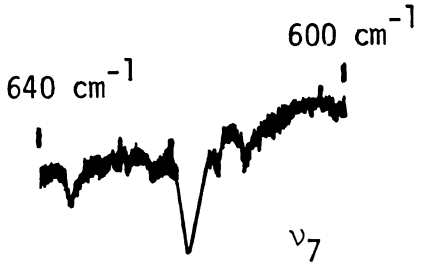
ν_5

The band observed at 1162 cm^{-1} in NNCHCN is assigned to the (ν_5) C=N stretching fundamental. This assignment finds support in the normal coordinate analysis results, which also show a significant contribution to this frequency from the CH wag, and the similar assignment of the 1165 cm^{-1} band observed in $HC{\equiv}CCHN_2$ and the 1170 cm^{-1} band observed

in CH_2N_2. This band is pictured on page 75. ν_5 is weak in the IR but strong in the Raman where it is observed at 1156.4 cm^{-1} (pure solid).

ν_6

No band attributable to ν_6 was observed in the matrix spectra. Normal coordinate analysis results predict it to be at 907.9 cm^{-1} and assigns it to the CC stretch. This vibration is expected to be very weak in the IR but rather strong in the Raman.[51] The band at 993.4 cm^{-1} observed in the spectrum of the pure solid is a likely candidate for this band, although lies quite far away from the predicted frequency.

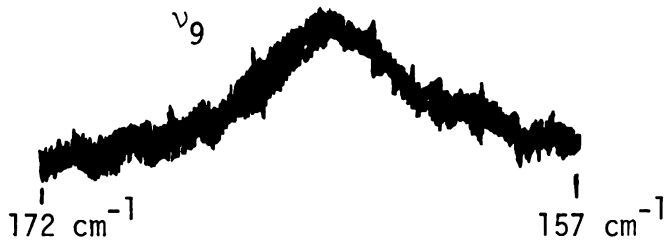


ν_7

The band observed at 620 cm^{-1} in NNCHCN and shifted to 612 cm^{-1} in $NNCH^{13}CN$ is assigned to the (ν_7) CNN in-plane bending fundamental. This band is very weak in the IR but of medium intensity in the Raman (623.3 cm^{-1}). It lies considerably higher than that of CH_2N_2 (421 cm^{-1}) while no useful correlation can be made with that of $HC{\equiv}CCHN_2$ due to the extensive internal mode coupling in the latter. This assignment is supported by the normal coordinate analysis results which show a significant contribution of the CC stretch in this frequency. This band $(\nu)_7$ is pictured above.

ν_8

No band which could be assigned to ν_8 was observed in the matrix or pure solid spectra. The normal coordinate analysis predicts ν_8 to be at 433.1 cm^{-1} and assigns it to CC≡N in-plane bending vibration.



ν_9

The band observed at 164 cm^{-1} in the Raman spectrum of NNCHCN in a N_2 matrix is assigned to the (ν_9) CC=N bending vibration. This assignment which is supported by the normal coordinate analysis results and the similar assignment of the 168 cm^{-1} band in HC≡NCNN$_2$, is in agreement with the results of the MW experiments.[65] In the latter, based on relative intensity measurements, a low-frequency deformation mode (predicted to be at 150 ±30 cm^{-1}) was tentatively assigned to the CC=N bending vibration. The 164 cm^{-1} band is pictured near the top of the page. ν_9 is also observed at 193.6 cm^{-1} in the Raman spectrum of the pure solid. Its IR analog could not be observed due to the fact that it lies outside the frequency range covered by our IR spectrophotometer. ν_9 along with the ν_2 are the only two fundamentals which could be observed in Raman matrix spectra.

