

ABSTRACT

VIBRATIONAL SPECTRA OF DIAZOPROPYNE AND ITS PHOTOLYSIS PRODUCT: THE PROPARGYLENE RADICAL

By

Frank K. Chi

Diazopropyne ($\text{H}-\text{C}\equiv\text{C}-\overset{\text{H}}{\underset{|}{\text{C}}}=\text{N}=\text{N}$) and a partially deuterated isotopic mixture ($\text{H}-\text{C}\equiv\text{C}-\text{CH}=\text{N}=\text{N}$, $\text{H}-\text{C}\equiv\text{C}-\text{CD}=\text{N}=\text{N}$, $\text{D}-\text{C}\equiv\text{C}-\text{CH}=\text{N}=\text{N}$ and $\text{D}-\text{C}\equiv\text{C}-\text{CD}=\text{N}=\text{N}$) were synthesized. Vibrational spectra have been obtained for diazopropyne and its mixed deuterated analogs in the gaseous and solid states, and in matrix isolation. A valence force field normal coordinate analysis has been performed on the basis of C_s symmetry, using molecular geometric parameters and initial force constants from related molecules, and refined to fit the infrared and Raman spectra of the isotopic species. Information regarding the electronic charge distribution of diazopropyne was provided by the final calculated force constants which suggest that diazopropyne has possible resonance structures, such as ($\text{H}-\text{C}\equiv\text{C}-\text{CH}=\text{N}=\text{N} \longleftrightarrow \text{H}-\text{C}\equiv\text{C}-\ddot{\text{C}}\text{H}-\text{N}\equiv\text{N} \longleftrightarrow \text{H}-\ddot{\text{C}}=\text{C}=\text{CH}-\text{N}\equiv\text{N}$).

Photolysis of matrix-isolated diazopropyne gives rise to several new spectral features, some attributable to the propargylene free radical. The existence of triplet $\text{H}-\dot{\text{C}}=\text{C}=\dot{\text{C}}-\text{H}$ in the matrix is confirmed by ESR measurements. The normal coordinate analysis of C_3H_2 , C_3HD , and C_3D_2 has

Frank K. Chi

been carried out on the basis of $D_{\infty h}$ symmetry ($C_{\infty v}$ for C_3HD). The final calculated force constants give frequencies in excellent agreement with the matrix infrared spectra, and suggest that the skeletal $C=C=C$ bonding situation in C_3H_2 is similar to that of C_3 and allene (C_3H_4). C_3H_2 has possible resonance structures ($H-\dot{C}=C=\dot{C}-H \leftrightarrow H-C\equiv C-\dot{C}-H \leftrightarrow H-\dot{C}-C\equiv C-H$) with outer orbital electron density distributed primarily at the end carbons of the radical. The $C=C=C$ bending force constant of C_3H_2 is intermediate between those of C_3 and CO_2 , supporting the correlation between the occupancy of the π_g orbital and the value of the central carbon bending force constant in molecules of this type.

VIBRATIONAL SPECTRA OF DIAZOPROPYNE AND ITS
PHOTOLYSIS PRODUCT: THE PROPARGYLENE RADICAL

By

Frank K. Chi

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1972

678854

To My Parents

ACKNOWLEDGMENTS

I wish to thank Professor George E. Leroi for his advice, interest and patience which have contributed greatly to this research and to my education.

I also wish to thank Professor R. H. Schwendeman for his help in the microwave study and Professor J. F. Harrison for his helpful discussions regarding the propargylene radical.

I would like to thank the members of the Molecular Spectroscopy group, especially, Glenn R. Elliott, and also Mrs. Naomi Hack, for their friendship.

Financial support from Michigan State University and the Office of Naval Research is appreciated.

Finally, I wish to thank my wife, May, for her patience and understanding.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
CHAPTER	
I. THE INFRARED AND RAMAN SPECTRA OF DIAZOPROPYNE	4
Experimental	5
Results and Discussion	20
Assignment of the Observed Fundamentals	42
Other Bands	59
An Outline of Normal Coordinate Analysis .	62
Vibrational Potential Function and Related Properties of Diazopropyne	64
Normal Coordinate Analysis	64
Vibrational Potential Function of Diazopropyne (A')	75
Vibrational Potential Function of Diazopropyne (A'')	79
Conclusion	82
II. INFRARED SPECTRUM OF THE PROPARGYLENE RADICAL	83
Experimental	84
Results and Discussion	86
Assignment of C ₃ H ₂ Fundamentals	92
Other Bands	101
Vibrational Potential Function and Related Properties of Propargylene	102
Normal Coordinate Analysis	102
Vibrational Potential Function of Propargylene	107
Conclusion	110
REFERENCES	111

LIST OF TABLES

TABLE		Page
I.	Observed infrared absorption bands of diazopropyne vapor (298 ⁰ K)	26
II.	Observed infrared absorption bands of a mix- ture of gaseous diazopropyne and its deuterated molecules	27
III.	Observed IR frequencies of matrix-isolated diazopropyne and its mixed deuterated molecules	43
IV.	Observed Raman shift frequencies of solid C ₃ H ₂ N ₂ and its mixed deuterated molecules	45
V.	Observed infrared frequencies of solid C ₃ H ₂ N ₂ and its mixed deuterated molecules . . .	46
VI.	Fundamental frequencies of diazopropyne .	60
VII.	Geometry and symmetry coordinates for diazopropyne	66
VIII.	Normal coordinate analysis of diazopropyne (C ₃ H ₂ N ₂)	70
IX.	Normal coordinate analysis of diazopropyne (C ₃ HDN ₂)	71
X.	Normal coordinate analysis of diazopropyne (C ₃ DHN ₂)	72
XI.	Normal coordinate analysis of diazopropyne (C ₃ D ₂ N ₂)	73
XII.	Normal coordinate analysis of diazopropyne (C ₃ H ₂ N ¹⁵ N)	74
XIII.	Valence force constants for diazopropyne .	80

LIST OF TABLES (Continued)

TABLE	Page
XIV. Bands occurring upon photolysis of diazo- propyne which disappear upon annealing .	90
XV. Symmetry coordinates for the propargylene radical	105
XVI. Normal coordinates analysis of the propargy- lene radical	106

LIST OF FIGURES

FIGURE	Page
1. Andonian Associates Model D-307 liquid helium dewar	10
2. Low temperature Raman cell	13
3. Spray-on infrared cell for Malaker refrigerator	15
4. Spray-on Raman cell for Malaker refrigerator	17
5. Infrared spectrum of gaseous diazopropyne .	23
6. Infrared spectrum of a mixture of gaseous diazopropyne and its deuterated molecules	25
7. Principle inertial axes of diazopropyne . .	29
8. Infrared spectrum of matrix (Kr)-isolated diazopropyne	35
9. Infrared spectrum of a mixture of matrix (Kr)-isolated diazopropyne and its deuterated molecules	37
10. Raman spectrum of solid diazopropyne . . .	39
11. Raman spectrum of a mixture of solid diazopropyne and its deuterated molecules . .	41
12. Infrared spectrum of a mixture of matrix-isolated diazopropyne and its deuterated molecules (expanded scale in the region 600-250 cm^{-1})	55
13. Internal coordinates for diazopropyne . . .	68
14. Infrared spectrum of photolyzed matrix-isolated diazopropyne	89

LIST OF FIGURES (Continued)

FIGURE	Page
15. Infrared spectra of photolyzed diazopropyne in krypton matrix ($2150 - 2000 \text{ cm}^{-1}$) . .	95
16. Infrared spectra of photolyzed mixed diazo- propyne and deuterated diazopropyne in kryp- ton matrix ($2150 - 2000 \text{ cm}^{-1}$)	97
17. Internal coordinates for the propargylene radical	104

INTRODUCTION

Free radicals have played an important role in the development of chemistry in this century. In 1918 Nernst suggested (1) that the individual atoms H and Cl were involved as intermediates in the photochemical reaction of hydrogen and chlorine molecules. In 1929, Paneth and Hofeditz (2) postulated that alkyl free radicals were formed upon thermal decomposition of metal alkyls, as accounted for by the removal of a metal film in the metal mirror experiments. Free radicals were subsequently proposed as reaction intermediates by many prominent chemists (3). The understanding of the nature of free radicals involved in reaction schemes can improve the validity of a proposed mechanism in a related chemical process.

Free radicals are defined as species which have one or more unpaired electrons. Thus they provide unique tests for the theory of chemical bonding, since the unpaired electrons of the free radical provide a great opportunity for electronic interaction with neighboring atoms and groups. Knowledge of the vibrational spectrum of simple free radicals can provide information regarding the structure and bonding of these interesting chemical species. Due to the extremely reactive nature of many free radicals, the direct detection

of free radicals by means of conventional spectroscopy was not possible. However, the use of rigid, inert host matrix materials such as argon and nitrogen for the isolation of guest molecules providing sources of free radical upon in situ photolysis was pioneered in the laboratory of Pimentel (Shittle et al., 1954) (4). Subsequent application of this technique by Milligan and Jacox (5) and many other workers has demonstrated its power for preparing and stabilizing free radicals and other reactive species for direct spectroscopic observation.

The purpose of this work is twofold: to elucidate the vibrational spectrum and structure of the propargylene free radical C_3H_2 ($H-\dot{C}=C=\dot{C}-H$), and concomitantly to study the vibrational spectrum of its parent molecule, diazopropyne, $C_3H_2N_2$ ($H-C\equiv C-CH=N=N$). Few diazo-compounds have been studied by vibrational spectroscopy, the only complete work being diazomethane, CH_2N_2 (6), which provides some helpful information for the vibrational study of diazopropyne.

The propargylene free radical has been observed by Skell (7), who has demonstrated by means of electron spin resonance spectroscopy that diazopropyne yields the propargylene radical when photolyzed in various organic solvents at liquid nitrogen temperature (77^0K). In addition the electronic absorption spectra of the propargylene radical and C_3 radical from the flash photolysis of diazopropyne were obtained by Merer (8), however, no ground state vibrational information was obtained in this study. The diazopropyne molecule thus offered the possibility of producing

the propargylene radical (via photolysis in an inert gas matrix) which could be detected by infrared and/or Raman spectroscopy. The vibrational study of the propargylene radical would add information on the correlation of electronic structures and vibrational force constants in some linear molecules with cumulated double bonds, such as C_3 (9), C_3O_2 (10), C_3S_2 (11), C_3N_2 (12), C_3H_4 (13), etc.

CHAPTER I

THE INFRARED AND RAMAN SPECTRA OF DIAZOPROPYNE

Diazopropyne, $C_3H_2N_2$, the molecule chosen in this work as the potential parent of the propargylene radical, has not been previously studied spectroscopically. There have been a number of studies of related molecules, such as diazomethane CH_2N_2 (6), dicyanodiazomethane $(CN)_2CN_2$ (12), and the propargyl halides $H-C\equiv C-CH_2X$ (14), which provide correlation in the assignment of fundamental frequencies for diazopropyne. A valence force field can be constructed using the force constants adapted from these related molecules and used as a starting point for the normal coordinate analysis of diazopropyne.

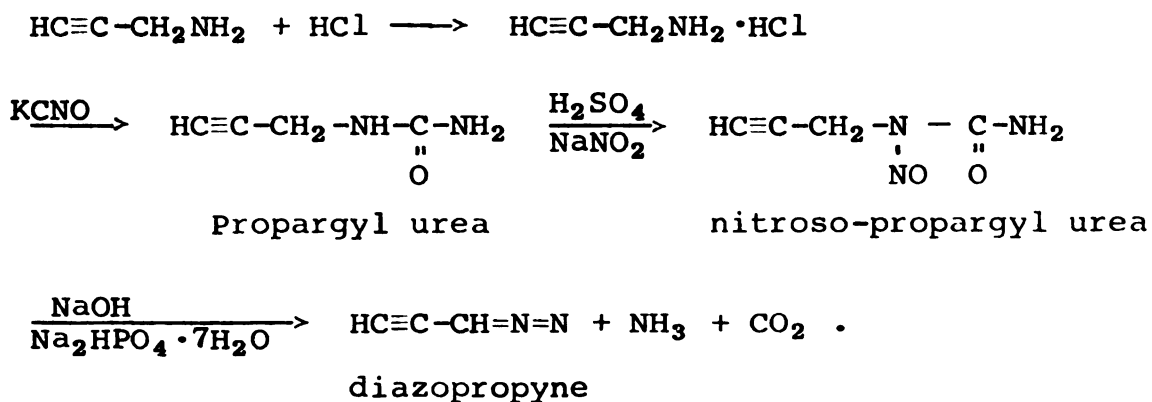
The relative positions of the vibrational fundamentals, such as the characteristic $N=N$ stretch and $C=N$ stretch, and the values of the associated force constants in the diazo-compound should provide some indication of the electronic distribution, for example the degree to which possible resonance structures are important in this molecule. The thorough understanding of the diazopropyne parent molecule will also provide assistance in the understanding of the vibrational spectra of the photolysis products, in particular the propargylene radical.

In this chapter, the author presents infrared spectral data concerning gaseous, solid and matrix-isolated diazopropyne $C_3H_2N_2$ ($H-C\equiv C-CH=N=N$), and its isotopic molecules C_3HDN_2 ($D-C\equiv C-CH=N=N$), C_3DHN_2 ($H-C\equiv C-CD=N=N$), $C_3D_2N_2$ ($D-C\equiv C-CD=N=N$), and $C_3H_2N^{15}N$ ($H-C\equiv C-CH=N=^{15}N$), and Raman spectral data regarding solid diazopropyne and its deuterated isotopic molecules C_3HDN_2 , C_3DHN_2 , and $C_3D_2N_2$. A complete vibrational analysis has been performed on diazopropyne; thus the vibrational assignment of the fundamentals is achieved.

Experimental

Preparation of diazopropyne:

As most diazo-compounds, diazopropyne is a very unstable material with a relatively high vapor pressure at room temperature. It decomposes quickly in the presence of light. Diazopropyne was prepared according to the general method for synthesizing diazo-compounds (15). The starting material used was propargyl amine; the entire process of preparation can be shown in the following reaction equations:



The final product diazopropyne was carried from aqueous solution by dry nitrogen gas into a trap which was connected through a second trap to a vacuum line. These two traps were immersed in liquid nitrogen contained in dewars. The resulting mixture was vacuum distilled at 80°K to remove the nitrogen gas, followed by vacuum distillation from 193°K (dry ice-acetone bath) to 80°K (liquid nitrogen) and from 273°K (salt-ice bath) to 193°K (dry ice-acetone bath), which gave essentially pure diazopropyne, confirmed by the absence of significant impurity absorption in the infrared spectrum. The final product was a bright yellow solid at liquid nitrogen temperature and a slightly darker yellow solid at 193°K. This indicates that solid diazopropyne might exist in two different solid phases at the two different temperatures.

Deuterated diazopropyne was also prepared, the procedure being simply the reaction of nitrosopropargyl urea, sodium hydroxide and sodium hydrogen phosphate in heavy water (D_2O) solution instead of normal water (H_2O) solution at the last step of the synthesis. There were four products formed at the end of this reaction, namely, $C_3H_2N_2$ ($H-C\equiv C-CH=N=N$), C_3HDN_2 ($D-C\equiv C-CH=N=N$), C_3DHN_2 ($H-C\equiv C-CD=N=N$) and $C_3D_2N_2$ ($D-C\equiv C-CD=N=N$).

Attempts to prepare pure $C_3D_2N_2$ by using NaOD and Na_2DPO_4 instead of NaOH and Na_2HPO_4 respectively in the last step of the reaction sequence were not successful; this might be due to the slow exchange rate between hydrogen and deuterium under the conditions of the synthesis.

The $\text{C}_3\text{H}_2\text{N}^{15}\text{N}$ was prepared by using $\text{Na}^{15}\text{NO}_2$ instead of NaNO_2 in the nitrosation of propargyl urea, the remaining reaction sequence being the same. Since only a small quantity of $\text{Na}^{15}\text{NO}_2$ was available, it was necessary to mix the labeled material with some normal NaNO_2 in this step in order to produce a satisfactory yield of the diazopropyne product for detection by infrared and Raman spectroscopy.

The decomposition of diazopropyne, especially in the gaseous phase, occurred when it was exposed to heat or radiation. Solid diazopropyne exploded readily at liquid nitrogen temperature under any kind of disturbance. Thus it is important that diazopropyne, especially in solid form, should be handled with extreme care. It is advisable to use no more than 1.5 grams of nitrosopropargyl urea for the reaction in base solution to produce diazopropyne, because the greater the quantity of diazopropyne present the harder it is to handle and to control. At the start of this work the author experienced several unpleasant explosions, but gradually it was learned how to handle diazopropyne with reasonable confidence.

Spectra of Diazopropyne:

(a) Gaseous diazopropyne was placed in a 10 cm long gas cell fitted with CsI windows. The gas phase infrared spectrum had to be taken in a short period of time since diazopropyne decomposed under exposure to the source radiation, as well as thermally.

(b) Pure liquid diazopropyne could not be obtained, and there were also no suitable solvents available. Ether and pentane are good solvents for diazopropyne, but their absorption bands overlap with diazopropyne's in the certain regions of the infrared spectrum. Therefore it was not possible to obtain the complete spectrum of diazopropyne in the liquid phase or in solution.

(c) The infrared spectra of solid diazopropyne at 80°K were obtained by spraying the sample onto a cooled CsI window which was installed in an Andonian Associates Model D-307 liquid helium dewar (Fig. 1). The coolant used in the inner jacket was liquid nitrogen instead of liquid helium. The temperature of the solid was in the neighborhood of 80°K.

The Andonian liquid helium dewar consists of two parts: (1) the outer jacket holding liquid nitrogen which also cools a radiation shield, and (2) the inner jacket which normally holds liquid helium. A stainless steel tube in which a variable pressure of helium gas which can be maintained in good thermal contact with the window holder passes through the coolant in the inner jacket. The pressure of the helium gas and an auxiliary heater can be used to control the temperature at the window holder. Helium gas is liquified in the bottom of this tube if the gas pressure is greater than one atmosphere when liquid helium is contained in the inner coolant reservoir. The space between the outer jacket and the inner jacket can be evacuated. The lower portion of the jacket can be rotated,

Figure 1. Andonian Associates Model D-307 liquid helium dewar.

- A Exchange gas port
- B Nitrogen fill
- C Helium fill and vent
- D Nitrogen vent
- E Dewar body outer shell
- F Nitrogen reservoir
- G Helium well
- H Vacuum insulation
- I Exchange gas chamber
- J Extended area heat exchanger
- K Outer tail
- L Nitrogen temperature radiation shield
- M Cold finger - sample mounting platform
- N Demountable window
- O Sample temperature radiation shield

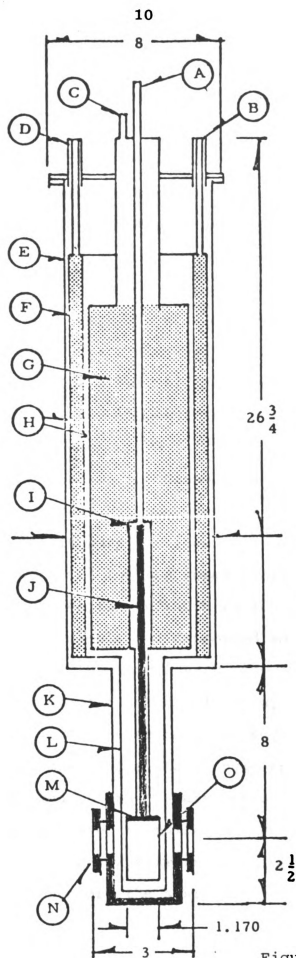


Figure 1.

allowing deposition and photolysis to be performed sequentially. For taking Raman spectra of solid diazopropyne at 80°K, an "L"-shaped Pyrex glass cryostat (Fig. 2) was used, which consists of two parts: (1) the outer portion for insulation, and (2) the concentric inner jacket holding liquid nitrogen. The copper deposition head is connected to the inner jacket with a Kovar metal-to-glass seal.

For the solid diazopropyne spectra at around 30°K, a Malaker Corp. Cryomite Mark VII-C closed-cycle helium refrigerator was used. A platinum resistor and a Zener diode were installed at the cold head of the Cryomite for monitoring and controlling the temperature. For taking solid and matrix-isolated diazopropyne infrared spectra a copper window holder was fitted on the Cryomite, and an inverted "T"-shaped brass outer jacket was used for insulation, spray-on and photolysis purposes (see details in Fig. 3). The windows used were CsI for the normal infrared region and polyethylene for the far infrared region. The substrate window upon which the sample was deposited was mounted in good thermal contact with the copper window holder to insure rapid dissipation of the thermal energy of the sample upon condensation. Indium spacers were used for this purpose. For obtaining Raman spectra, a sharp-angle spray-on copper sample head was fitted on the Cryomite (Fig. 4), and a glass outer jacket was used to maintain vacuum.

For matrix isolation experiments, noble gases such as neon, krypton and xenon are the best host materials, since

Figure 2. Low temperature Raman cell.

- a. Outer jacket for insulation
- b. Concentric inner jacket for holding liquid nitrogen
- c. 2" ground ball joint
- d. 1/2" Kovar seal
- e. Copper deposition head
- f. Spray-on nozzle
- g. Stopcock with 1/2" ground ball joint.

