

ISOTOPIC ANALYSIS OF NITROGEN IN AMMONIA BY  
FOURIER TRANSFORM INFRARED SPECTROSCOPY

by

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## VITA

Mohamed A. Abuzwida was born on October 12, 1953, in a small village called Shutt-Espan in Tagiura (a small city 15 km east of Tripoli, Libya). He attended primary schools in Tagiura and graduated from Tagiura High School in 1972.

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The author married Sharifa M. Kshid on September 29, 1977. A year later he received a scholarship for higher education; he attended the chemistry department at Kansas State University in Spring 1980.

## INTRODUCTION

Because of the chemical and biological importance of nitrogen there is a need to be able to perform isotopic tracer studies with this element. Up to the present the isotopic analysis of nitrogen has been primarily by mass spectrometry, but there has been some use made of emission spectra as well. My research has been a study of the isotopic analysis of nitrogen in ammonia by Fourier transform infrared spectroscopy (FT-IR).

Ammonia is the starting compound for a major part of nitrogen chemistry. The spectrum of ammonia has been studied extensively in both the microwave and the infrared region. Even though ammonia is a relatively simple molecule whose basic structural features and spectrum have long been recognized, there are a number of higher order interactions with spectral features which can be revealed readily under the high resolution that is possible with Fourier transform infrared spectrometry. For example, in my research I made use of highly resolved spectra associated with the bending vibrational motion  $\nu_2$  of the ammonia molecule. The inversion motion in the  $\nu_2$  fundamental mode of ammonia causes a splitting of vibrational levels and differing fundamental frequencies  $\nu_2$ "s" and  $\nu_2$ "a." When the ammonia is a mixture of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$ , the  $\nu_2$ "s" and  $\nu_2$ "a" will occur at different frequencies for the two molecules.

In the following pages I shall show high resolution infrared spectra of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the  $1000\text{-}800\text{ cm}^{-1}$  region and describe how these spectra may be used for analyzing the  $^{14}\text{N}$  and  $^{15}\text{N}$  content in ammonia samples.

## LITERATURE REVIEW

This literature review is focused on four areas:

- A) Early Studies of the Infrared Spectrum of Ammonia.
- B) Nitrogen Isotopic Effects on the Infrared Spectrum of Ammonia.
- C) Application of Fourier Transform Infrared Spectroscopy (FT-IR) to the Isotopic Analysis of Ammonia.
- D) Quantitative Determination of Ammonia by Infrared Spectroscopy.

## EARLY STUDIES OF THE INFRARED SPECTRUM OF AMMONIA

The absorption spectrum of ammonia occurring in the infrared has been studied repeatedly since the early days of infrared spectroscopy.

The rotational fine structure of the infrared spectrum of ordinary ammonia,  $^{14}\text{NH}_3$ , was first investigated by Spence (1) in 1925 and soon after this by Barker and coworkers (2-4). Barker (4) concluded on the basis of the relative line intensities that the ammonia molecule could be characterized as an oblate symmetric top. Additionally, he observed that many of the P and R lines of the  $1000\text{ cm}^{-1}$  band were doubled. He also investigated the  $1666.66\text{ cm}^{-1}$  perpendicular band. Although the resolution of the band was incomplete and many lines due to atmospheric water vapor interfered with his data, he was able to assign the strong transitions.

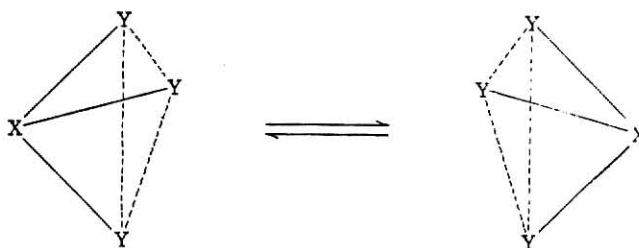
In 1950, Wood, et al. (5) made an intensive study on the vibration-rotation spectrum of ordinary ammonia,  $^{14}\text{NH}_3$ , making use of a grating spectrometer, in the region from  $1200$  to  $700\text{ cm}^{-1}$  with a resolution of  $0.4\text{ cm}^{-1}$ . Through their study 131 lines belonging to P- and R-branches of the symmetric deformation vibration band were determined and assigned.