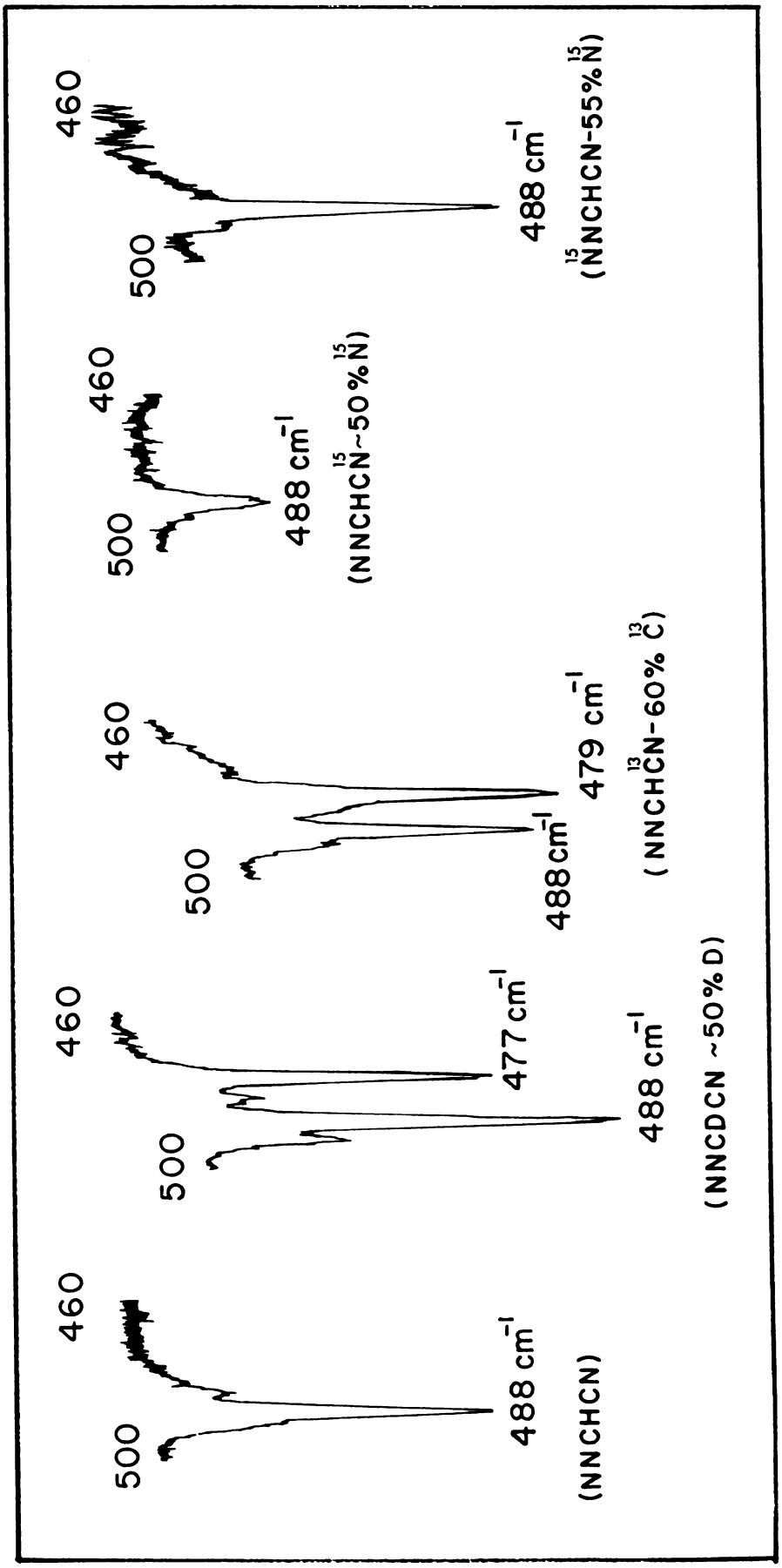


Figure 20. C≡N Out-of-Plane Bend (ν_{11}) of Diazoacetonitrile

A" Class

ν_{10}

No band assignable to ν_{10} was observed in the matrix or pure solid spectra. ν_{10} is predicted by the normal coordinate analysis at 719.1 cm^{-1} and assigned to the CNN out-of-plane bending vibration. This frequency like its in-plane analog, lies considerably higher than that of CH_2N_2 (564 cm^{-1}) and that of $HC{\equiv}CCHN_2$ (475 cm^{-1}).