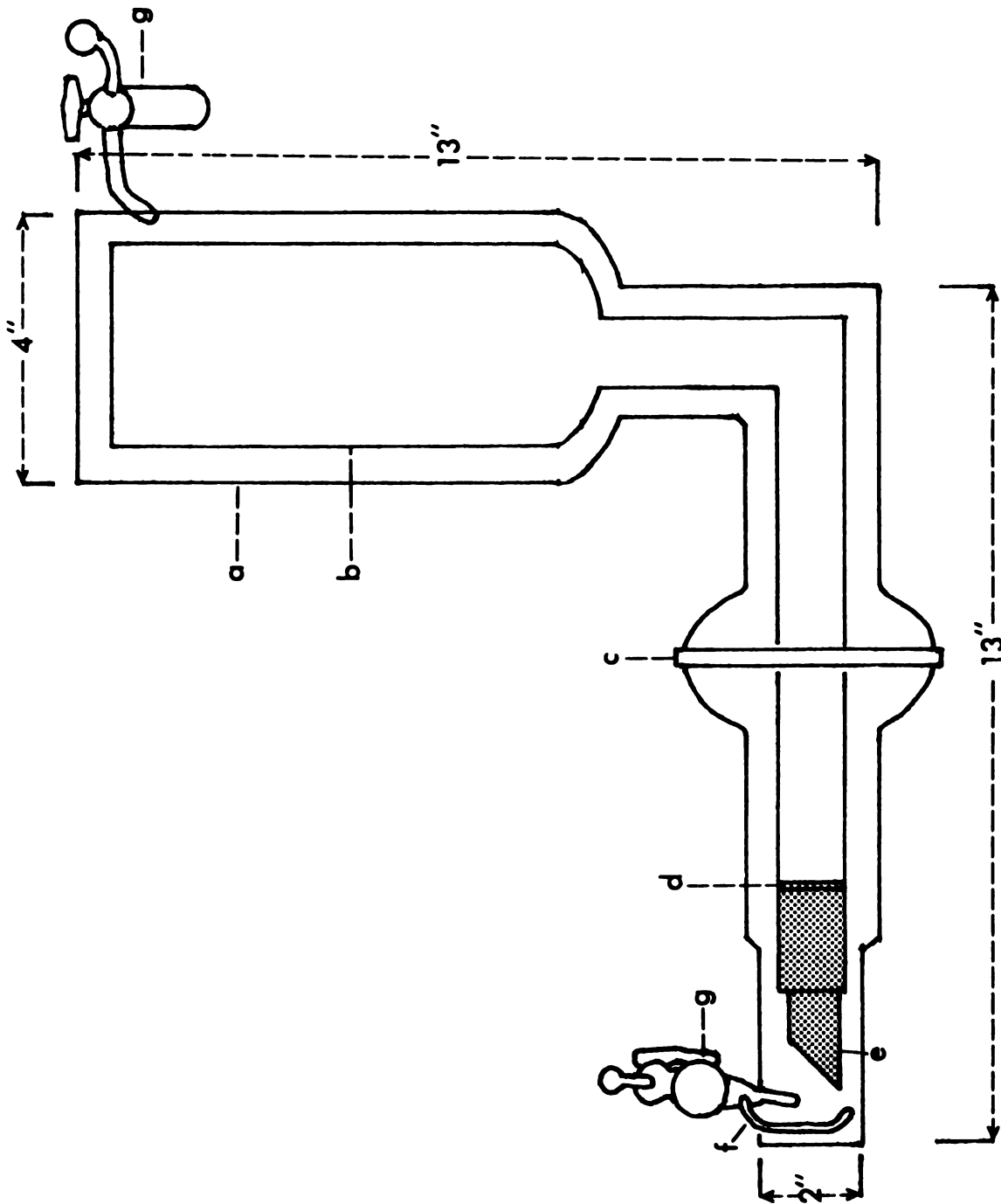
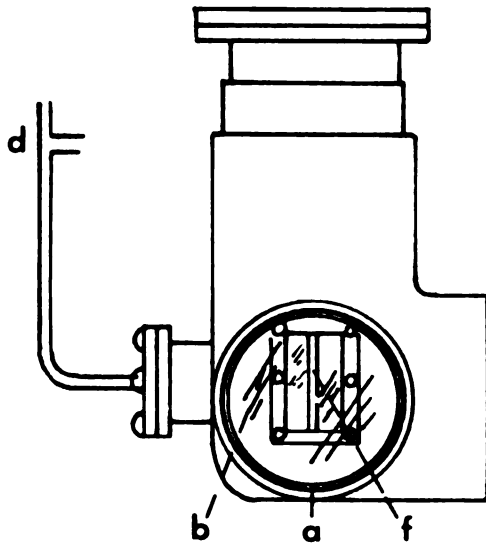


Figure 2.

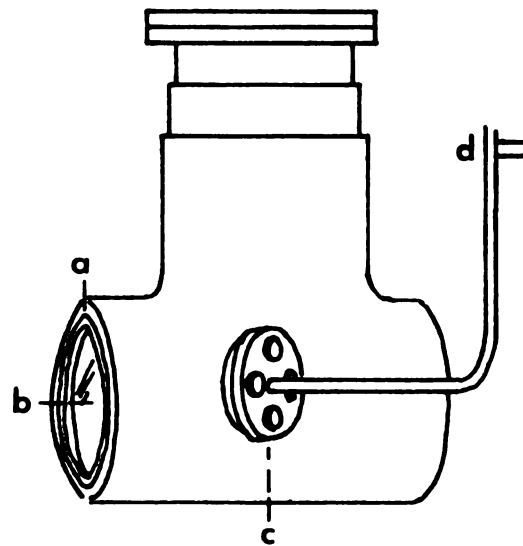
Figure 3. Spray-on infrared cell for Malaker refrigerator.

- a O-ring
- b CSI window for infrared spectrum taking.
- c Spray-on nozzle is soldered on a circular copper disk, which is pressed onto the cell with an aluminum flange.
- d Needle valve for controlling the flow of the gas mixture.
- e To place quartz window for photolysis purpose.
- f CSI window used for deposition purpose is placed in the copper window holder which is attached to the cryomite.
- g Connection to the cryomite, which enables rotation of the outer jacket for spray-on and photolysis purposes.

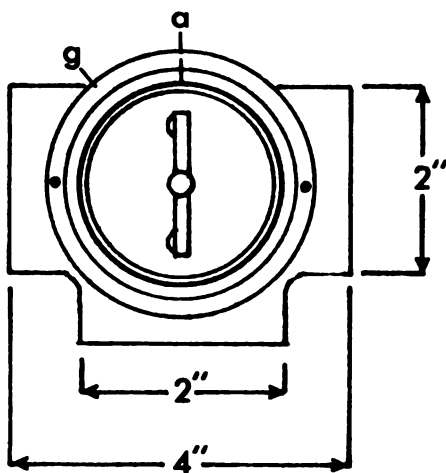
SIDE 1



FRONT



TOP



BACK

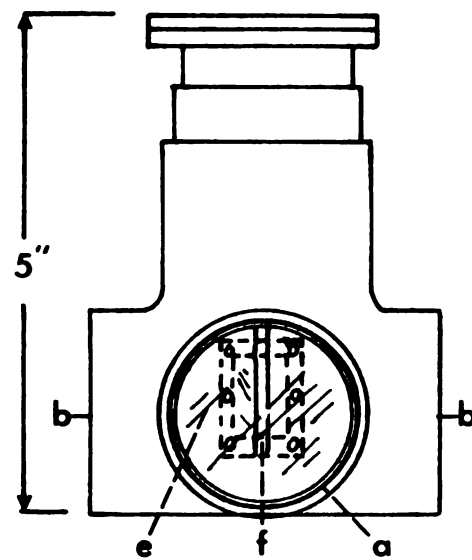


Figure 3.

- Figure 4. A. Spray-on cell for Malaker refrigerator.
- B. Closed sample head for Malaker refrigerator.
- a. Both sample cells were contained inside a 2-inch outer vacuum jacket
 - b. Attached to Malaker cold head
 - c. 1" Kovar seal
 - d. Spray-on nozzle
 - e. Remainder same as design B.
 - f. Silver soldered
 - g. 1/2" Kovar seal
 - h. 1/8" Kovar seal
 - i. 1/16" thin-walled stainless steel tubing coil
 - j. 1/2" outside vacuum jacket spacer with 1/16" tubing feed-thru

they are free from absorption in the vibrational frequency region. Nitrogen is also a good matrix material which is often used. Since the Cryomite in our laboratory cannot provide temperatures lower than 25°K, neon, argon and nitrogen could not be used for matrix material in our experiments. Experience from various experiments demonstrated that krypton was the best matrix material for diazopropyne at 25°K. Xenon was also suitable, but due to its large size it scattered quite strongly. Thus the matrix-isolated diazopropyne spectra in a krypton host were better than those obtained using xenon matrices. (Carbon tetrachloride, carbon monoxide and carbon dioxide were not good matrix materials for diazopropyne at 25°K).

Matrix samples are the collection of randomly oriented micro-crystals formed by rapid quenching from the gas. It is desired to produce a matrix with the maximum possible sample isolation within the host matrix, yet which is as transparent as possible in order to transmit the maximum amount of source radiation. The sample deposition rate is an important factor because it controls the degree of isolation of the sample within the host lattice and the transparency of the matrix. A relatively slow deposition rate of 1-3 m mole per hour was preferred, and the host-to-sample ratio was about 200 to 1 in the diazopropyne matrix isolation experiments. Several reviews of the matrix isolation technique have been published (16), which are most useful for planning and carrying through such experiments.

Infrared spectra were obtained using a Perkin-Elmer Model 225 grating spectrophotometer in the region 4000 cm^{-1} to 200 cm^{-1} , with resolution better than 1 cm^{-1} above 450 cm^{-1} and 1 to 2 cm^{-1} below 450 cm^{-1} . The spectrophotometer was calibrated against water vapor and carbon dioxide, and the reported frequencies should be accurate within $\pm 2\text{ cm}^{-1}$.

An RIIC - Beckman Model FS-720 Fourier Transform spectrometer (interferometer) was used for obtaining infrared spectra below 200 cm^{-1} . As mentioned earlier, the final product, diazopropyne, was collected from aqueous solution. Drying agents such as Drierite and silica gel were not used in the preparation since they adsorbed gaseous diazopropyne strongly. Since water vapor absorbs quite strongly below 300 cm^{-1} and the amount of diazopropyne was quite small, no gas phase diazopropyne spectra could be obtained in this range. Spectra of solid diazopropyne were obtained below 200 cm^{-1} with 2 cm^{-1} resolution. It required a large amount of sample in order to obtain a decent spectrum.

It was not possible to obtain infrared spectra of matrix isolated diazopropyne below 200 cm^{-1} . One potential cause of this problem might be the relatively poor thermal conductivity between the copper window holder and the polyethylene window, which could lead to the formation of a non-rigid matrix, with subsequent aggregation of the guest molecules.

Solid Raman spectra were obtained using a Spectra-Physics Model 125 He-Ne laser or a Coherent Radiation

Laboratory Model 52B krypton laser as excitation sources, and a Spex Model 1400 double monochromator to disperse the scattered radiation. The Raman spectrum above 3000 cm^{-1} was not obtainable since the sensitivity of the photomultipliers used (ITT-FW-130 and RCA C31034) decrease rapidly in this range when the red lines of the He - Ne or krypton laser are used as excitation sources. An argon ion laser could not be used since diazopropyne absorbs in the green (5145 Å) and blue (4880 Å), and may also decompose under the influence of the radiation from this laser. Resolution and frequency accuracy were approximately $\pm 4\text{ cm}^{-1}$ in the Raman studies.

Results and Discussion

From comparison with the related molecule diazoacetonitrile, $\text{N}\equiv\text{C}-\text{CH}=\text{N}=\text{N}$ (17), which has C_s symmetry, the diazopropyne is assumed to have the symmetry C_s ; $\Gamma_{\text{vib}} = 11 A' + 4 A''$. It follows that there will be fifteen distinct fundamental vibrational frequencies, of which eleven will belong to the A' symmetry class and four to the A'' symmetry class. All normal vibrations are both infrared and Raman active.

The gas phase spectrum of diazopropyne is preferred for the normal coordinate analysis. Since the molecules vibrate freely in the vapor, the observed gas phase frequencies represent the true vibrational frequencies, considering vibration-rotation interactions and other small

perturbations to be negligible. The spectra of gaseous diazopropyne and its mixed deuterated molecules $C_3H_2N_2$, C_3HDN_2 , C_3DHN_2 , and $C_3D_2N_2$ are shown in Figure 5 and Figure 6 respectively. The frequencies and their relative intensities are listed in Tables I and II.

In assigning the gas phase spectrum of diazopropyne, the following information was utilized: (1) type of rotation-vibration band envelope, (2) the frequencies of related molecules, (3) an initial normal coordinate calculation utilizing force constants transferred from similar bonding situations, (4) frequencies from spectra of solid and matrix-isolated diazopropyne, and (5) frequencies shifts upon isotopic substitution. Since there are only two symmetry classes in diazopropyne, the information from the type of band envelope is very helpful. Diazopropyne is an asymmetric top molecule, and thus all the vibrations in the molecular plane will give A-type or B-type bands (with higher intensity in the P, R branches or Q_1 , Q_2 branch), whereas vibrations out of the molecular plane will give C-type bands (with higher intensity in the Q branch) (18). On this basis, one should be able to assign all the absorption bands to their proper symmetry species, A' or A'' . The principal inertial axes of diazopropyne, which are calculated from bond angles and lengths (adapted from the related molecules, diazoacetonitrile and diazomethane) are depicted in Figure 7.

Microwave spectra of diazopropyne were taken in the regions, 26500-31000 MHz and 36380-39600 MHz. The spectra in the above ranges were quite decent. The spectrum in the range 18000-215000 MHz was also taken, but was not

Figure 5. Infrared spectrum of gaseous diazopropyne.

 10^2 cm^{-1}

Figure 5.

Figure 6. Infrared spectrum of a mixture of gaseous diazopropyne and its deuterated molecules.

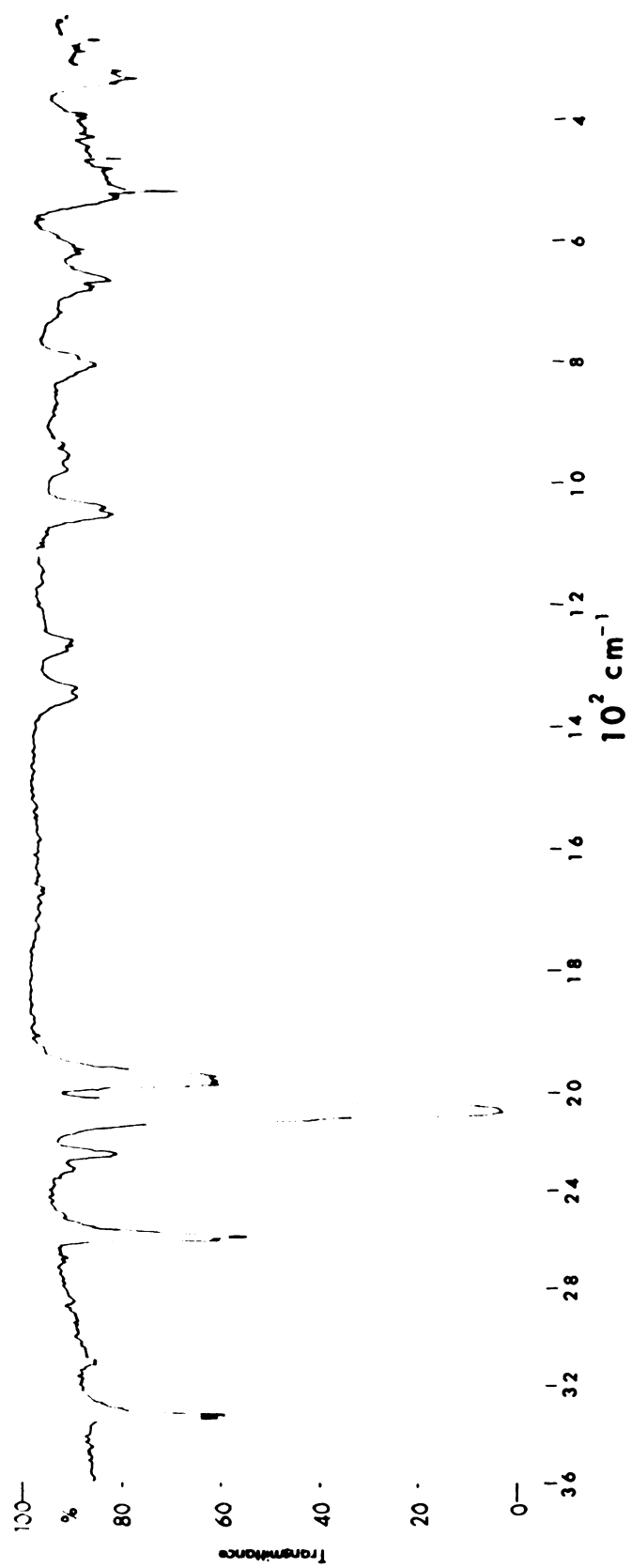


Figure 6.

Table I. Observed infrared absorption bands of diazopropyne vapor (298°K).

Frequency (cm ⁻¹)	Band Type	Frequency (cm ⁻¹)	Band Type
3338 Q (s)	B	832 R (w)	B
3325 Q (s)		818 P (w)	
3107 R (w)	B	689 R (m)	B
3093 P (w)		674 P (m)	
2335 R (w)	B	540 R (m)	C
2328 P (w)		531 Q (s)	
2126 Q (s)	B	504 (w)	?
2112 Q (s)			
2079 Q (vs)	B	476 (w)	C
2060 Q (vs)			
1364 R (m)	B	355 Q (s)	B
1353 P (m)		346 Q (s)	
1180 R (w)	B		
1168 Q (w)			
(1163) Q (w)			
(1150) P (w)			
1064 R (m)	B		
1053 P (m)			

Symbols: R, Q, P - branch designation.

vs - very strong, s - strong, m - medium,

w - weak, () - uncertain band.

Table II. Observed infrared absorption bands of a mixture of gaseous diazopropyne and its deuterated molecules.

Frequencies (cm^{-1})	Band Type	Frequencies (cm^{-1})	Band Type
3335 Q (s) 3320 Q (s)	B	(1172) (vw) (1152) (vw)	
3110 R (w) 3100 P (w)	B	1062 (m) 1050 (m)	B
2605 Q (s) 2594 Q (s)	B	816 R (w) 804 P (m)	B
2270 R (w) 2260 P (w)	B	688 R (w) 676 P (m)	B
2090 R (vs) 2075 Q (vs) 2060 P (vs)	A	540 R (m) 529 Q (s)	C
1985 R (m) 1975 P (m)	B	475 Q (m)	C
1360 R (w) 1346 P (w)	B	442 (w) 410 (w) 404 (w) 356 (sh) 346 (s) 332 (m) 288 (vw) 284 (w)	
1284 R (w) 1270 P (w)	B		

Symbols: R, Q, P - branch designation.

vs - very strong, s - strong, m - medium,

w - weak vw - very weak, sh - shoulder,

() - uncertain band.

Figure 7. Principle inertial axes of diazopropyne.

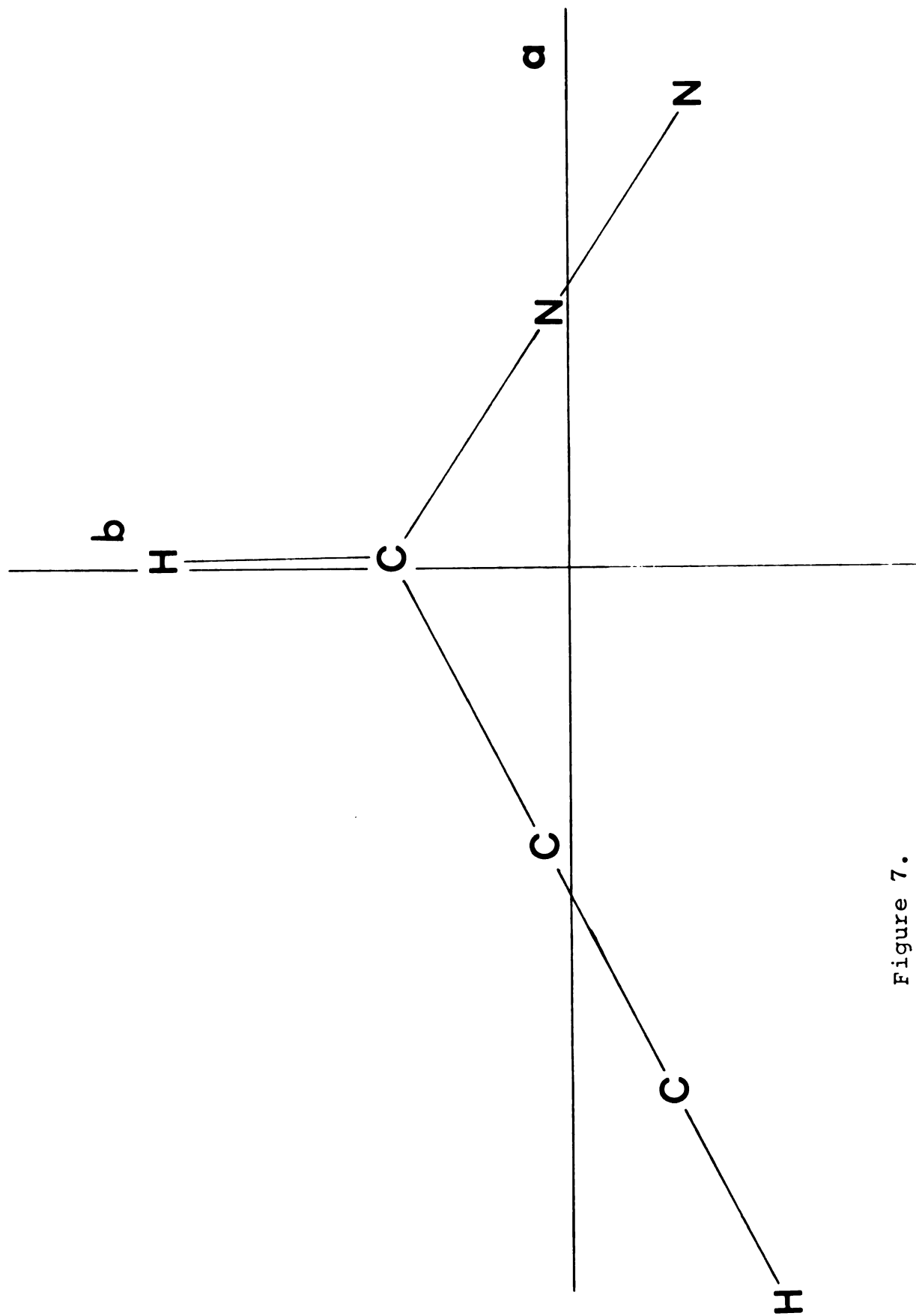


Figure 7.

satisfactory. Satellite bands of some transitions were observed. The satellite band has the same band shape as its parent transition (rotational transition in the ground vibrational state), but with less intensity, and is due to the rotational transition in the first excited vibrational state. Such satellite bands only occur when the first excited vibrational state lies not too far above the ground vibrational state. If the molecule has a low bending frequency (around 200 cm^{-1} or below), satellite bands will possibly be present in the microwave spectrum. From the intensities of the parent and satellite bands, a vibrational frequency for the transition from the vibrational ground state to first excited state can be approximately calculated by the Boltzmann equation.