Starting in 1957 Benedict, Plyler and Tidwell published a series of papers giving the fundamental and combination bands in the  $6666\text{ cm}^{-1}$  to  $1666.66\text{ cm}^{-1}$  region. Such studies have established that the nitrogen atom lies at the apex of a pyramid, approximately  $3.8 \times 10^{-9}\text{ cm}$  above the base. The three hydrogen atoms form the corners of the base. Analysis of rotational spectra established that the molecule has a structure that is an oblate symmetric top with a N-H bond length of  $1.01 \times 10^{-8}\text{ cm}$  (7-10).

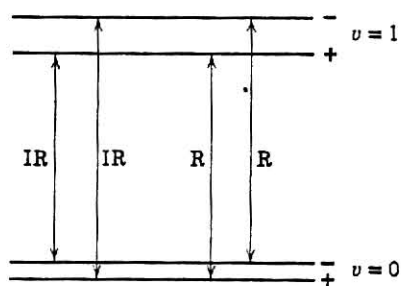
In 1959 Caring, et al. (11) re-examined the  $1600$ ,  $1000$ , and  $625\text{ cm}^{-1}$  band of  $^{14}\text{NH}_3$  making use of a vacuum grating spectrometer. The frequencies

of the observed lines are reported as well as the energy levels of the several vibrational modes (see Fig. 1(a), 1(b), 1(c)). Each of the four normal modes of vibration are split into two components as the result of the inversion of nitrogen through the plane of the hydrogen atoms to an equivalent pyramidal configuration (12). The effect of inversion on the  $\nu_2$  mode is described in the following paragraphs.

The effect of this inversion is a distinguishing feature in the infrared spectrum of  $\text{NH}_3$ . The two inversion forms are sketched below:



The potential barrier for transition between these two configurations is small enough so that the molecule may resonate between the two structures. As a result, each vibrational level splits into two levels, normally characterized as symmetric (+ or s) and antisymmetric (- or a).



Transitions between levels of different sign are allowed in the infrared spectrum, whereas those between the same sign are allowed in the Raman spectrum (13).



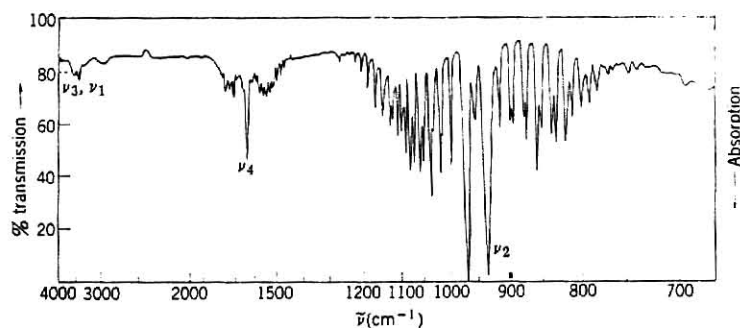


Figure 1a. Infrared Spectrum of Gaseous  $\text{NH}_3$ .

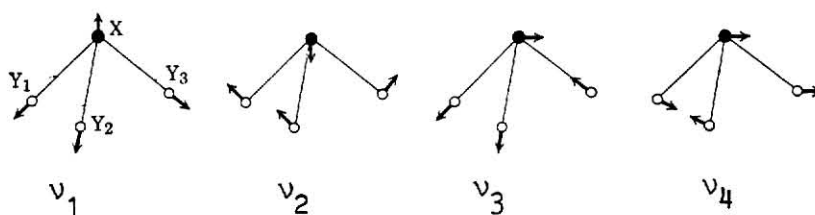


Figure 1b. Normal Modes of Vibration of Pyramidal  $\text{XY}_3$  Molecules.