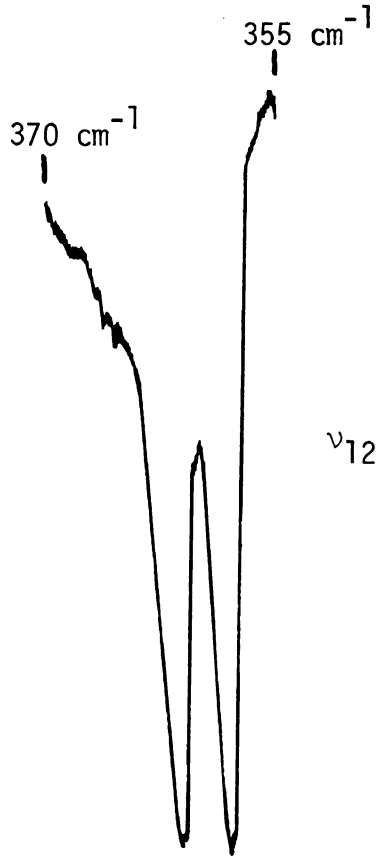
ν_{11}

The band observed at 488 cm^{-1} in NNCHCN, based on its isotopic frequency pattern and the normal coordinate analysis results, is assigned to the (ν_{11}) CC≡N out-of-plane bending vibration. ν_{11} and its counterparts in all five isotopes of diazoacetonitrile are shown in Figure 20. Normal Coordinate analysis shows a significant contribution to this frequency from the CH out-of-plane wag vibration. ν_{11} is strong in the IR but weak in the Raman where it is observed at 507.5 cm^{-1} (pure solid). It is interesting to note that ν_{11} lies very close to the frequency of the CCN bend in cyanoacetylene (500 cm^{-1}).[44]

ν_{12}

The band observed at 362 cm^{-1} in NNCHCN is shifted to 292 cm^{-1} in NNCDCN. This large deuterium shift alone implies that this is a hydrogen motion. Since the only hydrogen motion remaining is the CH out-of-plane wag vibration, it is assigned as such (ν_{12}). This assignment is supported by the normal coordinate analysis results and by a similar assignment made for the 406 cm^{-1} band in CH_2N_2. The analogous band in

$HC{\equiv}CCHN_2$ has not been observed. ν_{12} and its ^{13}C counterpart are pictured just below.



The Raman analog of this fundamental is probably the 394.8 cm^{-1} band (observed in the Raman spectrum of the pure solid). There is however a remote possibility that the latter is the Raman analog of the ν_8 fundamental (predicted at 433.1 cm^{-1} but not seen in matrix spectra). A depolarization ratio measurement of the 394.8 cm^{-1} band would probably solve the assignment problem. Unfortunately measurements of this nature cannot be made on pure solid samples (unless they are single crystals) since these samples scramble polarizations thoroughly.[66]

Other Bands

The band observed at 728 cm^{-1} in NNCHCN is assigned as the overtone of ν_{12} (362 × 2 = 724). Its isotopic frequency pattern supports this assignment fully (582 cm^{-1} in NNCDCN and 720 cm^{-1} in $NNCH^{13}CN$).

The band observed at 852 cm^{-1} in NNCHCN is assigned to the combination of ν_{11} and ν_{12} (488 + 362 = 850). This assignment is also supported by the isotopic frequency pattern (770 cm^{-1} in NNCDCN, 840 cm^{-1} in $NNCH^{13}CN$).

The band observed at 3062 cm^{-1} is assigned to the CH stretch of a polymer (perhaps a dimer) of NNCHCN (formed by hydrogen bonding). This assignment is supported by the large deuterium shift (792 cm^{-1}) and the intensity changes of the band with variation of the M/G ratio. Hydrogen bonding is known to occur in CH_2N_2 and is expected to be even more pronounced in NNCHCN due to the presence of the C≡N group which should increase the acidic character of the hydrogen atom.

Two bands (504 cm^{-1} and 367 cm^{-1}) observed as shoulders of ν_{11} and ν_{12} respectively are also assigned to a polymer of NNCHCN. These assignments are supported by IR spectra of low M/G ratios where the <u>only</u> bands observed in those frequency regions correspond to those high frequency shoulders.

The band at 2154 cm^{-1} which appears sometimes as a shoulder of the N≡N stretch and disappears upon photolysis could not be assigned to anything specific. The 1019.5 cm^{-1} band observed in the Raman spectrum of pure solid is assigned to a combination of the 623.3 cm^{-1} and 394.8 cm^{-1} bands (623.3 + 394.8 = 1018.1). Two other bands observed in the same spectrum (2087.6 cm^{-1} and 525.1 cm^{-1}) cannot be assigned to anything

specific at this time.

The Vibrational Potential Function of Diazoacetonitrile

The force constant of the CC stretch is calculated at 5.13 mdyn/Å and is very similar to that of $HC{\equiv}CCHN_2$ (5.0 mdyn/Å). Its value is a little larger that that of a CC single bond which is in accordance with the CC bond length obtained by the microwave spectra.

The force constant of the C≡N stretch is calculated at 16.99 mdyn/Å and is a little smaller than that of a typical CN triple bond, in accordance with the MW results. The force constant of the N≡N stretch is calculated at 17.642 mdyn/Å, which is larger than those of CH_2N_2 (16.89 mdyn/Å) and $HC{\equiv}CCHN_2$ (14.14 mdyn/Å). This correlates well with the fact that the N≡N bond is shorter in diazoacetonitrile than in CH_2N_2.