By using bond lengths and bond angles adapted from the related molecule diazoacetonitrile (17), and Professor R. H. Schwendeman's computer programs STRUCT and EIGVALS, a rotational analysis can be carried out to fit observed frequencies, and refined rotational constants of diazopropyne can be calculated. A reasonable fit was obtained in the 26500-31000 MHz and 36380-39600 MHz regions. The fit below 26500 MHz was not satisfactory; this is perhaps due to the uncertainty of the observed bands below 26500 MHz. Thus a harder search has to be made in the region below 26500 MHz. However, with the aid of the rotational calculation, a preliminary A-type assignment was achieved, which is not shown in detail in this dissertation. The

tentative rotational constants for diazopropyne are obtained as follows: $A = 28968$ MHz, $B = 2785$ MHz, and $C = 2653$ MHz.

Due to the unstable nature of the molecule, the amount of diazopropyne in the gas phase should decrease with time because of decomposition. The intensities of the vibrational absorption bands due to diazopropyne should be decreased proportionally as time elapses. For those bands which are not due to diazopropyne, the intensities should either grow or remain the same with respect to the time. Thus it is not too difficult to identify the vibrational absorption bands which are due to diazopropyne. Much higher resolution than is available in our laboratory would be required for an attempt to perform a rotational analysis of the vibration-rotation bands of diazopropyne. Only the envelopes of the bands were obtained for the gas phase spectra.

Based on the shapes of the band envelopes, the frequencies from related molecules, the results of an initial normal coordinate calculation, the frequencies of matrix isolated diazopropyne, and the deuterium - substitution study, most of the absorption bands have been assigned with certainty, except those bands below 600 cm^{-1} . There are four or five overlapping bands between 570 cm^{-1} and 440 cm^{-1} , with total band width of approximately 80 cm^{-1} (see Fig. 5). The normal A- or B-type band width is about 20 cm^{-1} for diazopropyne. The bands at 531 cm^{-1} and 476 cm^{-1} are the only two distinct C-type bands, which are due

to two of the out-of-plane bending motions of the diazopropyne molecule. The band at 540 cm^{-1} looked like an A- or B-type band overlapping with the 531 cm^{-1} band, but in the matrix spectrum, there is only one band at 525 cm^{-1} , corresponding to the 531 cm^{-1} band in the gas phase spectrum. The band at 540 cm^{-1} in the matrix spectrum is due to diazopropyne dimer or polymer since its intensity varies with different host-to-sample ratio. Thus, there is no band in the matrix spectrum corresponding to the 540 cm^{-1} band in the gas phase spectrum. Therefore, the band at 540 cm^{-1} is possibly the R branch of the 531 cm^{-1} band. The two bands between 531 cm^{-1} and 476 cm^{-1} are around 504 and 490 cm^{-1} respectively; the structures of these two bands are not distinctive. The former loses intensity, the latter gains intensity with time, so it is logical to eliminate the 490 cm^{-1} band from the list. Now the bands from 570 to 440 cm^{-1} are narrowed down to three. The frequency of the $\text{C-C}\equiv\text{C}$ out-of-plane bending motion in the propargyl halides (20) is about 300 cm^{-1} , but no bands are observed around 300 cm^{-1} in the gaseous diazopropyne spectrum.

The gas phase infrared spectra of deuterated mixtures of diazopropyne, namely $\text{C}_3\text{H}_2\text{N}_2$, C_3HDN_2 , C_3DHN_2 , and $\text{C}_3\text{D}_2\text{N}_2$, are relatively weak and the positions and shapes of many of the isotopic bands are not clearly evident. As mentioned in the experimental section, a most unfortunate problem is the difficulty in separating $\text{C}_3\text{H}_2\text{N}_2$, C_3HDN_2 , C_3DHN_2 , and $\text{C}_3\text{D}_2\text{N}_2$. Due to these problems with the gas phase infrared spectra of diazopropyne and its deuterated mixtures, it was

necessary to obtain solid phase Raman spectra as well as solid phase and matrix-isolated infrared spectra of diazopropyne and its deuterated mixtures in order to assign the fundamental vibrations.

The advantages of matrix isolation spectra are the similarity of the matrix isolated frequencies to the gas phase frequencies and the sharpness of the matrix isolated absorption bands, which permit us to identify some bands which cannot be resolved in the gas and solid phase spectra. In addition, the matrix isolated diazopropyne was used to prepare the propargylene free radical by photolysis with ultraviolet light; this work will constitute the second chapter of this dissertation.

Raman spectra of solid diazopropyne help identify those bands which have weak intensities in infrared spectra, but strong intensities in Raman spectra. For example, the 1165 cm^{-1} band is very weak in the infrared, but very strong in the Raman spectrum. In spectra of solid and matrix isolated diazopropyne, the identification of absorption bands due to diazopropyne was simply carried out by ultraviolet light photolysis. The bands due to diazopropyne should decrease in intensity, and those due to other molecules should increase in intensity or remain unchanged.

The infrared spectra of matrix-isolated diazopropyne and the deuterated isotopic mixture are shown in Figures 8 and 9. The solid Raman spectra of diazopropyne and its deuterated mixture are shown in Figures 10 and 11. The

Figure 8. Infrared spectrum of matrix (Kr)-isolated diazopropyne.

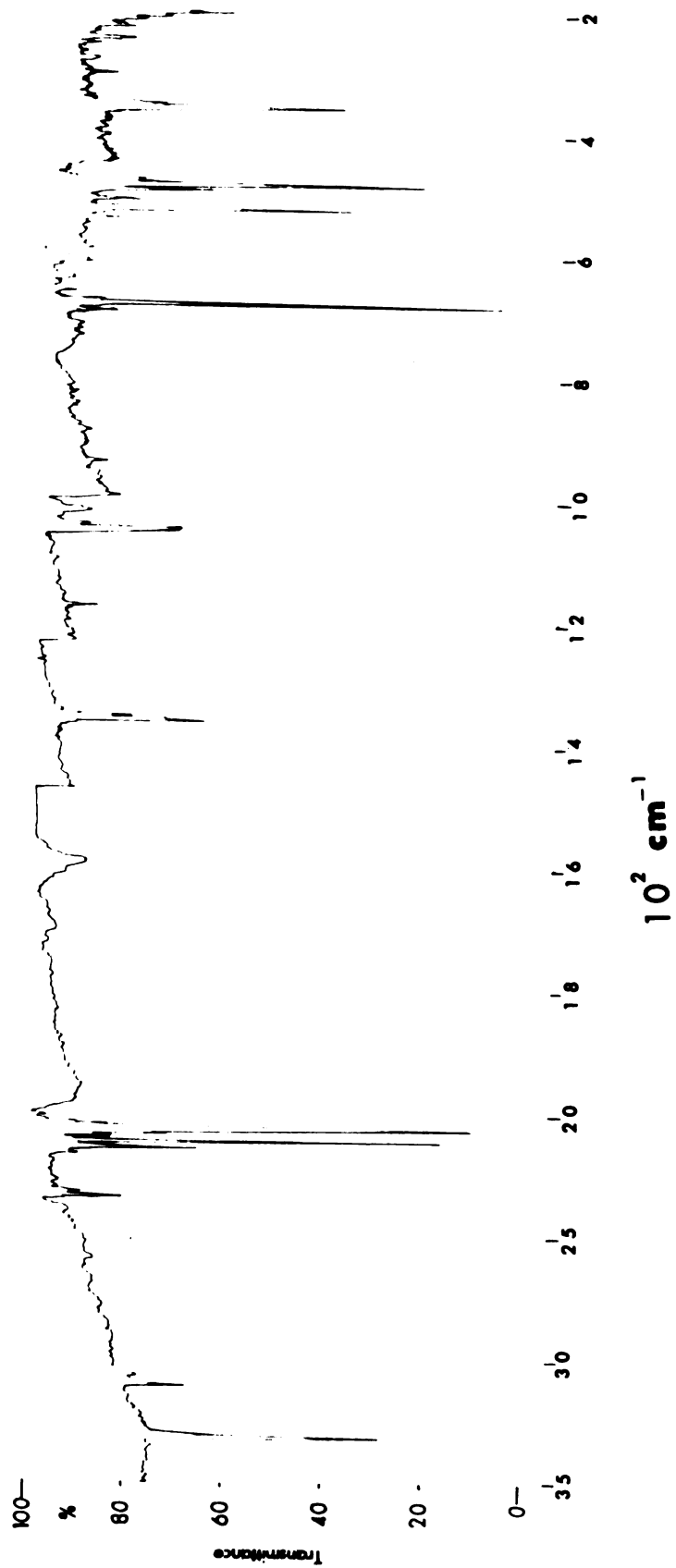


Figure 8.

Figure 9. Infrared spectrum of a mixture of matrix (Kr)-isolated diazopropyne and its deuterated molecules. The bands marked with X are not due to diazopropyne.

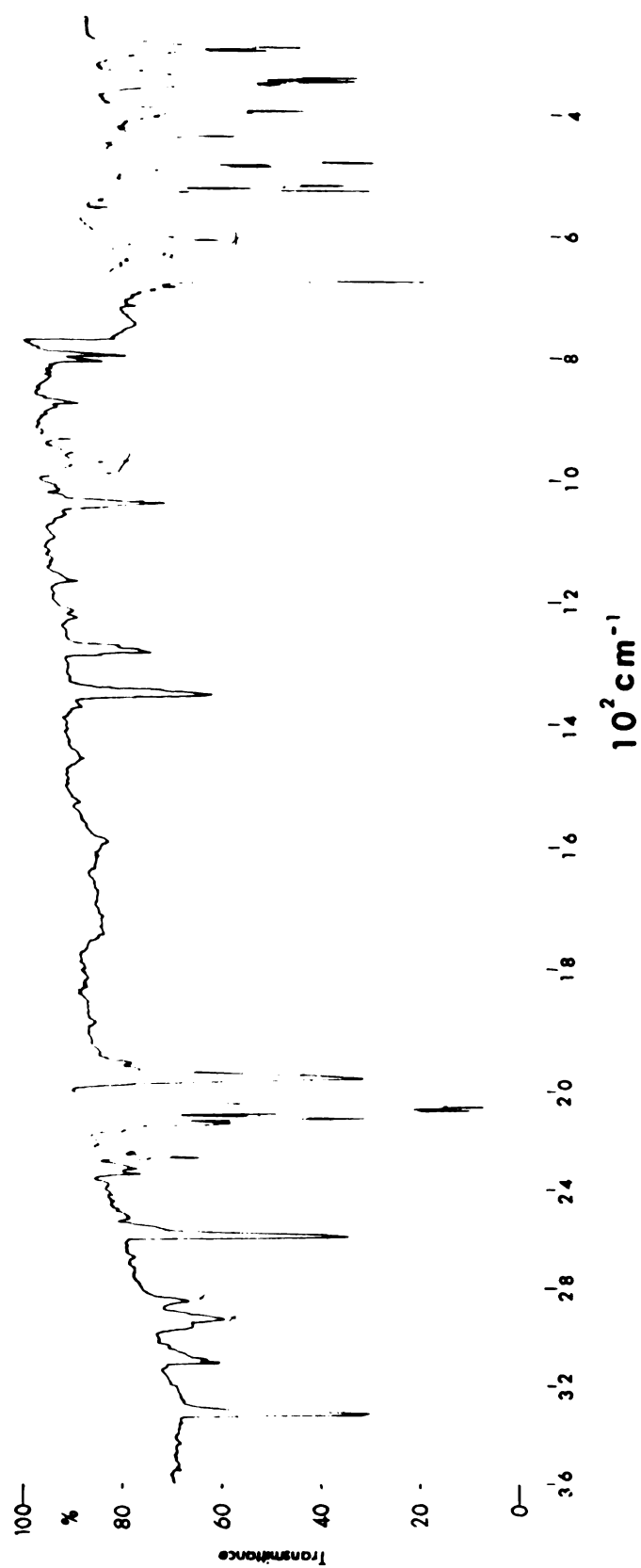
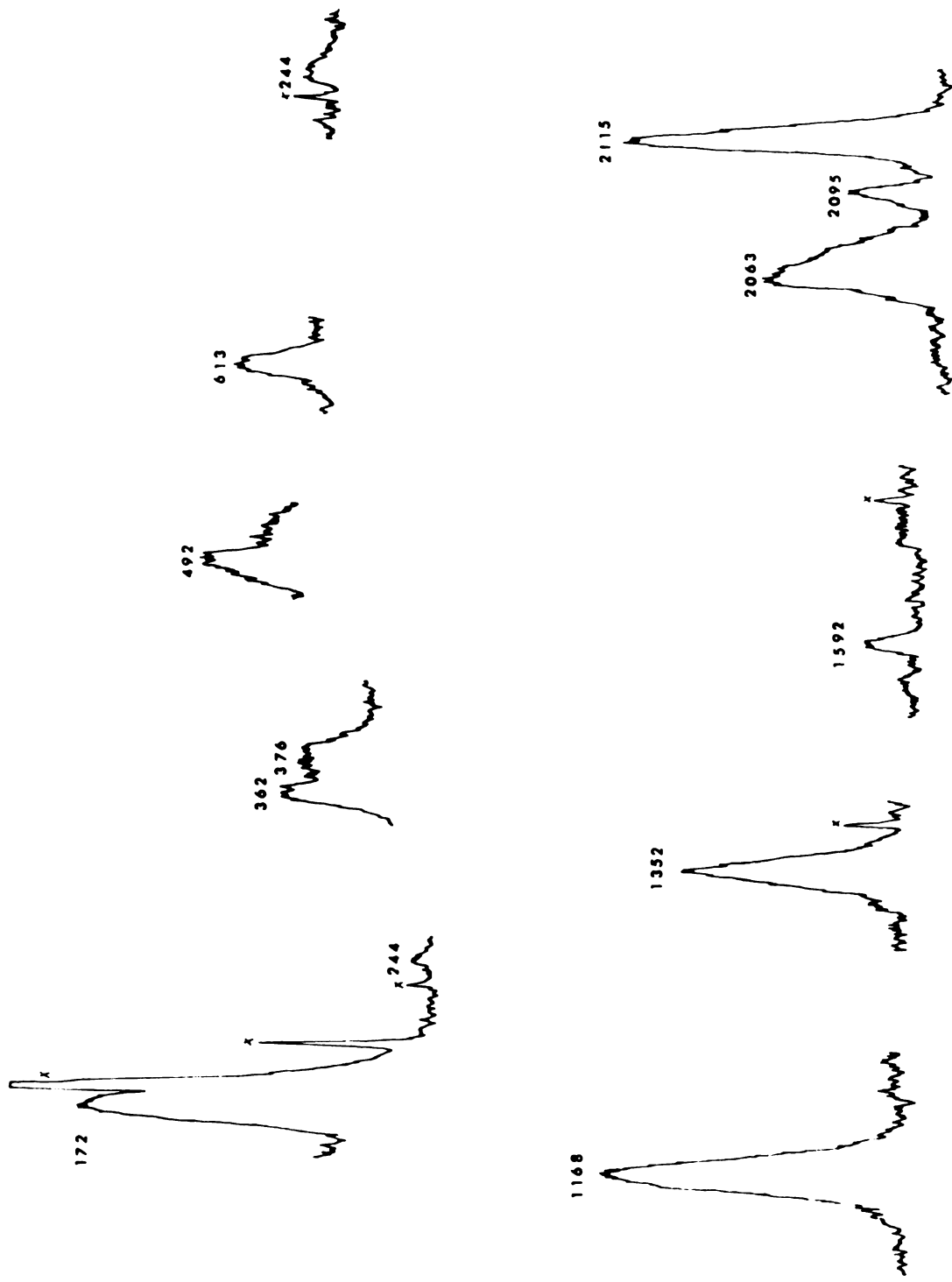


Figure 9.

Figure 10. Raman spectrum of solid diazopropyne.

The bands marked with X are fluorescence lines.



frequency (cm⁻¹)

Figure 10.

Figure 11. Raman spectrum of a mixture of solid diazopropyne and its deuterated molecules.

The bands marked with X are fluorescence lines.

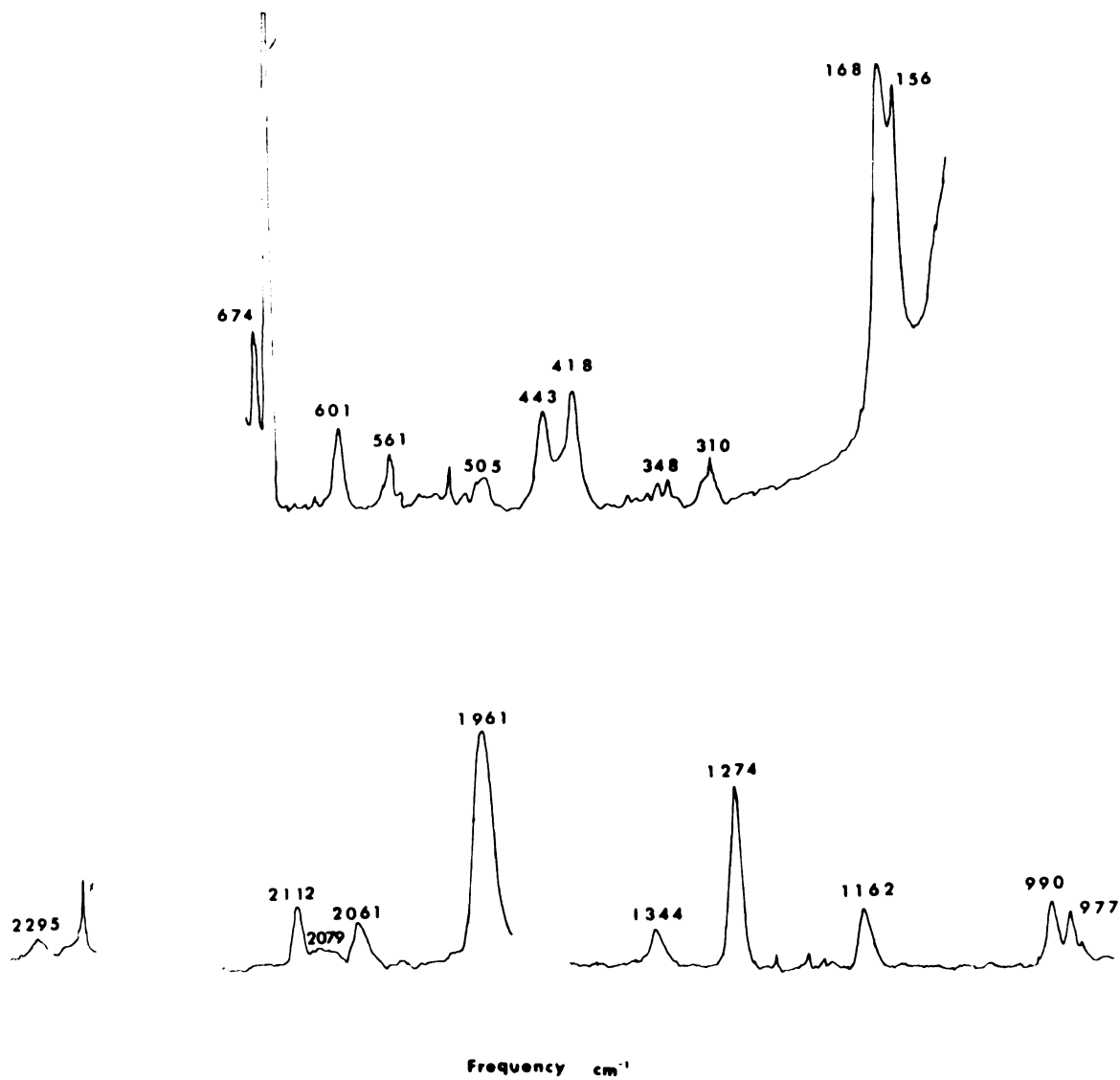


Figure 11.

frequencies and intensities of the vibrational bands observed in solid and matrix infrared and solid Raman spectra of diazopropyne and its deuterated mixture are given in Tables III - V.

Assignment of the Observed Fundamentals

A' symmetry class: (The bands in this class are due to in-plane vibrations with A- or B-type band envelopes in the gas phase spectrum.)