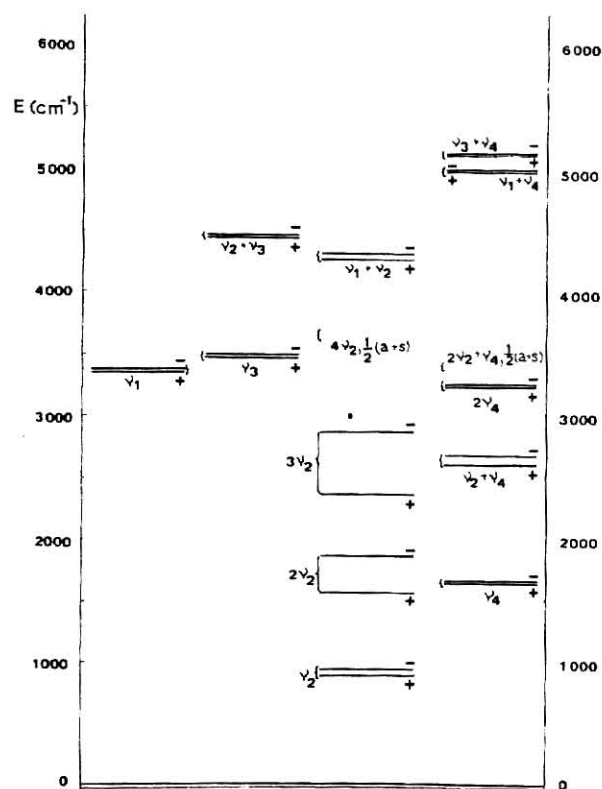


Figure 1c. The Lower Vibration and Inversion Energy Levels in  $\text{NH}_3$ .

There is an energy difference between the symmetric (s) and the antisymmetric (a) states with the symmetric state always being lower in energy. This so-called inversion splitting has been observed to increase as  $v$  increases until the energy level is above the top of the hill (see Figure 2), then the inversion splitting decreases. The potential well within which occur the various vibrational states of the molecule has a form somewhat like two overlapping parabolas with a hill in the middle of the well. The molecule may be on either side of the potential hill for any given vibrational state; that is, the N atom may be in either configuration with respect to the plane of the hydrogen atoms for a given vibrational state (14). Thus for example, in the ground state where  $v=0$  for  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ , the splitting is about  $0.79 \text{ cm}^{-1}$  for  $\nu_2$ , but for  $v=1$  for  $\nu_2$  and  $v=0$  for  $\nu_1$ ,  $\nu_3$ ,  $\nu_4$ , the splitting is of order of  $35.69 \text{ cm}^{-1}$  (15).

When designating the line or transition by a symbol, a set of two letters and two numbers is used. The first letter is an "a" or "s" to designate one or the other of the inversion levels of the lower state. The next is P, R, or Q, and the last two are rotational quantum numbers. Thus as shown by J. Curits (15) the symbol aR(J,K) refers to the transition from the lower vibrational level ( $v=0$ ) of antisymmetric inversion character and rotational quantum numbers J and K to upper vibrational level ( $v=1$ ) of symmetric inversion character and rotational quantum numbers J+1 and K (see Figure 3).

Allowed transitions in the infrared are from the lower level of the ground state inversion doublet to the upper level of the upper state doublet or from the upper level of the ground state doublet to the lower level of the upper state doublet (13). J. Curtis (15) showed that the difference between any two lines of the same type (i.e. those that differ

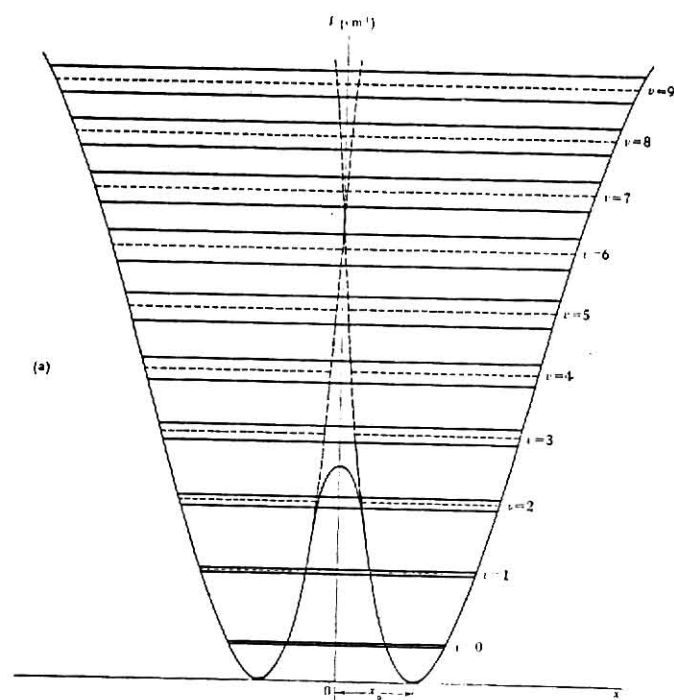


Figure 2. The Potential Energy in a Pyramidal  $XY_3$  Molecule as a Function of the Distance of the X Atom from the  $Y_3$  Plane.