The force constant of the C=N stretch is calculated at 7.26 mdyn/Å and is considerably smaller than that of CH_2N_2 (8.34 mdyn/Å) which is in disagreement with the relative order of the bond lengths in the two molecules.[65]

The force constant for the CH in-plane wag is calculated to 0.48 mdyn·Å and is very close to that of $HC{\equiv}CCHN_2$ (.456 mdyn·Å). The force constant for the CC=N bend is calculated at 0.408 mdyn·Å and is much lower than that of $HC{\equiv}CCHN_2$ (0.905 mdyn·Å).

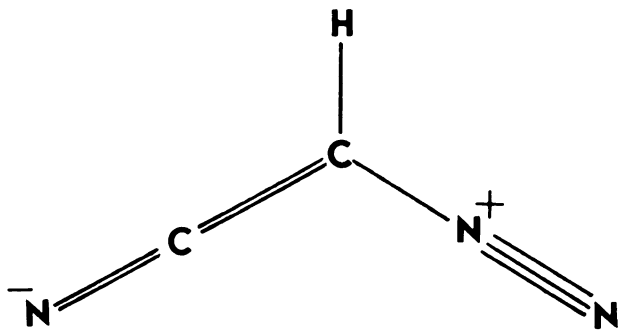
The force constants of the CNN in-plane (.836 mdyn·Å) and out-of-plane (.882 mdyn·Å) bends are much larger than those of CH_2N_2 (0.477 and .533 mdyn·Å) and $HC{\equiv}CCHN_2$ (.418 and .324 mdyn·Å).

The same situation is encountered for the CH out-of-plane wag force constant which is 0.121 mdyn·Å for diazoacetonitrile and 0.045 mdyn·Å

for CH_2N_2. The value for diazoacetonitrile is however closer to that of ketene (0.086 mdyn·Å), while still much lower than that of ethylene (0.23 mdyn·Å).

The force constants of the CC≡N in-plane (0.341 mdyn·Å) and out-of-plane (0.430 mdyn·Å) bends are not atypical of those of aliphatic nitriles, while the interaction force constants $F_{C=N,NN}$ (1.502 mdyn/Å), $F'_{C=N,CHwag}$ (-0.396 mdyn) and $F''_{CNN,CHwag}$ (0.008 mdyn·Å) for diazoacetonitrile are very similar to those of CH_2N_2 (1.23, -0.467 and 0.006 respectively).

Although several resonance structures can be written for CH_2N_2 and NNCHCN, there is one in particular which can be written for the latter but not for the former:



This structure weakens the CN bond of the CNN group and strengthens the CC bond. Thus it could be the reason for the difference between the $K_{C=N}$ force constants of the two molecules. This resonance structure can also explain the value of the K_{CC} force constant which is a little larger than that of a CC single bond. The slightly low value of the force constant for the C≡N bond can also be explained by this resonance structure.

Finally, it should be mentioned that only 11 out of the 12 diagonal force constants could be varied simultaneously for the normal coordinate analysis program to converge. This is not unexpected when the experimental information available is not complete (which is the case here, due to the 3 missing frequencies). In such a case the maximum amount of information, with regard to the vibrational potential function, that can be extracted from the experimental information consists of the following: a) the force constants that can be varied simultaneously and (b) the changes in the values of these force constants when the force constants whose values are assumed are changed. This allows one to see how accurate the values of the variable force constants are. When the change is large, with respect to the value of the force constant itself, it implies that the latter is not very accurate and when the change is small, the implication is that it is accurate.

The Table on the following page shows the accuracy of variable force constants as obtained from the normal coordinate analysis. Thus as one can see, the values of the following force constants should not be considered very accurate $H_{CC=N}$, $H'_{CC\equiv N}$, H'_{CHwag}, and $F''_{CNN,CHwag}$. The inaccuracy of the $H_{CC=N}$ force constant must be the reason for the large discrepancy between the latter and its analog in the $HC\equiv CCHN_2$ molecule mentioned earlier in this section.