ν_1 and ν_2

The gas phase bands of $\text{C}_3\text{H}_2\text{N}_2$ at 3330 cm^{-1} and 3100 cm^{-1} shift to 2599 cm^{-1} and 2263 cm^{-1} respectively in deuterated diazopropyne. According to the isotope shift calculation, and by comparing the frequencies with the isotopic shift of C-H stretching frequencies of related molecules (3335 to 2607 cm^{-1} from $\text{H-C}\equiv\text{C-CH}_2\text{Br}$ to $\text{D-C}\equiv\text{C-CH}_2\text{Br}$ [20,21] and 3077 to 2244 cm^{-1} from H_2CN_2 to D_2CN_2 [6]), the ν_1 and ν_2 bands at 3330 and 3100 cm^{-1} are assigned respectively to the stretching motion of the acetylenic C-H bond and the apex C-H bond in diazopropyne.

ν_3

The band at 2118 cm^{-1} in the gas shifts to 1980 cm^{-1} in the deuterated diazopropyne mixture. The matrix band at 2118 cm^{-1} shifts to 1982 cm^{-1} in the deuterated mixture, but there remain a couple of bands around 2118 cm^{-1} ; these are due to the presence of $\text{C}_3\text{H}_2\text{N}_2$ and C_3DHN_2 in the mixture.

Table III. Observed IR frequencies of matrix isolated diazopropyne and its mixed deuterated molecules.

$C_3H_2N_2$ in Kr	$C_3H_2N_2$ and Its Deuterated Isotopes in Kr	$C_3H_2N_2$ and $C_3H_2N^{15}N$ in Kr
3321(s)	3321(s)	3321(s)
3109(w)	3109(w)	
	2599(s), 2587(m)	
2320(w)		
	2280(w, sh), 2272(m)	
	2265(w, sh)	
2166(w)		
2141(m)	2141(w), 2138(w, sh)	2141(m)
2118(s)	2120(s), 2118(s)	2118(s), 2112(m)
2069(vs)	2085(vs), 2069(vs)	2068(vs), 2052(vs)
	1985(w, sh), 1982(s)	
	1972(vw, sh), 1960(vw, sh)	
1361(m), 1358(sh)	1355(m)	1357(m)
1352(w)	1352(sh), 1348(m, sh)	
	1291(w), 1285(m)	
	1282(m, sh), 1276(w, sh)	
1175(vw)	1175(vw)	
1050(m), 1047(m)	1045(m)	1047(w)
1040(w, sh)	1038(sh)	1040(w, sh)
	812(w), 809(w, sh)	
	803(m), 800(m, sh)	
691(w)	691(w)	692(m)
680(vs)	680(vs)	680(s)
540(w)	540(w), 532(s)	541(m), 532(w, sh)
525(s)	525(s), 523(s)	525(m)
510(w)	510(vw)	
494(m)	494(m)	494(m, sh)
485(vs)	485(vs)	485(s)
476(w, sh)	476(m, sh)	
	460(vw), 443(m)	
	405(m), 402(s)	
359(s)	359(s, sh)	359(s)
357(s, sh)	357(s, sh)	358(m, sh)
	352(s)	354(m, sh)
	346(s)	350(w, sh)
	340(m, sh)	
309(vw)		
	303(s)	
	297(s)	
	289(w, sh)	

Continued

Table III. (continued)

$C_3H_2N_2$ in Xe	$C_3H_2N_2$ and Its Deuterated Molecules in Xe
3309 (s)	3309 (m)
3090 (w)	2591 (s), 2580 (m)
	2268 (m), 2249 (w)
2135 (w)	2133 (vw)
2114 (vs)	2112 (m), 2110 (m)
2063 (vs)	2080 (vs), 2063 (vs)
	1978 (sh), 1975 (s), 1973 (m)
1356 (m)	1357 (m), 1355 (m)
	1285 (m), 1279 (m)
1044 (w)	1044 (w)
	1038 (w)
	807 (w), 798 (m)
685 (w, sh)	686 (w, sh)
679 (s)	679 (s)
535 (w)	531 (s)
523 (s)	523 (m), 520 (m)
492 (m, sh)	493 (m), 490 (w, sh)
483 (s)	484 (s), 483 (s)
	478 (m, sh)
	445 (w), 441 (m)
	402 (w, sh), 399 (s), 394 (w, sh)
359 (s)	358 (s)
354 (m)	354 (s)
350 (sh)	351 (s)
	346 (s)
	335 (w)
	303 (s)
	297 (s)
	289 (m)

Symbols: vs - very strong; s - strong; m - medium;
w - weak; sh - shoulder.

Table IV. Observed Raman shift frequencies of solid $C_3H_2N_2$ and its mixed deuterated molecules ($300K$)

$C_3H_2N_2$	$C_3H_2N_2$ and its mixed deuterated molecules
	(2295) (w)
2115 (vs)	2112 (m)
2095 (m)	2079 (w)
2063 (s)	2061 (s)
	1961 (s)
1352 (s)	1344 (m)
	1274 (vs)
1168 (vs)	1162 (s)
	695 (w)
	674 (m)
613 (m)	601 (w)
492 (m)	491 (w)
	443 (s)
	418 (m)
362 (m)	352 (w)
	342 (w)
(244) (vw)	310 (w)
172 (vs)	168 (vs)
	156 (vs)

Symbols: vs - very strong; s - strong; m - medium;
w - weak; vw - very weak; () - uncertain band

Table V. Observed infrared frequencies of solid $C_3H_2N_2$ and its mixed deuterated molecules.

$C_3H_2N_2$ (85°K)	$C_3H_2N_2$ and its mixed deuterated molecules (30°K)
	3315 (s)
3290 (s)	3285 (s)
3073 (m)	3072 (m)
	2581 (s)
	2575 (s)
	2265 (m)
	2250 (m)
2130 (m)	2140 (sh)
2112 (vs)	2116 (s)
	2088 (vs)
2062 (vs)	2068 (vs)
	1971 (s)
	1950 (w, sh)
1350 (m)	1348 (s)
	1276 (s)
1165 (vw)	1166 (vw)
	1160 (vw)
1050 (w)	1048 (w)
	836 (w)
	803 (w)
695 (m)	695 (m, sh)
	681 (s)
613 (w)	611 (m)
554 (m)	532 (s)
	495 (s)
487 (s)	490 (s)
	445 (s)
	403 (s)
360 (m, sh)	361 (s, sh)
358 (s)	355 (s)
	349 (s)
	305 (s)
	300 (s)

Symbols: vs - very strong; s - strong; m - medium;
w - weak; vw - very weak; sh - shoulder.

The $\text{C}\equiv\text{C}$ stretching frequency at 2138 cm^{-1} in propargyl bromide shifts to 2006 cm^{-1} in $\text{D-C}\equiv\text{C-CH}_2\text{Br}$ (21). From this comparison it is quite obvious that ν_3 the gas phase band at 2118 cm^{-1} is mainly due to the $\text{C}\equiv\text{C}$ stretch in diazopropyne.

ν_4

The gas phase band at 2069 cm^{-1} in diazopropyne shifts to around 2080 cm^{-1} in the deuterated mixture. The 2080 cm^{-1} band is difficult to locate with precision because of the presence of $\text{C}_3\text{H}_2\text{N}_2$, C_3HDN_2 , C_3DHN_2 , and $\text{C}_3\text{D}_2\text{N}_2$ in the gas mixture. In the matrix spectrum of the deuterated diazopropyne mixture, the 2069 cm^{-1} and 2086 cm^{-1} bands are quite distinct. In the matrix spectrum of the $\text{C}_3\text{H}_2\text{N}_2$ and $\text{C}_3\text{H}_2\text{N}^{15}\text{N}$ mixture, bands at 2068 and 2052 cm^{-1} are observed; the latter is due to participation of the N^{15}N stretch in the normal vibration. The observed deuterium and nitrogen-15 isotopic shifts are in good agreement with the normal coordinate calculation result, including the upward shift of this normal mode upon deuteration. Since the deuteration of the acetylenic hydrogen atom of diazopropyne can change the composition of this normal mode, this result is not completely unexpected. According to the isotopic shift results and from comparison with the frequencies of related molecules (2102 and 2147 cm^{-1} for $\text{N}=\text{N}$ stretches in diazomethane (6) and dicyanodiazomethane (12) respectively), the ν_4 band at 2069 cm^{-1} is mainly due to the $\text{N}=\text{N}$ stretching vibration.

ν_5

The band at 1358 cm^{-1} in gaseous diazopropyne shifts to 816 cm^{-1} in the deuterated diazopropyne mixture. The shift caused by replacing one or two hydrogen atoms with deuterium is quite large, so it is clear that hydrogen motion must contribute strongly to the 1358 cm^{-1} band. In acetaldehyde the C-H wagging frequency shifts from 1400 cm^{-1} to 849 cm^{-1} upon replacement of the hydrogen atom on the carbonyl group (22). It is evident that the C-H wagging motion in diazopropyne is the primary contributor to ν_5 .

 ν_6

The 1165 cm^{-1} band is quite weak in gas, solid and matrix isolated infrared spectra of diazopropyne, but it is strong in the Raman spectrum of the solid, so it is designated as a fundamental. The C=N stretching frequency in diazomethane is 1170 cm^{-1} and it shifts to 1157 cm^{-1} in CHDN_2 and 1213 cm^{-1} in CD_2N_2 (6). There is one band observed in the mixed deuterated diazopropyne gas phase spectrum at 1272 cm^{-1} and one band with strong intensity at 1274 cm^{-1} in the solid Raman spectrum of mixed deuterated diazopropyne. According to the normal coordinate calculation the C=N stretch contributes about 50 percent to this normal mode.

At this point, the author would like to stress that a given normal mode is often not representative of only one particular group vibration; sometimes it corresponds to the

combined vibrations of several groups, each contributing in different weight. The percentage of the contribution of each vibration to the normal mode is calculated in the normal coordinate analysis and is listed in the output of the computer program under the title of potential energy distribution (PED). For instance, ν_1 and ν_2 of diazopropyne are due almost solely to the acetylenic C-H and apex C-H stretches respectively; this is because C-H stretching motions normally do not couple with other vibrations due to their high frequency nature. (However, a C-H motion will couple with other C-H stretching vibrations if they are geometrically close to each other in the molecule.) However, if some groups are close to one another structurally in the molecule and their individual frequencies are not too far apart then they will have a tendency to couple with one another. The normal mode represents the resultant frequency of a particular coupling of internal coordinates.

ν_7

According to the normal coordinate calculation, the gas phase band at 1058 cm^{-1} is due to a complex vibration of several groups, including the C-H wag, C-C stretch, and C-C $\equiv$ N bend, each contributing less than 50 percent to the potential energy distribution. It is thus not appropriate to assign the 1058 cm^{-1} band (ν_7) to any one of the group vibrations mentioned above. A similar situation is encountered in the mixed deuterated diazopropyne gas phase

spectrum. As mentioned above, a band at 1272 cm^{-1} is observed, which is not observed in the gaseous diazopropyne spectrum. It is obviously due to the isotopic shift, but it is difficult to tell precisely to which band in diazopropyne it corresponds. According to the normal coordinate calculation, the 1272 cm^{-1} band is due to the complex contributions of the $\text{C}=\text{N}$ stretch, $\text{C}-\text{C}$ stretch, $\text{C}-\text{D}$ wag, $\text{N}=\text{N}$ stretch, and $\text{C}\equiv\text{C}$ stretch, and it is assigned to ν_5 in $\text{C}_3\text{D}_2\text{N}_2$. In fact in the Raman spectrum of the solid deuterated diazopropyne mixture, the 1274 cm^{-1} band is quite strong and the 1162 cm^{-1} band, which is due mainly to the $\text{C}=\text{N}$ stretch and is very strong in diazopropyne, is relatively less strong than the 1274 cm^{-1} band, so it is not surprising that 1274 cm^{-1} band has some contribution from the $\text{C}=\text{N}$ stretch.

ν_8

In the gas phase spectrum, the deuterium isotope shift of the 681 cm^{-1} band of $\text{C}_3\text{H}_2\text{N}_2$ is difficult to observe, because the deuterium-shifted frequency overlaps the 531 cm^{-1} (C-type) band of diazopropyne. However, in the mixed deuterated diazopropyne matrix spectrum, bands at 691, 680, and 532 cm^{-1} are observed. The 691 cm^{-1} band is probably due to the dimer or a polymer of diazopropyne, since it is present in the matrix diazopropyne spectrum and its intensity varies with different matrix-to-sample ratios. The 680 cm^{-1} band is due to $\text{C}_3\text{H}_2\text{N}_2$ and/or C_3DHN_2 (deuterium

substitution at the apex hydrogen atom). The 532 cm^{-1} absorption is due to $\text{C}_3\text{D}_2\text{N}_2$ and/or C_3HDN_2 (deuterium substitution at the acetylenic hydrogen atom), since it is not present in the matrix diazopropyne spectrum. This assignment also receives support from the deuterium isotope study of propargyl bromide (21), in which the $\text{C}\equiv\text{C-H}$ bending frequency shifts from 637 to 501 cm^{-1} upon replacement of the acetylenic hydrogen atom with deuterium. The frequencies from the normal coordinate analysis are 678 and 537 cm^{-1} for the $\text{C}\equiv\text{C-H}$ and $\text{C}\equiv\text{C-D}$ bends respectively, which are in good agreement with observed frequencies at 681 and 532 cm^{-1} for diazopropyne and its deuterated molecule. Thus the ν_8 band at 681 cm^{-1} is due to the $\text{C}\equiv\text{C-H}$ in-plane bend and is assigned to ν_8 .

The author assigns the 680 cm^{-1} band to the $\text{C}\equiv\text{C-H}$ bends in $\text{C}_3\text{H}_2\text{N}_2$ and C_3DHN_2 , and the 532 cm^{-1} band to the $\text{C}\equiv\text{C-D}$ bends in $\text{C}_3\text{D}_2\text{N}_2$ and C_3HDN_2 . This is based on the similarity of the structures. The replacement of the non-acetylenic hydrogen atom with a deuterium atom on $\text{C}_3\text{H}_2\text{N}_2$ does not affect the $\text{C}\equiv\text{C-H}$ bending motion, and the same is true for the $\text{C}\equiv\text{C-D}$ bending motion upon the replacement of the non-acetylenic deuterium atom with an hydrogen atom on $\text{C}_3\text{D}_2\text{N}_2$. This assignment receives support from the normal coordinate analysis.

ν_9

The band at 494 cm^{-1} for diazopropyne in a Kr matrix has medium intensity. From comparisons with acetaldehyde (22) and fumaronitrile (23), the former having the $\text{C}-\text{C}=\text{O}$ bending frequency at 509 cm^{-1} and the latter the $\text{C}-\text{C}=\text{C}$ bending frequency at 538 cm^{-1} , the band at 494 cm^{-1} in diazopropyne is probably related to the $\text{C}-\text{C}=\text{N}$ bend.

The 509 cm^{-1} band shifts to 500 cm^{-1} in monodeutero acetaldehyde (CH_3CDO) (22), and it is also indicated in the normal coordinate analysis that this isotopic substitution of acetaldehyde does not appreciably affect the $\text{C}-\text{C}=\text{O}$ bending frequency. In the gas phase diazopropyne spectrum, there is a rather indistinct band around 504 cm^{-1} , which corresponds to the 494 cm^{-1} band in the matrix. The normal coordinate analysis shows that the $\text{C}-\text{C}=\text{N}$ bend, $\text{C}-\text{C}$ stretch and $\text{C}=\text{N}=\text{N}$ bend are jointly responsible for this normal mode at 494 cm^{-1} , and it also predicts that deuteration should not affect the frequency appreciably. Indeed, there are no bands observed between 494 and 460 cm^{-1} in the mixed deuterated diazopropyne matrix spectrum.

 ν_{10}

In the gas phase spectrum of diazopropyne, a strong distinct B-type band at 351 cm^{-1} is observed. In the diazopropyne matrix (Kr) spectrum a strong band at 359 cm^{-1} is observed with shoulder at 357 cm^{-1} . The shoulder at 357 cm^{-1} is not distinct. In the corresponding mixed deuterated

diazopropyne matrix spectrum there are five bands observed, namely: 359, 357, 352, 346, and 340 cm^{-1} (Fig. 12). They are present with good intensities except that 340 cm^{-1} band is only a weak shoulder. The three lower frequency bands are absent in the diazopropyne matrix spectrum and the 357 cm^{-1} band increase in intensity with respect to 359 cm^{-1} band in the mixed deuterated diazopropyne matrix spectrum. According to a relative intensity study of these bands in matrix infrared spectra with different isotopic distributions, the 359, 357, 352, and 346 cm^{-1} bands are assigned to $\text{C}_3\text{H}_2\text{N}_2$, C_3DHN_2 , C_3HDN_2 , and $\text{C}_3\text{D}_2\text{N}_2$ respectively.

The observed deuterium isotope shifts are in good agreement with the normal coordinate calculation result. In the $\text{C}_3\text{H}_2\text{N}_2/\text{C}_3\text{H}_2\text{N}^{15}\text{N}$ mixed matrix (Kr) spectrum bands at 360, 358, 354, and 350 cm^{-1} are observed, the last three being shoulders. The 354 cm^{-1} feature is due to the nitrogen-15 isotope shift. Thus the 351 cm^{-1} band in the gas phase spectrum of diazopropyne is due to some vibration involving the terminal nitrogen atom. Since the frequency of this band is rather low, it is likely this vibration is the $\text{C}=\text{N}=\text{N}$ bend.

The $\text{C}=\text{N}=\text{N}$ bending frequencies are between 380 and 420 cm^{-1} for diazomethane and its various deuterated analogs (6). For example, the $\text{C}=\text{N}=\text{N}$ in-plane bending frequency of diazomethane shifts from 421 to 393 cm^{-1} upon replacing one hydrogen atom with deuterium. Therefore, the gas phase band ν_{10} at 351 cm^{-1} is assigned to the $\text{C}=\text{N}=\text{N}$ in-plane bend.

Figure 12. Infrared spectrum of a mixture of matrix isolate diazopropyne and -1 , its deuterated molecules (expanded scale in the region 600-250 cm^{-1}).

A. Infrared spectrum of $\text{C}_3\text{H}_2\text{N}_2$ in Kr matrix.

B. Infrared spectrum of $(\text{C}_3\text{H}_2\text{N}_2 + \text{C}_3\text{HDN}_2 + \text{C}_3\text{D}_2\text{N}_2)$ in Kr matrix.

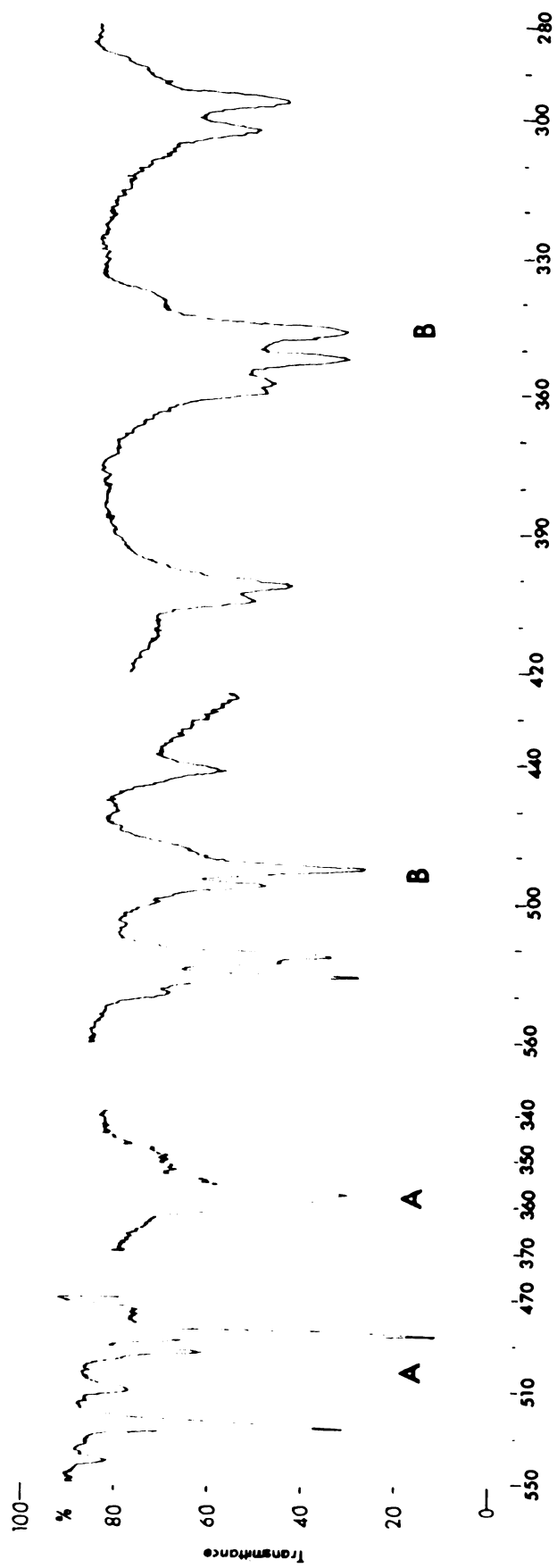


Figure 12.

ν_{11}

Bands at 168 and 170 cm^{-1} are observed in the Raman and infrared spectra of solid diazopropyne respectively. In addition to the 168 cm^{-1} band, a band at 156 cm^{-1} is observed in the Raman spectrum of mixed solid deuterated diazopropyne. In the related molecule propargyl bromide (20,21), the $\text{C}\equiv\text{C}-\text{C}$ in-plane bending frequency shifts from 186 to 165 cm^{-1} when the acetylenic hydrogen atom is replaced with deuterium. Thus ν_{11} , the last band in the A' symmetry class, is assigned as the $\text{C}-\text{C}\equiv\text{C}$ bend at 168 cm^{-1} .

A'' symmetry class: (The bands in this class are due to out-of-plane vibrations with C-type band envelopes in the gas phase spectrum.)

 ν_{12} and ν_{13}

Two distinct C-type bands are observed, at 530 cm^{-1} and 475 cm^{-1} respectively, in the gaseous diazopropyne spectrum. The corresponding isotopic shift bands in the mixed deuterated diazopropyne gas spectrum are at 442 and 404 cm^{-1} . However, their intensities are quite weak and their band shapes are rather structureless. In the mixed deuterated diazopropyne matrix spectrum, bands at 525, 523, 485, 443, 405, and 402 cm^{-1} are observed. The 525, 485 cm^{-1} bands correspond respectively to the 530 and 475 cm^{-1} bands in the gas phase spectrum, and are also present in the diazopropyne matrix spectrum. Thus, the remaining absorptions

must be due to deuterated diazopropyne molecules. In related molecules, the $\text{C}=\text{N}=\text{N}$ out-of-plane bending frequency shifts from 564 to 528 cm^{-1} , from H_2CN_2 to D_2CN_2 (6) and the $\text{C}-\text{H}$ out-of-plane bending frequency shifts from 637 to 501 cm^{-1} , from propargyl bromide to acetylenic deuterated propargyl bromide (21). According to the normal coordinate calculation result, the observed matrix frequencies 523 (C_3DHN_2), 405 (C_3HDN_2), and 402 cm^{-1} ($\text{C}_3\text{D}_2\text{N}_2$) are the deuterium-shifted frequencies corresponding to the 525 cm^{-1} band ($\text{C}_3\text{H}_2\text{N}_2$), and 443 cm^{-1} is the deuterium-shifted frequency for the 485 cm^{-1} band of $\text{C}_3\text{H}_2\text{N}_2$.

In addition to the above information, the author also has observed a C-type band around 480 cm^{-1} in a preliminary gas phase infrared spectrum of diazoacetonitrile.* There should be only two out-of-plane bending frequencies in the region of 500 to 300 cm^{-1} for diazoacetonitrile, namely the $\text{C}-\text{C}\equiv\text{N}$ and $\text{C}=\text{N}=\text{N}$ out-of-plane bends. The former should have a frequency around 350 cm^{-1} (24), so the 480 cm^{-1} band is probably due to the $\text{C}=\text{N}=\text{N}$ out-of-plane bend. This supports the assignment from the normal coordinate calculation and frequencies from related molecules of ν_{12} and ν_{13} , the gas bands at 530 and 476 cm^{-1} in diazopropyne, as the $\text{H}-\text{C}\equiv\text{C}$ and $\text{C}=\text{N}=\text{N}$ out-of-plane bends respectively.

*The author attempted to obtain an infrared spectrum for diazoacetonitrile ($\text{N}\equiv\text{C}-\text{CH}=\text{N}=\text{N}$) which would be a strong support to the assignment of the vibrational spectrum of diazopropyne, since their structures are so similar. Unfortunately, the complete spectrum of diazoacetonitrile was not obtainable because its vapor pressure is not adequate for infrared spectroscopic study.

ν_{14}

In the infrared spectrum of the mixed deuterated diazopropyne matrix (Kr), distinct bands at 303 cm^{-1} , 297 cm^{-1} and a weak shoulder at 290 cm^{-1} , are observed. They are absent in the diazopropyne matrix (Kr) spectrum. According to the normal coordination calculation prediction, four bands at 309 , 308 , 295 , and 291 cm^{-1} are expected, corresponding to the out-of-plane $\text{C}\equiv\text{C}-\text{C}$ bends in $\text{C}_3\text{H}_2\text{N}_2$, C_3DHN_2 , C_3HDN_2 , and $\text{C}_3\text{D}_2\text{N}_2$, respectively. Indeed, there is a band observed at around 309 cm^{-1} in the $\text{C}_3\text{H}_2\text{N}_2$ matrix; however, it is quite weak in comparison with its counterpart in the mixed deuterated matrix (Kr) diazopropyne spectrum. The $\text{C}\equiv\text{C}-\text{C}$ out-of-plane bending frequency of propargyl bromide shifts from 314 to 296 cm^{-1} (21) upon deuteration of the acetylenic hydrogen atom. Upon this rather meager evidence, the weak band at 309 cm^{-1} is tentatively assigned to the $\text{C}\equiv\text{C}-\text{C}$ out-of-plane bend.

 ν_{15}

The only remaining fundamental is the out-of-plane C-H wag, which is predicted at about 245 cm^{-1} for diazopropyne by the normal coordinate calculation using force constants transferred from diazomethane. No band is observed around 245 cm^{-1} in the diazopropyne infrared spectrum. A weak band is found at around 244 cm^{-1} in the Raman spectrum of solid diazopropyne. This band can be only tentatively assigned as ν_{15} . Further investigation is necessary.

According to the preliminary microwave study, by calculating from the intensities of a certain transition (transition in the vibrational ground state) and its first satellite (transition in the vibrational first excited state), there should be at least two vibrational transitions below 250 cm^{-1} , so the C-H out-of-plane wagging frequency is likely to fall around 250 cm^{-1} or below. The fundamental frequencies of diazopropyne are summarized in Table VI.

Other Bands (These bands are not due to fundamentals of diazopropyne.)

In the gas phase infrared spectrum of diazopropyne (see Fig. 5), the intensities of the bands at around 2315 and 824 cm^{-1} decrease with time. Thus they are due to diazopropyne; the former may be due to a combination band ($\nu_5 + 2\nu_{13}$) and the latter is absent in the infrared spectra of solid and matrix isolated diazopropyne, and is also possibly due to a combination band ($\nu_9 + \nu_{10}$). The intensities of the bands from 645 to 600 cm^{-1} , and the band at 490 cm^{-1} increase with time. Thus, they are due to the decomposition products of diazopropyne, which increase in quantity as time elapses.

In the infrared spectrum of matrix isolated diazopropyne (see Fig. 8), the band at 2340 cm^{-1} is due to carbon dioxide, which is probably contained in the mixture of the host gas and gaseous diazopropyne. The band at 2320 cm^{-1} corresponds to the 2315 cm^{-1} band in the gas phase spectrum. The infrared spectrum of matrix isolated

Table VI. Fundamental frequencies of diazopropyne.

A'		A''	
ν_1	3331.0	ν_{12}	531 .0
ν_2	3100.0	ν_{13}	476 .0
ν_3	2118.0	ν_{14}	(309 .0) ⁺
ν_4	2069.0	ν_{15}	---
ν_5	1358.0		
ν_6	1165.0		
ν_7	1058.0		
ν_8	681.0		
ν_9	*494.0		
ν_{10}	351.0		
ν_{11}	(168.0)		

* Matrix frequency

() Solid Raman frequency

()⁺ Uncertain band

diazopropyne is somewhat similar to that of the solid phase spectrum in the range 2170-2000 cm^{-1} . Both have two strong absorption bands corresponding to ν_3 and ν_4 (the frequencies are not quite the same in the matrix isolated and the solid spectra), and a less strong band on the higher frequency side around 2140 cm^{-1} which may be due to the overtone, $2\nu_7$. The minor splitting in this region (2170-2000 cm^{-1}) of the matrix spectrum of diazopropyne probably arises from the interaction between diazopropyne and its host lattice or the interaction between/among diazopropyne molecules. The broad band around 1600 cm^{-1} is due to the absorption of solid water. A shoulder (1357 cm^{-1}) and a sharp band (1353 cm^{-1}) are observed at the low frequency side of the ν_5 which are probably due respectively to the overtone band $2\nu_8$ and the interaction between diazopropyne molecules in the host lattice (since a band at around 1347 cm^{-1} was observed in the solid phase spectrum of diazopropyne). A band with medium intensity at 1046 cm^{-1} and a weak sharp band at 1040 cm^{-1} appear at the low frequency side of ν_7 . They perhaps arise respectively from the overtone $2\nu_{12}$, and interaction between diazopropyne molecules in the host lattice. The bands from 670 to 600 cm^{-1} are due to decomposition products since their intensities increase upon photolysis. The bands at 690, 540, and 475 cm^{-1} are due to dimer or polymer of diazopropyne, since their intensities vary with different host matrix-to-sample ratios, M/S. The weak band at 510 cm^{-1} is possibly due to the combination

($\nu_{10} + \nu_{11}$). The bands below 300 cm^{-1} are not due to diazopropyne since they do not disappear upon photolysis.

An Outline of Normal Coordinate Analysis

A normal coordinate analysis is a powerful tool in the study of vibrational spectra, for it enables structural and bonding information concerning the molecules under investigation to be obtained. Vibrational analysis can also help in the assignment of the fundamental frequencies of the molecules being studied. In relation to the work described in this dissertation several vibrational analyses have been carried out, so it would seem appropriate for the author to outline the procedure for a normal coordinate analysis. A more detailed treatment can be found in Wilson, Decius and Cross' Molecular Vibrations (25).

The potential energy of a molecule can be written as

$$2V = \tilde{R}FR \quad (1)$$

Where R is a column matrix in terms of the internal coordinates, $\tilde{R}$ is the transpose of R and F is a matrix whose components are force constants. The kinetic energy of a molecule can be written as

$$2T = \tilde{R}G\dot{R}. \quad (2)$$

The G matrix is defined as $G = BM^{-1}B$. Here $\dot{R}$ is the first derivative of R with respect to time and M^{-1} is a diagonal matrix whose components are μ_i , where μ_i is the reciprocal of the mass of the i^{th} atom. The B matrix is

defined through the relation $R = BX$, where R and X are column matrices whose components are the internal and rectangular coordinates, respectively. If equations (1) and (2) are combined with Lagrange's equation,

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{R}} \right) + \frac{\partial V}{\partial R} = 0 \quad (\text{equation of motion}),$$

$$|F - G^{-1}\lambda| = 0 \quad (3)$$

is obtained. Equation (3) can be transformed to $|GF - E\lambda| = 0$, where $\lambda = 4\pi^2 C^2 \tilde{\nu}^2$ is an eigenvalue and $\tilde{\nu}$ is the related frequency. λ can be solved for if G and F are known. The G matrix can be constructed by the Wilson S-vector technique (25).

If unit vectors are considered, $R = BX$ can be written in a more convenient form with vector notation, $R = S \cdot \rho$. Here ρ is a column matrix written in terms of the displacement vector of the atoms in the molecule. S is called the S-matrix, and its components (S-vector) can be expressed by bond stretching and/or angle bending in the molecule. By using the S-matrix, $G = BM^{-1}B$ can be written as $G = SM^{-1}S$, and thus the G matrix is constructed for the molecule. A generalized valence force field or Urey-Bradley force field can be used to construct the F matrix.

For simplicity in solving the secular equation symmetry coordinates are usually introduced in the vibrational analysis. The symmetry coordinate is defined as $R' = UR$, where R is a column matrix whose components are internal

coordinates and U is an orthogonal matrix whose elements must satisfy the relations $\sum_k (U_{jk})^2 = 1$ and $\sum_k U_{jk} U_{\ell k} = 0$. Furthermore, the symmetry of the molecule must be taken into consideration. The advantage of using symmetry coordinates is that one can factor the G and F matrices according to their symmetry classes into symmetry blocks; thus the secular equation can be reduced and more easily solved. The method of transforming the G matrix and F matrix to symmetrized G and F matrices is prescribed by Wilson, Decius, and Cross (25). The secular equation was solved by two Jacobi diagonalizations, with the actual calculation being carried out using a computer program originally due to Schachtschneider (26,27).

Vibrational Potential Function and Related Properties of Diazopropyne

Normal Coordinate Analysis

The object of carrying out a normal coordinate analysis is fourfold: to provide information for the assignment of the fundamentals, to test the value of transferring force constants from related molecules (and thus the general utility of calculating such potential constants), to understand the nature of each normal vibration by calculating the potential energy contribution of each force constant to the normal modes, and finally to seek qualitative information on the correlation of electronic structures and vibrational force constants in molecules of interest. In the

usual procedure the vibrational problem is solved in the harmonic approximation. However, the observed frequencies are not harmonic frequencies, and on occasion in the present work matrix frequencies are used in the analysis. Under these circumstances, the author will not attempt to achieve a perfect fit between observed and calculated frequencies. As a matter of fact, for some molecules a perfect fit can't be achieved using the valence force field alone in the normal coordinate calculation.

In this calculation the bond lengths and bond angles listed in Table VII were used, assumed by analogy with related molecules: diazomethane (6), dicyanodiazomethane (12), the propargyl halides (14), and diazoacetonitrile (17). In Figure 13, where the internal coordinates are depicted, the bending coordinates in (a) are perpendicular to those in (b). In order to proceed further, it is necessary to form the symmetry coordinates for diazopropyne. The symmetry coordinates used in the vibrational analysis are also listed in Table VII. The redundant coordinate O_R is in the A' symmetry block.

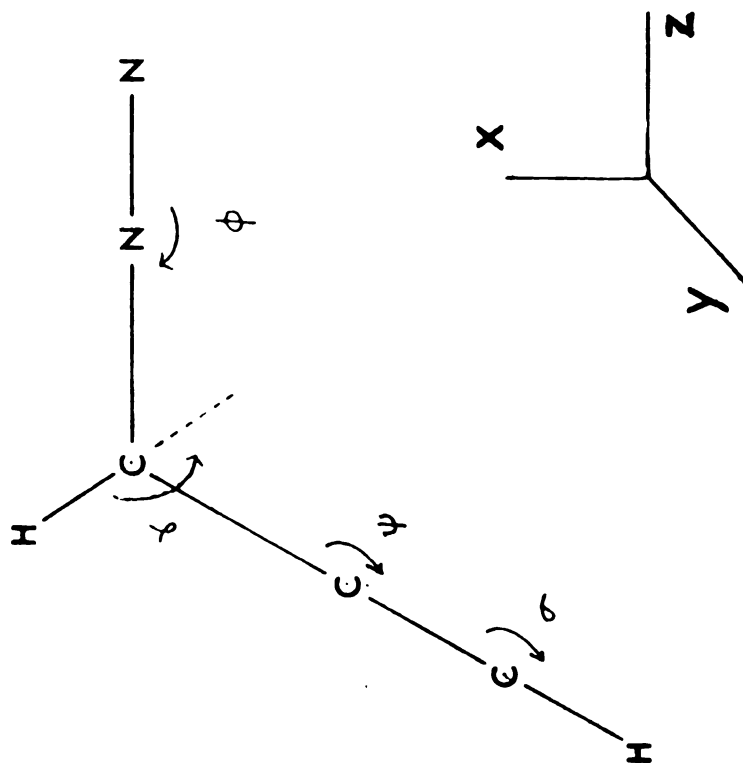
Using the molecular parameters such as bond lengths, bond angles and the mass of each individual atom, a G matrix can be constructed. With the G matrix and force constants transferred from the related molecules, diazomethane H_2CNN (6), dicyanodiazomethane $(CN)_2CNN$ (12), and the propargyl halides $HC\equiv C-CH_2X$ (14), one can obtain the general pattern expected for the vibrational fundamentals

Table VII. Geometry and symmetry coordinates for diazopropyne.

Bond Lengths ($\text{\AA}$)	Bond Angles
$r_{12} = 1.28$	$\angle\beta_1 = 123.5^\circ$
$r_{23} = 1.139$	$\angle\alpha = 119.5^\circ$
$r_{14} = 1.075$	$\angle\beta_2 = 117.0^\circ$
$r_{15} = 1.424$	
$r_{56} = 1.21$	
$r_{67} = 1.06$	
A'	A''
$S_1 = \Delta r_{12}$	$S_{13} = \Delta\phi$
$S_2 = \Delta r_{15}$	$S_{14} = \Delta\psi$
$S_3 = \Delta r_{23}$	$S_{15} = \Delta\sigma$
$S_4 = \Delta r_{14}$	$S_{16} = \Delta\gamma$
$S_5 = \Delta r_{56}$	
$S_6 = \Delta r_{67}$	
$S_7 = 2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2$	
$S_8 = \Delta\alpha + \Delta\beta_1 + \Delta\beta_2 = O_R$	
$S_9 = \Delta\beta_1 - \Delta\beta_2$	
$S_{10} = \Delta\theta$	
$S_{11} = \Delta\tau$	
$S_{12} = \Delta\epsilon$	

Figure 13. Internal coordinates for diazopropyne.

b



a

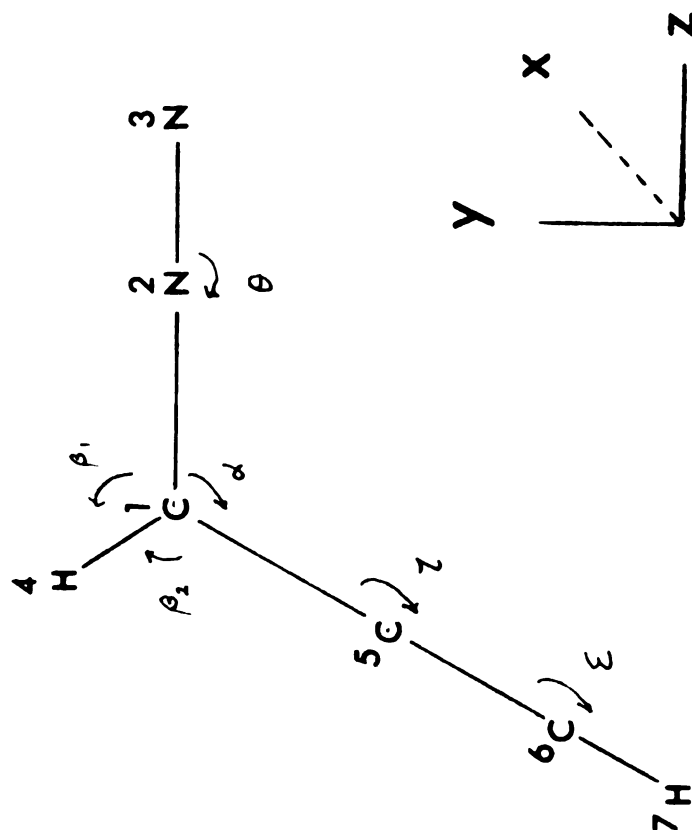


Figure 13.

of diazopropyne. The calculation was carried out on a CDC 6500 computer in the Computer Center at Michigan State University using computer programs written by Schachtschneider (26,27). One of the subroutines in the program can adjust the input force constants by using a least squares method which iterates the force constants until the calculated frequencies give a best fit with the observed frequencies.

For convenience in carrying out the calculation, the A, and A" symmetry classes may be treated separately as two molecules.

A' symmetry class:

Forty-six frequencies for the isotopes $C_3H_2N_2$, $C_3D_2N_2$, C_3HDN_2 , C_3DHN_2 , and $C_3H_2N^{15}N$ are used as input data for the force constant calculation. Due to the previously noted problems in the mixed deuterated diazopropyne gas phase spectrum, matrix frequencies are used for some fundamentals. The normal frequencies of $C_3H_2N^{15}N$ are similar to those of $C_3H_2N_2$, except in a few cases where the ^{15}N atom is heavily involved in the vibrations.

A reasonable fit (average error 6.3 cm^{-1} or 0.5%) of the 46 frequencies is obtained for this class using a total of 18 force constants: eleven diagonal force constants and seven off-diagonal force constants. Three interaction force constants are particularly vital, namely: $F_{CN,CH\text{ wag}}$, $F_{CC,CCN}$, and $F_{C\equiv C,\equiv C-H}$. The calculated results are compared to experiment in Tables VIII - XII, together with the

Table VIII. Normal coordinate analysis of diazopropyne ($\text{C}_3\text{H}_2\text{N}_2$).

Frequencies (cm^{-1})					Primary Contributors (P.E.D)
ν	obs.	Calc.	$\Delta\nu$		
A' ν_1	3331.0	3331.3	-0.3	C-H (95)	
ν_2	3100.0	3080.9	19.1	C-H (98)	
ν_3	2118.0	2123.5	-5.5	$\text{C}\equiv\text{C}$ (69), C-C (15)	
ν_4	2069.0	2071.5	-2.5	$\text{N}\equiv\text{N}$ (63), $\text{C}\equiv\text{N}$ (25), $\text{C}\equiv\text{C}$ (10)	
ν_5	1358.0	1352.4	5.6	C-H wag (53), C-C (20), $\text{C}\equiv\text{N}$ (17), $\text{C}\equiv\text{N}$ wag (-12)	
ν_6	1165.0	1156.0	9.0	$\text{C}\equiv\text{N}$ (47), $\text{N}=\text{N}$ (24)	
ν_7	1058.0	1055.0	3.0	C-H wag (40), C-C (19), CCN (17), CC (15)	
ν_8	681.0	678.6	2.4	$\text{C}\equiv\text{C-H}$ (107), CCH (-12)	
ν_9	*494.0	496.0	-2.0	C-C (50), CCN (42), CNN (31), CC (37)	
ν_{10}	*359.0	361.0	-2.0	CCC (50), CNN (45)	
ν_{11}	(168.0) ^a	161.1	--	CCC (48), CCN (42), CNN (20), C-C (13) CC CCN (-20)	
A" ν_{12}	*525.0	517.4	7.6	H-C $\equiv$ C (101), CCC (9), CCC	
ν_{13}	475.0	459.6	15.4	CNN (62), C-H wag (22)	
ν_{14}	(309.0) ^b	309.1	--	CCC (77), CNN (23)	
ν_{15}	---	247.5	--	C-H wag (68), CCC (15), CNN (13)	

* Matrix frequency.

()^a Raman frequency of solid, not used in force constant calculation.()^b Uncertain band, not used in force constant calculation.

Table IX. Normal coordinate analysis of diazopropyne (C_3HND_2).