Table XV. P Matrix Elements of Diazoacetonitrile

Force Constant		P Element
f	Value	$\partial f/\partial H_{CNN}$
K_{CC}	5.130	-0.065
K_{CH}	5.281	0.017
$K_{C\equiv N}$	16.990	-0.008
$K_{C=N}$	7.260	-0.016
K_{NN}	17.642	-0.001
H_{CHwag}	0.480	0.025
$H_{CC=N}$	0.408	-0.288
$H_{CC\equiv N}$	0.341	-0.049
H'_{CNN}	0.882	-0.011
$H'_{CC\equiv N}$	0.430	-0.317
H'_{CHwag}	0.121	-0.087
$F'_{C=N,CHwag}$	-0.396	-0.012
$F_{C=N,NN}$	1.502	-0.004
$F''_{CNN,CHwag}$	0.008	0.08

Conclusion

Nine of the twelve fundamental frequencies of diazoacetonitrile were observed and properly assigned, based on the isotopic frequency pattern, group frequency concept and the results of normal coordinate analyses. The three missing frequencies are also predicted by the latter and accordingly assigned. The valence force field is surprisingly accurate, despite the 3 missing fundamentals, as was shown in the previous section.

Overall, the results of the vibrational study are in very good agreement with the results of the MW experiment. The force constants of diazoacetonitrile, in general, correlate well with those of $HC{\equiv}CCHN_2$ and CH_2N_2. Whenever large discrepancies occur, these can be explained by invoking the concept of resonance or the results of the study on the accuracy of the obtained force constants from the normal coordinate analysis. Despite the difference between the refined force constants for the three molecules, they are considered transferrable from the point of view that the initial set of calculated frequencies of diazoacetonitrile based on the force constants of CH_2N_2 and $HC{\equiv}CCHN_2$ correlates very well with its frequencies which are observed experimentally.

The group frequency concept seems to hold for the stretching motions in the CNN group. However, due to the intensive mixing of the internal valence modes, the group frequency concept does not seem to hold for the bending motions associated with the CNN group.

Finally, it should be mentioned that, if a better estimate of the force field of diazoacetonitrile is to be obtained, further investigation for the determination of the missing frequencies is necessary.

The Electronic Aborption Spectrum of Diazoacetonitrile

Although irrelevant to the vibrational work on diazoacetonitrile, it seems appropriate to at least report the data obtained regarding the electronic spectrum of diazoacetonitrile. These data were obtained in the process of trying to observe the electronic spectrum of HCCN on one hand and establish the wavelength range of the photolyzing radiation on the other.

The electronic spectrum of diazoacetonitrile in an Ar matrix at 15 K was scanned between 185 nm and 800 nm. There were no bands observed in the visible part of the spectrum. One very strong band was observed in the UV part and is shown in Figure 10 on page 47 (dotted line). This band (2280 Å) disappears with photolyzing radiation of $\lambda > 3500$ Å.

The electronic spectrum of diazoacetonitrile in CH_2Cl_2 at room temperature was also scanned between 185 and 800 nm. Two bands were observed. One was very broad and weak covering the wavelength range from ~4800 Å to ~3000 Å and seemingly peaked at ~4050 Å. The other was a very strong band which began at ~3500 Å and went off scale at ~2500 Å. As the concentration of diazoacetonitrile in CH_2Cl_2 was lowered by dilution, the band in the visible became weaker and finally disappeared while the band in the UV was still off scale. This is the reason why the band in the visible could not be observed in the matrix, since the light scattering becomes a severe problem when the thickness of the matrix exceeds a certain point.

The electronic spectrum of diazoacetonitrile seems to follow the pattern exhibited by other diazo compounds.[67] The weak, broad band in the visible must be the one responsible for the photodissociation of

diazoacetonitrile when it is irradiated with $\lambda > 3{,}500$ Å. Indeed the frequency range covered by this band corresponds to energies higher than the dissociation energy of the C=N bond[68] and is certainly outside the frequency range that corresponds to energies close to the dissociation energy predicted for the CH bond.[69] The latter is in agreement with the fact that no other free radicals were observed in the matrix.

APPENDIX

APPENDIX A

The uncertainties listed in parentheses next to the force constants in Tables VII and XIV are obtained from the following equation:[33]

$$u(K_h) = \left[\frac{(\tilde{J}WJ)^{-1}_{hh}\, S}{(n-m)}\right]^{1/2}$$

where: $u(K_h)$ = uncertainty in force constant K_h

n = number of frequencies

m = number of force constants

W = diagonal matrix whose elements give the weights assigned to corresponding observed frequencies

J = Jacobian matrix given by the equation $\Delta\nu = J\Delta K$ (where $\Delta\nu$ is the frequency change vector and ΔK is the force constant change vector)

S = weighted sum of squared deviations defined by $(\tilde{\nu}_{obs} - \tilde{\nu}_{calc.})(W)(\nu_{obs} - \nu_{calc})$

ν = column frequency vector

$\tilde{\nu}$ = row frequency vector

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