Frequencies (cm^{-1})					Primary Contributors (P.E.D.)
	ν	obs.	Calc.	$\Delta\nu$	
A'	ν_1	3100.0	3081.0	19.0	C-H (98)
	ν_2	2599.0	2596.0	3.0	$\equiv$ C-D (68), $C\equiv C$ (28)
	ν_3	*2085.0	2080.3	4.7	N=N (67), C=N (30)
	ν_4	*1982.0	1976.5	5.5	$C\equiv C$ (52), $\equiv$ C-D (29), C-C (14)
	ν_5	*1348.0	1344.6	3.4	C-H wag (55), C=N (18), C-C (17), CN wag (-12)
	ν_6	1165.0	1155.7	9.3	C=N (47), N=N (24), CH wag (10)
	ν_7	*1045.0	1048.5	-3.5	C-H wag (37), C-C (19), CCN (18), C-C (15)
	ν_8	*532.0	537.3	-5.3	$C\equiv C$ -D (107), CCD (-24)
	ν_9	*494.0	491.5	1.5	C-C (48), CCN (39), CNN (33), C-C (-36)
	ν_{10}	*352.0	348.0	4.0	CNN (44), CCC (42)
A''	ν_{11}	(156.0) ^a	154.6	--	CCC (50), CCN (41), CNN (18), C-C (13), C-C (-19)
	ν_{12}	475.0	468.2	6.8	CNN (55), C-H wag (20), CCC (16'), $C\equiv C$ -D (10)
	ν_{13}	*405.0	408.7	-3.7	$C\equiv C$ -D (91), CCC (13), CNN (13), CCC $C\equiv C$ -D (-17)
	ν_{14}	*297.0	295.4	1.6	CCC (54), CNN (24), C-H wag (21)
	ν_{15}	---	241.5	--	C-H wag (58), CCC (23), CNN (10)

* Matrix frequency.

() ^a Raman frequency of solid, not used in force constant calculation.

Table X. Normal coordinate analysis of diazopropyne (C_3DHN_2).

Frequencies (cm^{-1})					Primary Contributors (P.E.D.)
ν	obs.	Calc.	$\Delta\nu$		
A' ν_1	3331.0	3331.3	-0.3	$\equiv C-H$ (95)	
ν_2	*2272.0	2312.7	-40.7	C-D (85)	
ν_3	*2120.0	2121.4	-1.4	$C\equiv C$ (62), C-C (13), N=N (12), C=N (8)	
ν_4	---	2048.5	--	N=N (56), C=N (18), $C\equiv C$ (16)	
ν_5	*1292.0	1293.3	-1.3	C=N (32), C-C (27), C-D wag (19), N=N (14), $C\equiv C$ (16)	
ν_6	---	1090.0	--	C=N (33), CCN (21), N=N (13)	
ν_7	816.0	827.5	-11.5	C-D wag (80)	
ν_8	681.0	677.7	3.3	$C\equiv C-H$ (107), CCH (-11)	
ν_9	*494.0	495.5	-1.5	C-C (50), CCN (41), CNN (32), C-C (-37)	
ν_{10}	*357.0	355.1	-1.9	CCC (50), CNN (44)	
ν_{11}	(168.0) ^a	160.4	--	CCC (48), CCN (43), CNN (20), C-C (13), C-C (-19)	
ν_{12}	*523.0	517.3	5.7	$C\equiv C-H$ (102), CCC (9), $C\equiv C-H$ (-15)	
ν_{13}	*443.0	452.4	-9.4	CNN (68), C-D wag (16)	
ν_{14}	*303.0	307.8	-4.8	CCC (85), CNN (18)	
ν_{15}	---	196.2	--	C-D wag (79), CNN (12)	

* Matrix frequency

()^a Raman frequency of solid, not used in force constant calculation.

Table XI. Normal coordinate analysis of diazopropyne ($C_3D_2N_2$).

Frequencies (cm^{-1})				$\Delta\nu$	Primary Contributors (P.E.D.)
ν	obs.	Calc.			
A' ν_1	2599.0	2597.0	2.0	$\equiv C-D$ (68), $C\equiv C$ (28)	
ν_2	*2265.0	2308.0	-43.3	C-D (88)	
ν_3	2069.0	2069.5	-0.5	$N=N$ (62), $C=N$ (26)	
ν_4	*1972.0	1964.8	7.2	$C\equiv C$ (51), $\equiv C-D$ (27), C-C (12)	
ν_5	*1282.0	1284.6	-2.6	$C=N$ (34), C-C (25), C-D wag (19), $N=N$ (15), $C\equiv C$ (10), $C-D$ wag (-10)	
ν_6	---	1086.2	--	$C=N$ (31), CCN (22), $N=N$ (12), $C-C$ (10)	
ν_7	816.0	826.0	-10.0	C-D wag (80)	
ν_8	*532.0	535.7	-3.7	$C\equiv C-D$ (107), CCN (39), CNN (34), $C-C$ (-36)	
ν_9	*494.0	491.3	2.7	C-C (49), CCN (39), CNN (34), $C-C$ (-36)	
ν_{10}	*346.0	342.7	3.3	CNN (43), CCC (42)	
ν_{11}	(156.0) ^a	153.9	--	CCC (50), CCN (41), CNN (18), C-C (13), $C-C$ (-19)	
A" ν_{12}	*443.0	462.3	-19.3	CNN (57), CCC (18), C-D wag (15), $C\equiv C-D$ (13)	
ν_{13}	*402.0	407.2	-5.2	C C-D (88), CNN (17), CCC (12), CCC (-16)	
ν_{14}	*290.0	291.2	-1.2	CCC (67), CNN (16), C-D wag (10)	
ν_{15}	---	192.9	--	C-D wag (75), CNN (11), CCC (10)	

^a Matrix frequency.

(^a) Raman frequency of solid, not used in force constant calculation.

Table XII. Normal coordinate analysis of diazopropyne ($C_3H_2N^{15}N$).

Frequencies (cm^{-1})					Primary Contributors (P.E.D.)
	ν	obs.	Calc.	$\Delta\nu$	
A'	ν_1	3331.0	3331.3	-0.3	C-H (95)
	ν_2	3100.0	3080.9	19.1	C-H (98)
	ν_3	2112.0	2122.1	-10.1	C C (73), C-C (15)
	ν_4	*2052.0	2053.3	-1.9	$N^{15}N$ (65), CN (28)
	ν_5	1358.0	1350.3	7.7	CH wag (54), C-C (20), CN (15), CH wag (-12)
	ν_6	---	1143.7	--	CN (47), $N^{15}N$ (26)
	ν_7	1058.0	1054.9	3.1	CH wag (40), C-C (19), CCN (17), CC (15)
	ν_8	681.0	678.6	2.4	$C\equiv C-H$ (108), CCH (-12)
	ν_9	*494.0	494.0	0.0	C-C (50), CCN (42), $CN^{15}N$ (30), CC (-38)
	ν_{10}	*354.0	359.0	5.0	CCC (51), $CN^{15}N$ (45)
A''	ν_{11}	---	159.3	--	CCC (47), CCN (42), $CN^{15}N$ (20), C-C (13), CC (-20)
	ν_{12}	*525.0	517.3	7.7	$C\equiv C-H$ (101)
	ν_{13}	475.0	458.1	16.9	$CN^{15}N$ (61), C-H wag (23)
	ν_{14}	---	308.4	--	CCC (78), $CN^{15}N$ (23)
	ν_{15}	---	247.0	--	C-H wag (68), CCC (15), $CN^{15}N$ (14)

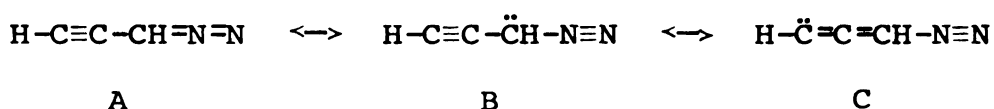
* Matrix frequency.

potential energy distribution among the symmetry coordinates for each normal mode. (Only those symmetry coordinates contributing more than 10% to each normal mode are listed in the Tables.) Introduction of additional interaction force constants brought about no significant improvement in the agreement between the calculated and observed frequencies. The main source of the frequency error shown in Tables VIII-XII is probably anharmonicity, most of it occurring in vibrations where hydrogen atoms are involved. For instance, the calculated deuterium shifts of the apex C-H stretching frequency (3081 cm^{-1} to 2308 and 2313 cm^{-1} from $\text{C}_3\text{H}_2\text{N}_2$ to $\text{C}_3\text{D}_2\text{N}_2$ and C_3DHN_2 respectively) do not agree with the observed frequencies (3100 cm^{-1} to 2265 and 2272 cm^{-1} from $\text{C}_3\text{H}_2\text{N}_2$ to $\text{C}_3\text{D}_2\text{N}_2$ and C_3DHN_2 respectively). These frequency errors seem too big to be accounted for solely by anharmonicity. The same discrepancy occurs in the normal coordinate calculation of CH_3CHO and CH_3CDO (22). In the calculated 2308 and 2313 cm^{-1} normal modes, about 5% C=N and N=N stretches are contributed respectively to the potential energy distribution for each normal mode. Introduction of CH, CN and CH, NN stretching interaction force constants fails to improve the calculated frequencies.

Vibrational Potential Function of Diazopropyne (A')

The C-N bond force constant $K_{11} = 8.92 \times 10^5\text{ dyn/cm}$ is between a single and a double bond (28). The C-N force constant is close to the corresponding C-N force constant,

8.34×10^5 dyn/cm, in diazomethane (6). The interaction force constant between the C-N stretch and the in-plane C-H wag, $F_{19} = 0.402 \times 10^{-3}$ dyn/rad, is fairly large; it makes about a 12% potential energy contribution of ν_5 . This interaction force constant is significant in the valence force field for diazopropyne and it has the same sign and is comparable in magnitude to that of HN_3 (0.466×10^{-3} dyn/rad) (29). In order to rationalize the final calculated force constants and the importance of some interaction force constants, three valence bond resonance structures for diazopropyne are drawn below:



It is well established that relatively large stretch-bend interaction force constants are required to fit the observed vibrational spectra for molecules where intermediate hybridization is implied by such resonance forms (6,12,29,32).

The C-C stretching force constant, $K_{22} = 5.00 \times 10^5$ dyn/cm, is greater than a normal C-C single bond. The bond length of $1.424 \text{ \AA}$ is shorter than an ordinary single bond. The interaction force constant between the C-C=N deformation and the C-C stretch is fairly large ($F_{27} = -0.876 \times 10^{-3}$ dyn/rad); it makes about 15%, 38% and 20% potential energy contributions to ν_7 , ν_9 , and ν_{11} respectively.

The N-N force constant, $K_{33} = 14.13 \times 10^5$ dyn/cm is not quite analogous to that of N_2O : 18.3×10^5 dyn/cm (34) or that of CH_2N_2 : 16.9×10^5 dyn/cm (6). Addition of an interaction force constant between the N-N and C-N stretches failed to improve the calculated frequencies and contributed insignificantly to the potential energy. However, the N-N force constant is greater than that of diazirine (CH_2N_2): 11.18×10^5 dyn/cm (30) and that of CF_2N_2 : 11.18×10^5 dyn/cm (31), and the N-N bond length is shorter than that of these two molecules: both = $1.228 \text{ \AA}$ (31). The N-N bond force constant and bond length in diazirine CH_2N_2 are characteristic of a typical N-N double bond. Thus the final calculated force constants K_{11} and K_{33} support the importance of the suggested resonance structures. The contribution of resonance structures (B) and (C) tends to weaken the C-N bond and strengthen the N-N bond relative to double bonds.

The apex C-H force constant, $K_{44} = 5.14 \times 10^5$ dyn/cm, and the bond length, $1.075 \text{ \AA}$, are close to those of ketene (32) and diazomethane (6). The $C \equiv C$ force constant, $K_{55} = 15.00 \times 10^5$ dyn/cm, is smaller than that of methylacetylene (15.58×10^5 dyn/cm (19)) and that of acetylene (15.80×10^5 dyn/cm (33)). The somewhat low value of the $C \equiv C$ stretching force constant and high value of the C-C stretching force constant may be rationalized by considering the resonance structure (C), which tends to weaken the $C \equiv C$ bond and strengthen the C-C bond.

The acetylenic C-H force constant, $K_{66} = 5.89 \times 10^5$ dyn/cm, is close to that of methylacetylene (5.85×10^5 dyn/cm (19)) and that of the propargyl halides (5.96×10^5 dyn/cm (14)). The acetylenic C-H bond length is a normal value 1.06 Å.

The C-C=N bending force constant $H_{77} = 0.905 \times 10^{-11}$ erg/rad² and the C-H wagging force constant $H_{88} = 0.456 \times 10^{-11}$ erg/rad² are close to the C-C=O bending force constant (1.0×10^{-11} erg/rad²) and the C-H wagging force constant (0.43×10^{-11} erg/rad²) of acetaldehyde (22), respectively.

The in-plane C=N=N bending force constant, $H_{99} = 0.418 \times 10^{-11}$ erg/rad², is close to that of diazomethane (0.48×10^{-11} erg/rad²). The C≡C-C and H-C≡C in-plane skeletal bending force constants, $H_{10,10} = 0.291 \times 10^{-11}$ erg/rad²; $H_{11,11} = 0.245 \times 10^{-11}$ erg/rad² respectively, are close to those of the propargyl halides (C≡C-C bending force constant 0.26×10^{-11} erg/rad² and C≡C-H bending force constant 0.19×10^{-11} erg/rad² (14)). The interaction force constant between the C≡C-C bend and the C≡C-H bend, $F_{10,11} = 0.086 \times 10^{-11}$ erg/rad², contributes about 12% and 9% in potential energy to ν_8 and ν_{11} , respectively. This interaction force constant also supports the existence of resonance structure (C).

The remaining interaction force constants do improve the calculated frequencies slightly, but they contribute

insignificantly to the potential energy. The final calculated force constants are listed in Table XIII.

A" symmetry class:

The A" symmetry class is composed of four out-of-plane internal coordinates. Thirteen frequencies for the isotopes $\text{C}_3\text{H}_2\text{N}_2$, $\text{C}_3\text{D}_2\text{N}_2$, C_3HDN_2 , C_3DHN_2 , and $\text{C}_3\text{H}_2\text{N}^{15}\text{N}$ were used as input data for the force constant calculation. These 13 frequencies were fitted by 9 force constants: 4 diagonal and 5 off-diagonal force constants. The frequency fit was not quite as satisfactory, with an average error of 8 cm^{-1} or 1.8%.

The normal coordinate calculation should be quite simple since only 4×4 matrices are involved in the calculation. However, the potential energy distribution in the normal coordinate calculation indicates that three internal coordinates namely, $\text{C}\equiv\text{C}-\text{C}$, $\text{C}=\text{N}=\text{N}$ out-of-plane bend and C-H out-of-plane wag are involved in ν_{13} , ν_{14} , and ν_{15} . Due to the uncertainty in ν_{14} and the absence of ν_{15} , coupled with the high mixing of internal coordinates in the normal modes, the normal coordinate calculation result is not completely satisfactory in the A" symmetry class.

Vibrational Potential Function of Diazopropyne (A")

The out-of-plane $\text{C}=\text{N}=\text{N}$ bending force constant, $H'_{11} = 0.324 \times 10^{-11}\text{ erg/rad}^2$, is somewhat smaller than that of diazomethane ($0.53 \times 10^{-11}\text{ erg/rad}^2$ (6)) and that of ketene ($0.57 \times 10^{-11}\text{ erg/rad}^2$ (32)).

Table XIII. Valence force constants for diazopropyne.

A' (In-plane vibrations)				
K_{CN}	8.92	K_{C-C}	5.00	K_{NN} 14.13 K_{C-H} 5.14
$K_{C\equiv C}$	15.00	$K_{\equiv C-H}$	5.89	H_{CCH} 0.905 H_{CH} wag 0.456
H_{CNN}	0.418	H_{CCC}	0.291	$H_{H-C\equiv C}$ 0.245 F_{CN} 0.402 CH wag
F_{CC} CCN	-0.876	F_{CNN} CCC	0.010	F_{CNN} 0.026 F_{CCC} 0.086 $H-C\equiv C$
$F_{C\equiv C}$ C-H	-0.155	F_{CC} CH wag	0.016	
A'' (out-of-plane vibrations)				
H'_{CNN}	0.324	H'_{CCC}	0.239	H'_{CH} wag 0.042 $H'_{C\equiv C-H}$ 0.140
F'_{CNN} CCC	0.005	F'_{CNN} CH wag	0.007	F'_{CCC} 0.045 F'_{CCC} CH wag -0.008 $C\equiv C-H$
F'_{CNN} $C\equiv C-H$	-0.011			

Units: 10^5 dyn/cm for stretching force constants, 10^{-11} erg/rad² for bending, and 10^{-3} dyn/rad for stretch-bend interactions.

The out-of-plane $\text{C}\equiv\text{C}-\text{C}$ and $\text{C}\equiv\text{C}-\text{H}$ bending force constants, $H_{22}' = 0.239 \times 10^{-11}$ erg/rad² and $H_{33}' = 0.140 \times 10^{-11}$ erg/rad² respectively, also do not correlate closely with those of the propargyl halides (14): 0.33×10^{-11} erg/rad² and 0.19×10^{-11} erg/rad² for the $\text{C}\equiv\text{C}-\text{C}$ out-of-plane bending force constants, respectively.

The out-of-plane C-H wagging force constant cannot be calculated, since no observed frequency is assigned to ν_{15} . However, due to the similarity between diazomethane and diazopropyne, the author used the out-of-plane CH_2 wagging force constant of diazomethane, 0.042×10^{-11} erg/rad², in the normal coordinate analysis. Further work should be done on the out-of-plane C-H wag of diazopropyne, which may well lie below the most efficient region of the Perkin-Elmer 225 infrared spectrophotometer.

The interaction force constant between the $\text{C}\equiv\text{C}-\text{C}$ and $\text{C}\equiv\text{C}-\text{H}$ out-of-plane bends, $F_{23}' = 0.045 \times 10^{-11}$ erg/rad², contributes about 15% to the potential energy distribution for ν_{12} . The remaining interaction force constants are relatively small in value, and contribute no more than 5% to the potential energy distribution of any normal mode, but introduction of these interaction force constants does improve the calculated frequencies in A'' symmetry class. The final calculated force constants of A'' symmetry class are also listed in Table XIII.

Conclusion

From a comparison of the force constants of diazopropyne with those of diazomethane, the propargyl halides, and with some typical force constants such as those for ordinary $\text{N}=\text{N}$ double bonds, $\text{C}\equiv\text{C}$ triple bonds, $\text{C}-\text{C}$ single bonds, and $\text{C}=\text{N}$ double bonds, it is concluded that the electronic structure of diazopropyne is slightly different from that of diazomethane and of the propargyl halides. However, diazopropyne has possible resonance structures, such as (A), (B), and (C) which cannot be written for these prototype molecules. Although properly a molecular orbital population analysis should be carried out to better describe the electronic structure of diazopropyne, many of the force constants derived from the normal coordinate analysis can be rationalized in terms of contributions from these valence bond structures.

CHAPTER II

INFRARED SPECTRUM OF THE PROPARGYLENE FREE RADICAL

Having established a background spectrum of diazopropyne, the author proceeds to seek, identify and characterize the photolysis products of this fairly unstable molecule. Of special interest is the propargylene radical, C_3H_2 , which has been observed by Skell and coworkers (7) who demonstrated by means of electron spin resonance spectroscopy that diazopropyne yields the propargylene radical when photolyzed in organic solvents at $77^{\circ}K$. Analysis of the ESR spectrum showed the C_3H_2 radical to be linear in the organic solvent (7). The author has reproduced the ESR spectrum of the propargylene radical in ether and polychlorotrifluoroethylene at $77^{\circ}K$. The infrared spectra of matrix isolated propargylene radical and of isotopic propargylene produced by photolysis of matrix-isolated mixed deuterated diazopropyne were obtained, and provided information regarding the symmetry of this radical, which is established as $D_{\infty h}$. Attempts to obtain a Raman spectrum of matrix-isolated diazopropyne were made, but due to the weak scattering activity of the dilute guest molecules the experiment was not successful. Thus the Raman spectrum of propargylene radical could not be obtained.

Experimental

Photolysis studies using matrix isolation can be performed in two ways: photolysis after deposition (deposition followed by in situ photolysis) and photolysis during deposition. If in situ photolysis is successful, it gives the most clear-cut results. A matrix containing parent molecules is deposited and the intensity of the parent molecules absorption monitored. After a period of photolysis ranging from five minutes to one hour the spectrum is studied. A decrease in the intensity of the absorption bands of the parent molecule, and the appearance of new absorptions clearly indicate the formation of new molecules or radicals. Unfortunately, in situ photolysis is often inefficient. The "cage effect" is used to explain this inefficiency. In the matrix the parent molecule is "locked" in the host lattice. If the molecule is dissociated by the radiation one of the fragments must have sufficient energy to penetrate the wall of the site it occupies and attain a different site. If this does not occur, generally the fragments will recombine and no result will have been achieved by the photolysis of the parent molecules. This is so-called "cage effect". One way to overcome the "cage effect" is to photolyze during deposition. In this case, fragments from molecules photolyzed in the gas phase separate before they are condensed on the sample window, and under these circumstances the "cage effect" operates to prevent recombination. If molecules are photolyzed as they

condense they can also separate on the surface in the few instants before the matrix becomes truly rigid. In the diazopropyne case, since the fragment N_2 is quite stable, in situ photolysis will be relatively efficient.

As mentioned in the Experimental section of Chapter I, a Malaker Corp. Cryomite VII-C closed cycle helium refrigerator was used, which was fitted with a spray-on copper window holder and an inverted "T"-shaped brass outer jacket (see detail on Fig. 3, Chapter I) for the present infrared matrix isolation and photolysis study. In the diazopropyne matrix isolation experiment the matrix-to-sample ratio M/S was about 200 to 1, and the deposition rate was 1-3 m mole per hour. This deposition rate was controlled with a needle valve and was chosen to give minimum scattering and maximum transparency. The deposition period was about 2-3 hours for each experiment. The entire sample was deposited at 30°K before initiating photolysis. The in situ photolysis was carried out using a Bausch and Lomb 33-86-20 xenon light source with 150 W output, and in some experiments a Dow Corning CS051 filter was placed in front of the xenon lamp to cut off wave lengths of less than 3500 Å. The purpose of applying a Pyrex glass filter was to distinguish the various photolysis products which were induced by photons with different energies. After taking a few spectra, the Pyrex glass filter was removed and a few more spectra were taken after unfiltered photolysis.

An infrared study was performed over the range of 200 to 4000 cm^{-1} with a purged Perkin Elmer 225 grating infrared spectrophotometer which has resolution of better than 1 cm^{-1} above 450 cm^{-1} and better than 2 cm^{-1} below 450 cm^{-1} . The reported frequencies should be accurate to within $\pm 2\text{ cm}^{-1}$. The matrix gases used were research grade krypton and xenon from the Matheson Gas Company. The propargylene radical was also produced for ESR study by trapping gaseous diazopropyne in polychlorotrifluoroethylene at liquid nitrogen temperature and then photolyzing with the xenon discharge lamp. The ESR spectrum was obtained on a Varian V-4500-108 X-band spectrometer.

Results and Discussion

Based on the conclusion of Skell's ESR study (7), that the propargylene radical is linear, the author assumes $D_{\infty h}$ symmetry for C_3H_2 . Thus it should have ten normal modes, of which three are degenerate, so there should be seven distinct fundamental frequencies for C_3H_2 . Two belong to Σ_g^+ symmetry, two to Σ_u^+ symmetry, one to π_g symmetry and two to π_u symmetry. The Σ_u^+ and π_u vibrations are infrared active and the Σ_g^+ and π_g vibrations are Raman active. However, for the monodeutero propargylene radical, C_3HD , the symmetry is lowered to $C_{\infty v}$. In this case four fundamentals belong to Σ^+ symmetry and three to π symmetry; all showing both infrared and Raman activity. The infrared spectra of diazopropyne and of mixed deuterated

diazopropyne in krypton matrices after photolysis with light from a xenon discharge lamp are shown in Figure 14. The frequencies of new absorption bands occurring upon photolysis and disappearing upon annealing in these matrix spectra are shown in Table XIV.

The identification of the absorption bands due to photolysis products, in particular free radicals is achieved by observing the growth of the new absorption bands upon continued photolysis and the decrease or disappearance of these new absorption bands upon controlled annealing. The annealing softens the matrix and permits the diffusion of the isolated reactive species. The absorption bands due to the same reactive species should behave in the same fashion (change of band intensity) upon photolysis and annealing. Furthermore, photolysis through various filters may help distinguish different photolysis products.

Bands at 3285, 3279, 2140, 408, 402, 259, and 249 cm^{-1} are suggested as being due to the C_3H_2 radical. The growth rate of these bands is effectively unchanged when the Pyrex glass filter is placed in front of the xenon photolysis lamp. The species responsible for these absorptions is thus formed by radiation with wavelength longer than 3500 Å. This is in agreement with the probable mechanism of the formation of the C_3H_2 radical, since the formation of C_3H_2 requires only enough energy to break the very labile N_2 group away from $\text{C}_3\text{H}_2\text{N}_2$. The formation of other possible free radicals would probably require higher energy radiation.

Figure 14. Infrared spectrum of photolyzed matrix-isolated diazopropyne.

- A. $C_3H_2N_2$ after photolysis without Pyrex glass filter.
- B. A mixture of $C_3H_2N_2$, C_3HDN_2 , C_3DHN_2 , and $C_3D_2N_2$ after photolysis with Pyrex glass filter.

The bands marked with a check are due to propargylene radical and its deuterated analogs, C_3HD and C_3D_2 .

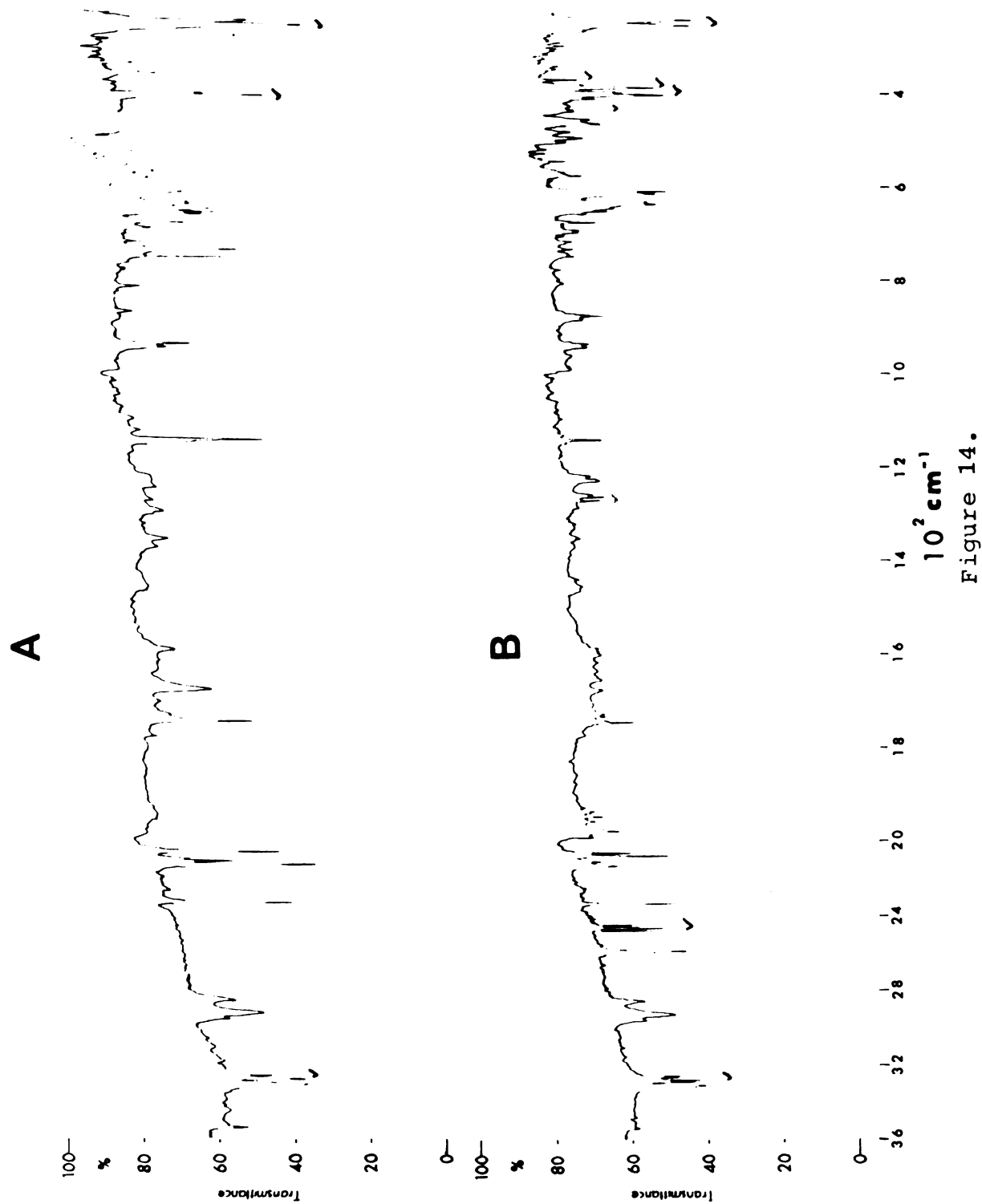


Table XIV. Bands occurring upon photolysis of diazopropyne which disappear upon annealing.

$C_3H_2N_2 \xrightarrow{h\nu}$	$C_3H_2N_2, C_3HDN_2 \xrightarrow{h\nu}$ $C_3DHN_2, C_3D_2N_2$
Frequencies (cm^{-1})	Frequencies (cm^{-1})
*3285 (s)	*3291 (m)
*3279 (w, sh)	*3285 (s)
*3260 (m)	*3270 (w)
	*3260 (m)
	*2482 (m)
	*2471 (s)
	*2469 (m)
	*2458 (m)
2145 (m) ^a	2145 (m) ^a
*2140 (w)	*2140 (vw)
	*2115 (vw)
1747 (m)	1747 (w), 1745 (vw)
	1264 (vw)
1150 (w, sh)	1150 (w, sh)
1146 (m)	1146 (w)
754 (w)	754 (w)
738 (w)	738 (w)
581 (m)	581 (m)
550 (m)	550 (m)
	* 416 (w)
* 408 (s)	* 408 (s)
* 402 (sh)	* 402 (s)
	* 392 (s)
	* 386 (w, sh)
	* 375 (w)
* 259 (s)	* 259 (s)
* 257 (sh)	* 257 (sh)
	* 254 (sh)
* 249 (m)	* 249 (s)
* 247 (m)	* 247 (s)

*The bands which behave in same fashion are due to C_3H_2 or its deuterium isotopes C_3D_2 and C_3HD .

^aDue to CO monomer.

These absorption bands show corresponding intensity behavior upon photolysis and annealing, and the suggested assignment receives support from the deuterium isotopic shift study and the normal coordinate analysis.

Assignment of C_3H_2 Fundamentals

Assuming that propargylene is a linear, symmetric molecule, the infrared spectrum should exhibit four fundamentals: two each in the Σ_u^+ and π_u symmetry classes. These are designated ν_3 , ν_4 , ν_6 , and ν_7 according to the accepted numbering scheme (18). As in Chapter I, only frequencies observed in krypton matrices will be discussed in the text.

ν_3

Bands at 3285, 3279, and 3260 cm^{-1} are observed in the photolyzed diazopropyne matrix spectrum Figure 14. The 3285 cm^{-1} band is the strongest among them, 3279 cm^{-1} is a very weak shoulder, and the 3260 cm^{-1} band is relatively weak. The weak shoulder at 3279 cm^{-1} is possibly due to a "matrix site effect" (the propargylene radicals occupying two different kinds of sites in the host matrix lattice), since its frequency is quite close to 3285 cm^{-1} and its intensity is so weak. The band at 3260 cm^{-1} may be due to the perturbation of the propargylene radical by a single N_2 , also a photolysis product, located on a site adjacent to the propargylene radical (35). The 3285 cm^{-1}

band is within the range of frequencies for an acetylenic C-H stretching motion, and this motion is expected for C_3H_2 since the outer carbon atoms have sp hybridization character. In the photolyzed mixed deuterated diazopropyne matrix spectrum (Fig. 14), two sets of related bands are observed: 3291, 3285, 3270, 3260 cm^{-1} and 2482, 2471, 2469, 2458 cm^{-1} . In the first set, the four bands appear as two pairs, at 3285 and 3260 cm^{-1} and at 3291 and 3270 cm^{-1} , the lower frequency in each pair may be due to the perturbation by N_2 . The first pair is obviously due to C_3H_2 , and the second doublet represents the corresponding C-H motion in C_3HD . Again, the stronger component (3291 cm^{-1}) was chosen as the vibrational frequency for the normal coordinate analysis. The same situation is encountered in the C-D stretching region. The pair of bands at 2471 and 2458 cm^{-1} grows together and is assigned to C_3HD . The 2471 cm^{-1} band is normally the strongest in this set. One would expect more C_3HD formed than C_3D_2 in the photolysis of the deuterated mixture, and relative intensities of parent molecule absorptions support this expectation. The pair of bands at 2482 and 2469 cm^{-1} grow in the same fashion, and are due to C_3D_2 . Again, the 2469 and 2458 cm^{-1} bands may be due to the perturbation by N_2 . Thus, the bands at 3291 and 3285 cm^{-1} are respectively assigned to the C-H stretch (ν_1) in C_3HD and the antisymmetric C-H stretch (ν_3) in C_3H_2 . The bands at 2482 and 2471 cm^{-1} are assigned respectively to the antisymmetric C-D stretch (ν_3) in C_3D_2

and the C-D stretch (ν_2) in C_3HD . These assignments receive support from the normal coordinate calculation.

ν_4

In a previous experimental investigation of carbon vapor condensed in an argon matrix at 4^0K , a band at 2040 cm^{-1} was observed, and assigned to the antisymmetric stretching mode in the C_3 radical (9). Also bands due to the C=C antisymmetric stretch were observed at 1957, 1940 and 1921 cm^{-1} in the spectra of allene (C_3H_4) and the isotopic allenes $C_3H_2D_2$ and C_3D_4 respectively (13). On the basis of this information, one would expect that the C=C antisymmetric stretching vibrations should fall in the neighborhood of 2000 cm^{-1} for the propargylene radical and its deuterated isotopes, since the carbon-carbon bonding situation is similar in all these cases.

When matrix-isolated $C_3H_2N_2$ is photolyzed with near ultraviolet radiation ($3500\text{ \AA}$) a band is observed at 2140 cm^{-1} in the infrared spectrum, Figure 15. The intensity of this band is difficult to follow, since this region is complicated by absorption from monomeric and aggregated CO (36). A weak band at 2115 cm^{-1} , Figure 16, remains in the matrix infrared spectrum of the deuterated diazopropyne mixture after complete photolysis of the parent molecules. A weak shoulder at about 2065 cm^{-1} is also sometimes observed on a strong parent molecule absorption in the latter experiments. These bands appear to grow upon continued

Figure 15. Infrared spectra of photolyzed diazopropyne in krypton matrix (2150 - 2000 cm^{-1}).

- A. Before photolysis
- B. After photolysis
- C. After photolysis and partial annealing at 60°K
- D. Expanded scale of B
- E. Expanded scale of C

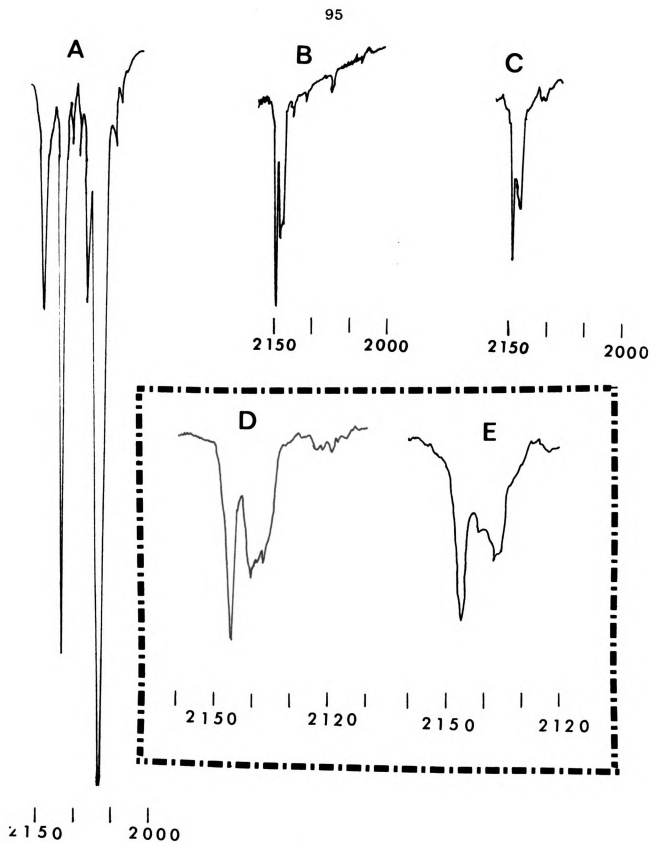


Figure 15.

Figure 16. Infrared spectra of photolyzed mixed diazopropyne and deuterated diazopropyne in krypton matrix ($2150 - 2000 \text{ cm}^{-1}$).

- A. Before photolysis
- B. After photolysis
- C. After photolysis and partial annealing at 60°K

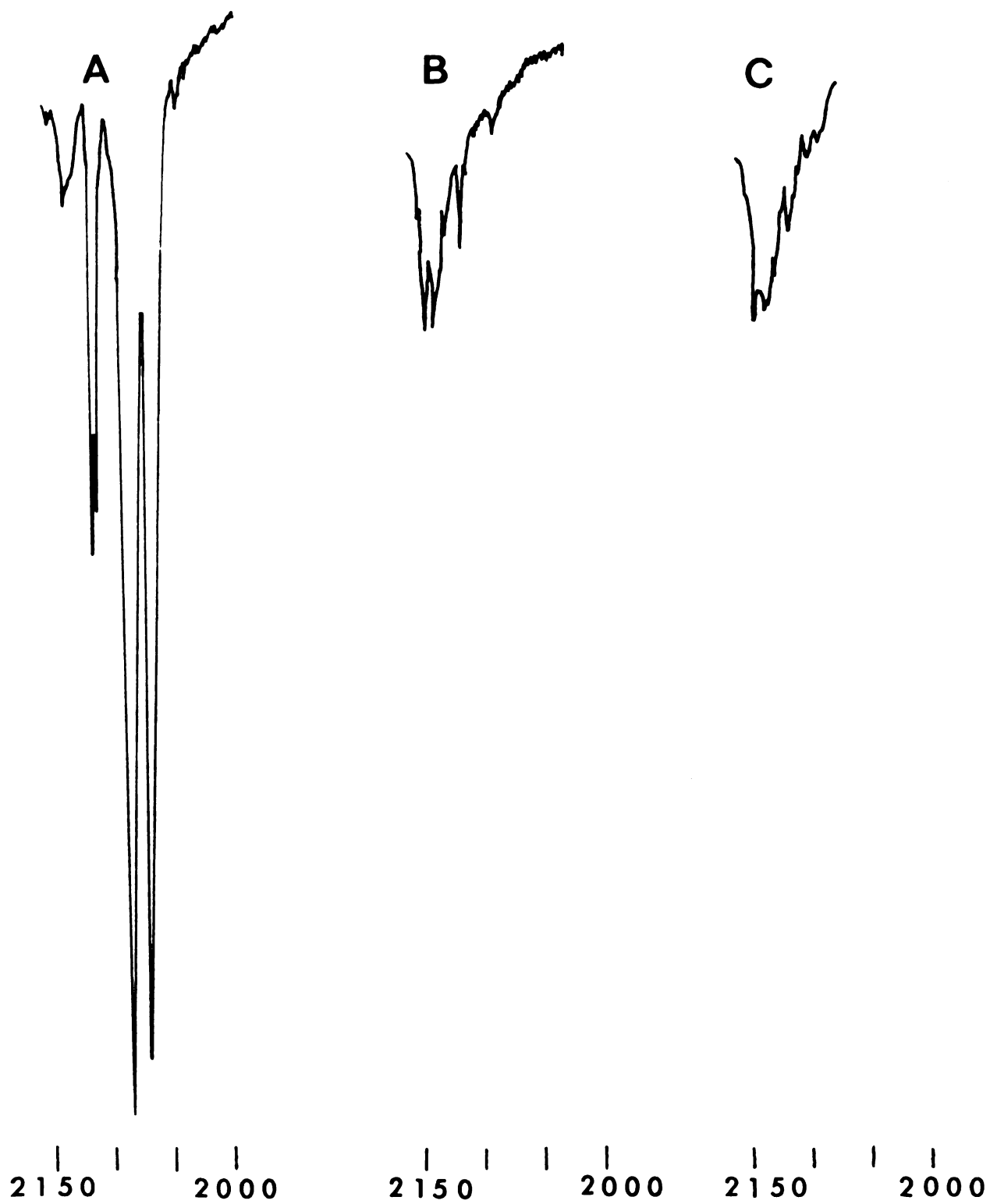


Figure 16.

photolysis, and disappear upon annealing, and they are therefore attributed to the isotopic propargylene radicals. The intensities of these absorptions are extremely weak in comparison to the C-H and C-D stretching vibrations. On the basis of the normal coordinate calculation, the bands at 2140 (ν_4) and 2115 cm^{-1} (ν_3) are C=C antisymmetric stretching vibrations in C_3H_2 and C_3HD . The absorption near 2065 cm^{-1} is less well established. However, the calculated frequency for the antisymmetric C=C stretch of C_3D_2 is 2064 cm^{-1} , so one may tentatively assign the shoulder at 2065 cm^{-1} to ν_4 of perdeuteropropargylene.

A very weak band at 1264 cm^{-1} was also observed in the infrared spectrum of mixed deuterated propargylene radical. It grows and disappears respectively upon photolysis and annealing. On the basis of normal coordinate calculation the band at 1264 cm^{-1} is assigned to ν_4 of C_3HD , the "symmetric stretching" vibration.

π_u symmetry class

ν_6

A strong band at 408 cm^{-1} and a medium intensity band at 402 cm^{-1} are observed in the photolyzed diazopropyne matrix spectrum, the latter is perhaps due to the perturbation of C_3H_2 by N_2 . After photolysis of mixed deuterated diazopropyne matrices bands at 416, 408, 402, 392, 386, and 375 cm^{-1} are observed. It should be noted that since C_3HD

has $C_{\infty v}$ symmetry, the π_g mode in $D_{\infty h}$ changes into a π mode and becomes infrared active. Thus one more band is expected to be observed in C_3HD than in C_3H_2 or C_3D_2 in the π symmetry class.

The 416 and 375 cm^{-1} bands grow and disappear respectively upon photolysis and annealing in the same fashion as the 3291 and 2471 cm^{-1} bands (ν_1 and ν_2 in C_3HD), and the behavior of the 392 and 386 cm^{-1} bands parallel that of the 2482 cm^{-1} band (ν_3 in C_3D_2) with respect to varying isotopic distributions in all experiments.

According to the normal coordinate calculation, the deuterium isotopic shift, the relative intensity behavior, and a comparison of frequencies with those of related molecules [C_3S_2 (11) and C_3N_2 (12) have ν_6 frequencies of 462 and 392 cm^{-1} respectively], the 408 cm^{-1} band in the photolyzed diazopropyne matrix spectrum is assigned to ν_6 for the C_3H_2 radical and the 416, 375, and 392 cm^{-1} bands in the photolyzed mixed deuterated diazopropyne matrix spectrum are assigned to ν_5 and ν_6 for the C_3HD radical and ν_6 for the C_3D_2 radical respectively. Because of the change in symmetry, and the consequent different contribution of the internal modes to the normal modes of vibration, the C_3HD frequencies (ν_5 and ν_6) span the values of ν_6 for C_3H_2 and C_3D_2 . This complication also affects the relative intensities of these motions.

ν_7

There are few bands observed below 300 cm^{-1} in the photolyzed diazopropyne matrix spectrum. A strong, poorly resolved doublet is noted at 259 and 257 cm^{-1} , along with medium intensity feature at 249 and 247 cm^{-1} . (The latter pair may be due to the perturbation of C_3H_2 by N_2 .) The intensities of the bands at 259 and 247 cm^{-1} are approximately equal in the infrared spectrum of the photolyzed deuterated mixture, in contrast with their counterparts in photolyzed diazopropyne matrix spectrum. The increase in intensity at 247 cm^{-1} in the deuterated spectrum is probably due to the presence of some other photolysis product since the 247 cm^{-1} band does not disappear proportionately with 259 cm^{-1} band upon annealing. The 259 cm^{-1} band behaves in the same fashion upon photolysis and annealing as the 3285 and 408 cm^{-1} bands. Thus the 259 cm^{-1} band is assigned to ν_7 for C_3H_2 . The deuterium shifts of this absorption in C_3HD and C_3D_2 were not observed. According to the normal coordinate calculation, ν_7 for C_3D_2 is around 200 cm^{-1} and ν_7 for C_3HD is around 220 cm^{-1} ; the former is probably beyond the effective low-frequency limit of the infrared instrument, and the latter is perhaps too weak to be observed. (The other bending modes of C_3HD are quite weak.)

According to the normal coordinate analysis, the ν_6 and ν_7 normal modes of C_3H_2 correspond to a mixture of CCH and CCC bends. It is expected that the electron

density around $C=C=C$ and $C=C-H$ in C_3H_2 will change when the C_3H_2 radical is bent. In other words, there will be interactions between $C=C-H$ and $C=C=C$ bends. Therefore, the mixing of these two bending vibrations in the normal modes is expected, and it is not appropriate to assign individual group frequencies to ν_6 and ν_7 .

Other Bands

Bands at 1747, 1146, 754, 738, 581, and 550 cm^{-1} are also observed both in infrared spectra of photolyzed matrix isolated diazopropyne and mixed deuterated diazopropyne. All of these bands behave like reactive species. The intensities of the 1747, 1146, 754, and 738 cm^{-1} bands are quite strong when the Pyrex glass filter is not used in the photolysis, but weak in filtered photolysis. The intensities of the 581 and 550 cm^{-1} bands do not grow and disappear, in photolysis and annealing experiment, proportionately with bands assigned to C_3H_2 . Furthermore, there are no corresponding deuterium isotope shifts observed for any of the bands discussed in this section. Thus one must conclude that these bands are not due to C_3H_2 . Thus a further study of these bands is suggested.

Vibrational Potential Function and Related Properties of Propargylene

Normal Coordinate Analysis

Due to the absence of the six Raman active fundamentals of the C_3H_2 and C_3D_2 radicals, a complete normal coordinate analysis cannot be carried out for propargylene. However, there are still enough frequencies from infrared active fundamentals of C_3H_2 , C_3D_2 , and C_3HD to carry out the normal coordinate calculation and obtain meaningful valence force field potential constants.

The calculation is carried out by the same method used for diazopropyne. The internal and symmetry coordinates for the propargylene radical are shown respectively in Figure 17 and Table XV. The skeletal structure parameters $r_{CH} = 1.07 \text{ \AA}$ and $r_{CC} = 1.30 \text{ \AA}$ are taken from the related molecule allene (13). The initial force constants were transferred from the related molecules allene (13) and C_3 (9).

Twelve frequencies for the isotopes C_3H_2 , C_3D_2 , and C_3HD radicals were used as input data for the force constant calculation. These twelve frequencies were fit by eight independent force constants, of which four interaction force constants ($F_{CC,CH}$, $F_{CC,CC}$, $F_{CCH,CCH}$, and $F_{CCC,CCH}$) were important in the analysis. The calculated results are compared to experiment in Table XVI, together with the potential energy distribution among the internal coordinates

1000

Figure 17. Internal coordinates for the propargylene radical.

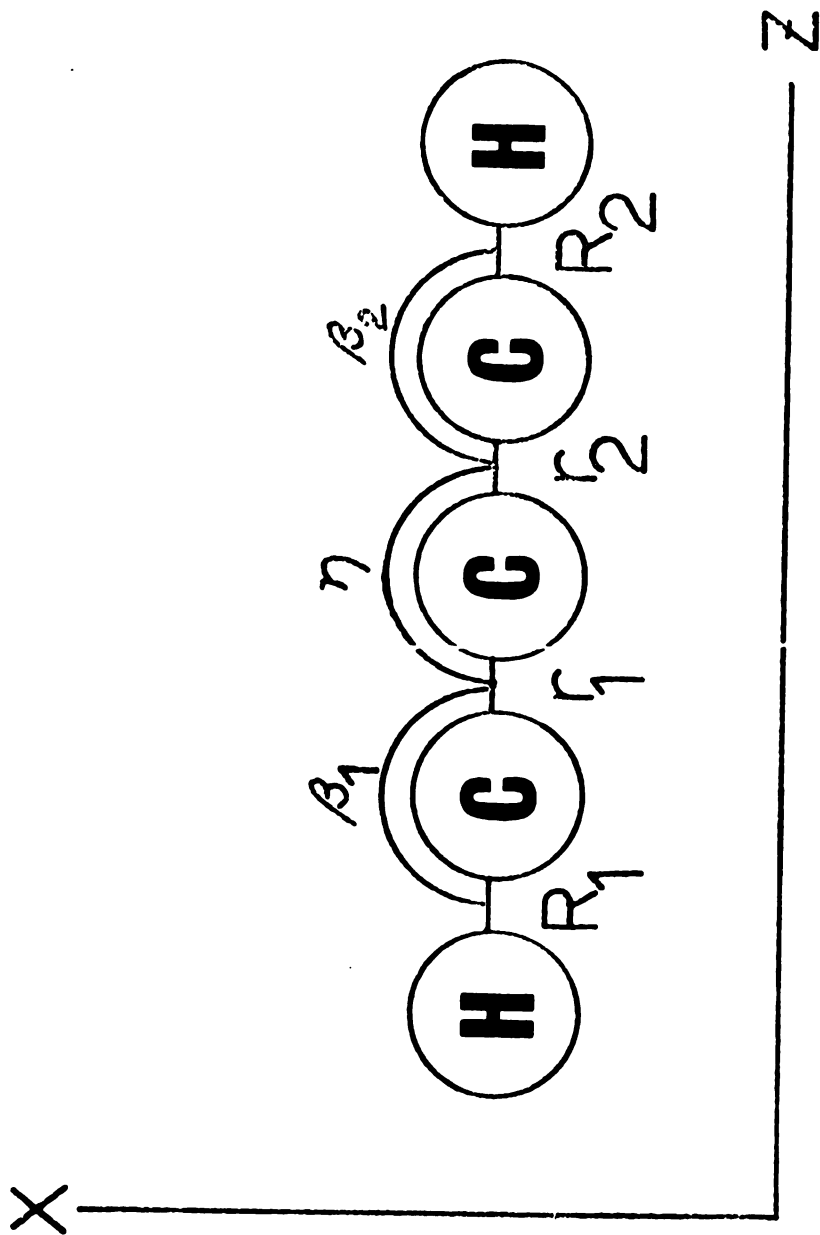


Figure 17.

Table XV. Symmetry coordinates for the propargylene radical.

Σ_g^+	
	$S_1 = \Delta R_1 + \Delta R_2$
	$S_2 = \Delta r_1 + \Delta r_2$
Σ_u^+	
	$S_3 = \Delta R_1 - \Delta R_2$
	$S_4 = \Delta r_1 - \Delta r_2$
π_g	
	$S_5 = \Delta\beta_1 - \Delta\beta_2$
π_u	
	$S_6 = \Delta\eta$
	$S_7 = \Delta\beta_1 + \Delta\beta_2$

Table XVI. Normal coordinate analysis of the propargylene radical.

		Frequencies (cm ⁻¹)			Primary Contributors		
ν		Obs.	Calc.	$\Delta\nu$	(PED)		
C₃H₂							
Σ_g^+	ν_1	--	3288.0	--	C-H (100)		
	ν_2	--	1297.2	--	C=C 92, $\begin{smallmatrix} \text{C}=\text{C} \\ \text{C}=\text{C} \end{smallmatrix}$] (7)		
Σ_u^+	ν_3	3295.0	3286.7	-1.7	C-H (100)		
	ν_4	2140.0	2149.0	-9.0	C=C 106, $\begin{smallmatrix} \text{C}=\text{C} \\ \text{C}=\text{C} \end{smallmatrix}$] (-7)		
π_g	ν_5	--	430.9	--	$\beta + \beta\beta$ (100)		
π_u	ν_6	408.0	409.2	-1.2	$\beta - \beta\beta$ (52), $\eta - \beta\eta$ (48)		
	ν_7	259.0	257.7	1.3	$\beta - \beta\beta$ (48), $\eta + \beta\eta$ (52)		
C₃D₂							
Σ_g^+	ν_1	--	2445.8	--	C-D (96)		
	ν_2	--	1233.3	--	C=C 87, $\begin{smallmatrix} \text{C}=\text{C} \\ \text{C}=\text{C} \end{smallmatrix}$] (16)		
Σ_u^+	ν_3	2482.0	2483.2	-1.1	C-D (81), C=C (26)		
	ν_4	(2065.0)	2063.6	--	C=C (82), C-D (19)		
π_g	ν_5	--	336.2	--	$\beta + \beta\beta$ (100)		
π_u	ν_6	392.0	390.8	1.2	$\eta - \beta\eta$ (67), $\beta - \beta\beta$ (33)		
	ν_7	--	195.8	--	$\beta - \beta\beta$ (67), $\eta + \beta\eta$ (33)		
C₃HD							
Σ^+	ν_1	3291.0	3287.7	3.3	C-H (100)		
	ν_2	2471.0	2466.3	4.7	C-D (87), C=C (18)		
	ν_3	2115.0	2105.3	9.7	C=C (92), C-H (11)		
	ν_4	1264.0	1264.3	-0.3	C=C (90), $\begin{smallmatrix} \text{C} & \text{C} \\ \text{C} & \text{C} \end{smallmatrix}$] (7)		
π	ν_5	416.0	416.0	0.0	$\beta - \beta\beta$ (75), $\eta - \beta\eta$ (24)		
	ν_6	375.0	375.1	-0.1	$\beta + \beta\beta$ (61), $\eta - \beta\eta$ (38)		
	ν_7	--	219.5	--	$\beta - \beta\beta$ (63), $\eta + \beta\eta$ (36)		
$K_{\text{C-H}}$	K_{CC}	K_{CCH}	H_{CCC}	$F_{\text{CH}}^{\text{CC}}$ CC	$F_{\text{CC}}^{\text{CC}}$ CC	$F_{\text{CCH}}^{\text{CCH}}$	$F_{\text{CCC}}^{\text{CCH}}$
5.93	12.05	0.078	0.246	0.564	0.868	-0.020	0.006

() uncertain band not used in force constant calculation.

Units: 10^5 dyn/cm for stretching force constants, 10^{-11} erg/rad² for bending, and 10^{-3} dyn/rad for bend-stretch interactions.

for each normal mode (only those contributing more than 10% to each normal mode are listed), and the final calculated force constants. The fit of the calculated frequencies with those observed is excellent, with average error 2.7 cm^{-1} or 0.11%.

Vibrational Potential Function of Propargylene

The C-H stretching force constant, $K_{\text{C-H}} = 5.93 \times 10^5 \text{ dyne/cm}$, is close to that of propargyl halides ($5.96 \times 10^5 \text{ dyne/cm}$) (14) and that of methylacetylene ($5.85 \times 10^5 \text{ dyne/cm}$) (19) a prototype acetylenic C-H stretching force constant. This indicates that the C-H bond in the propargylene radical has acetylenic character.

The C-C stretching force constant, $K_{\text{C-C}} = 12.05 \times 10^5 \text{ dyne/cm}$, of C_3H_2 is slightly higher than that of C_3H_4 ($10.08 \times 10^5 \text{ dyne/cm}$) (13), since in the latter case the outer carbon atoms are sp^2 hybridized, but in the former case the outer carbon atoms are sp hybridized.

The H-C=C bending force constant, $H_{\text{HCC}} = 0.078 \times 10^{-11} \text{ erg/rad}^2$, is somewhat smaller than the H-C≡C bending force constant of propargyl halides ($0.14 \times 10^{-11} \text{ erg/rad}^2$) (14). However, the bonding situation is rather different in the present case. The unpaired spin density on the terminal carbon atoms would tend to more readily permit the rehybridization which accompanies CCH bending, and thus lead to a lower bending force constant.

The C=C=C bending force constant, $H_{\text{CCC}} = 0.246 \times 10^{-11}$ erg/rad², falls between that of allene (0.40×10^{-11} erg/rad²) (13) and that of the first excited state of the C₃ radical (0.11×10^{-11} erg/rad²) (37).

The C=C=C bending force constant is worth special discussion, since it can be correlated with the electronic structures of some simple linear molecules with cumulated double bonds, such as C₃, C₃H₂, C₃H₄, etc. Considering first the C=C=C bending force constant of the ground state of the C₃ radical, and extremely low value (around 0.005×10^{-11} erg/rad²) is found (37). However, the same bending force constant increases to 0.11×10^{-11} erg/rad² in the first excited state of C₃ radical. This may be understood in light of the suggested correlation between central carbon atom electron density and ease of bending. The electron density in the π_u orbital of ground state C₃ radical ($\sigma_u^2 \pi_u^4$), as calculated by Clementi and McLean (38), is primarily located on the central carbon atom and therefore would remain relatively unaffected by a change in geometry such as that of the bending motion. Thus an extremely small bending force constant is expected. The low bending force constant of C₃ also receives support from a recent ab initio calculation (39). The bending potential for this normal mode is quite anharmonic (near to a square well with minimum at a central carbon angle around 180°), which would lead to a low bending frequency.

However a similar calculation for CO_2 ($\sigma_u^2 \pi_u^4 \pi_g^4$) (40) shows that the π_g orbital has a "dumbbell" shape. For the case of first excited state of the C_3 radical ($\sigma_u^2 \pi_u^3 \pi_g$), the promoted electron density is distributed primarily on the ends of the molecule. Undoubtedly, bending either molecule would increase electronic repulsion considerably, with a much greater effect for CO_2 . Thus a relatively large bending force constant is expected.

Following the same argument, the $\text{C}=\text{C}=\text{C}$ bending force constant of the C_3H_2 radical ($\sigma_u^2 \pi_u^4 \pi_g^2$) would be between the CO_2 bending force constant (0.57×10^{-11} erg/rad²) (18) and that of the first excited state of the C_3 radical (0.11×10^{-11} erg/rad²). Indeed, this prediction is borne out by the present normal coordinate analysis; the C_3H_2 radical has a CCC bending force constant of 0.246×10^{-11} erg/rad².

Although the stretching interaction force constants, $F_{\text{CH,CC}} = 0.564 \times 10^5$ dyne/cm and $F_{\text{CC,CC}} = 0.869 \times 10^5$ dyne/cm, contribute no more than 10% to the potential energy distribution of the related normal modes, the introduction of these two interaction force constants certainly improves the fit between the observed and calculated frequencies. The relatively large $F_{\text{CC,CC}}$ interaction force constant suggests the possible resonance structures $\text{H}-\dot{\text{C}}=\text{C}=\dot{\text{C}}-\text{H} \longleftrightarrow \text{H}-\ddot{\text{C}}-\text{C}\equiv\text{C}-\text{H} \longleftrightarrow \text{H}-\text{C}\equiv\text{C}-\ddot{\text{C}}-\text{H}$, similar to those which may be drawn for CO_2 ($\text{O}=\text{C}=\text{O} \longleftrightarrow \text{O}-\text{C}\equiv\text{O} \longleftrightarrow \text{O}\equiv\text{C}-\text{O}$) (41). Introduction of the $F_{\text{CH,CC}}$ interaction force constant

improves the calculated frequencies in the Σ_u^+ symmetry block a great deal. The bending interaction force constants, $F_{CCH,CCH} = 0.020 \times 10^{-11}$ erg/rad² and $F_{CCC,CCH} = 0.006 \times 10^{-11}$ erg/rad², contribute significantly to the potential energy of ν_6, ν_7 (C_3H_2 and C_3D_2) and ν_5, ν_6, ν_7 (C_3HD) respectively. Thus they too must be included in the normal coordinate calculation.

Conclusion

Only one C-H stretching frequency is observed in the infrared spectrum of the C_3H_2 radical, which implies that the two hydrogen atoms in propargylene are equivalent. The acetylenic C-H stretching force constant and large C=C=C bending force constant for the molecule indicate that the electron density in the outermost valence orbital is located primarily on the terminal carbon atoms of the radical. The value of the calculated bending force constant, H_{CCC} , is in line with the expected occupancy of this "dumbbell shape" orbital, intermediate between that of C_3 and CO_2 . All of the observations in the infrared spectra of the matrix-isolated isotopic propargylenes support the expected $D_{\infty h}$ symmetry for this radical.

REFERENCES

REFERENCES

1. W. Nernst, Z. Elektrochem. 24, 335 (1918).
2. F. Paneth and W. Hofeditz, Chem. Ber. 62, 1335 (1929).
3. E. W. R. Steacie, Atomic and Free Radical Reactions (Reinhold, New York) 2nd ed. (1954).
4. E. Whittle, D. A. Dows, and G. C. Pimentel, J. Chem. Phys. 22, 1943 (1954).
5. D. E. Milligan and M. E. Jacox, In Physical Chemistry, An Advanced Treatise, 4, Chap. 4 (Academic, New York), (1969).
6. C. B. Moore and G. C. Pimentel, J. Chem. Phys. 40, 342 (1964).
7. R. A. Bernheim, R. J. Kempf, J. V. Gramas and P. S. Skell, J. Chem. Phys. 43, 196 (1965).
8. A. J. Merer, Can. J. Phys. 43, 1795 (1965).
9. W. Weltner, Jr. and D. McLeod, Jr., J. Chem. Phys. 45, 3096 (1966).
10. W. H. Smith and G. E. Leroi, J. Chem. Phys. 45, 1767 (1966).
11. W. H. Smith and G. E. Leroi, J. Chem. Phys. 45, 1778 (1966).
12. W. H. Smith and G. E. Leroi, Spectrochim. Acta 25A, 1917 (1969).
13. W. H. Fletcher and W. T. Thompson, J. Mol. Spectry. 25, 240 (1968).
14. G. Zerbi and M. Gussoni, J. Chem. Phys. 41, 456 (1964).
15. Organic Syntheses Collective Vol. 2, 165, 461 (John Wiley and Sons Inc., New York) (1944).

16. L. Andrews, In Annual Review of Physical Chemistry, 22, Chap. 5 (1971).
17. C. C. Costain, J. Chem. Phys. 45, 1961 (1966).
18. G. Herzberg, Molecular Spectra and Molecular Structure, Infrared and Raman Spectra of Polyatomic Molecules. Vol. 2, (D. Van Nostrand Co., Inc., Princeton, N.J.) (1966).
19. B. L. Crawford, Jr., J. Chem. Phys. 8, 526 (1940).
20. J. C. Evans and R. A. Nyquist, Spectrochim. Acta 19, 1153 (1963).
21. R. A. Nyquist, T. L. Reder, F. F. Stee and G. J. Kallos, Spectrochim. Acta 27A, 897 (1971).
22. P. Cossee and J. H. Schachtschneider, J. Chem. Phys. 44, 97 (1966).
23. F. A. Miller, O. Sala, P. Devlin, J. Overend, E. Lippert, W. Luder, H. Moser and J. Varchmin, Spectrochim. Acta 20, 1233 (1964).
24. T. Fujiyama and T. Shimanouchi, Spectrochim. Acta 20, 1233 (1964).
25. E. B. Wilson, J. C. Decius and P. C. Cross, Molecular Vibration (McGraw-Hill Book Co., Inc., New York).
26. J. H. Schachtschneider, Shell Development Co., Tech. Rep. No. 231-64.
27. J. H. Schachtschneider, Shell Development Co., Tech. Rept. No. 57-65.
28. W. J. Orville-Thomas, Chem. Rev. 57, 1179 (1957).
29. W. T. Thompson and W. H. Fletcher, Spectrochim. Acta 22, 1907 (1967).
30. R. Ettinger, J. Chem. Phys. 40, 1693 (1964).
31. C. W. Bjork, N. C. Craig, R. A. Mitsch and J. Overend, J. Am. Chem. Soc. 87(6), 1186 (1965).
32. C. B. Moore and G. C. Pimentel, J. Chem. Phys. 38, 2816 (1963).
33. F. Stitt, J. Chem. Phys. 8, 56 (1940).

34. J. L. Griggs, Jr., K. N. Rao, L. H. Jones, and R. M. Potter, J. Mol. Spectry. 18, 212 (1965).
35. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 278 (1967).
36. G. E. Leroi, G. E. Ewing and G. C. Pimentel, J. Chem. Phys. 40, 2298 (1964).
37. L. Gausset, G. Herzberg, A. Lagerqvist and B. Rosen, Astrophys. J. 142, 45 (1965).
38. E. Clementi and A. D. McLean, J. Chem. Phys. 36, 45 (1962).
39. D. H. Liskow, C. F. Bender and H. F. Schaefer III, J. Chem. Phys. 56, 5075 (1972).
40. A. D. McLean, J. Chem. Phys. 38, 1347 (1963).
41. H. W. Thompson and J. W. Linnett, J. Chem. Soc. 138 (1937).