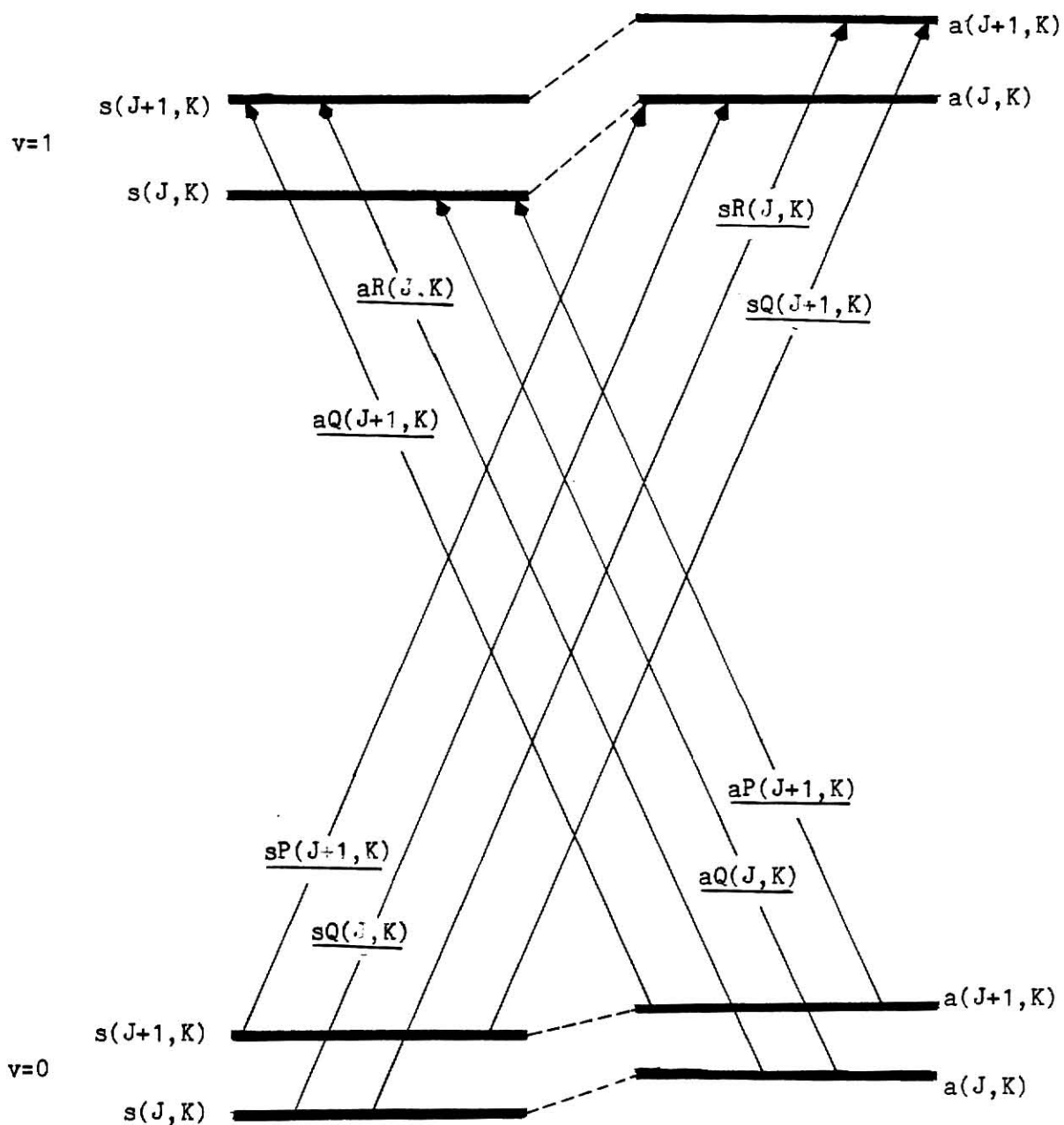
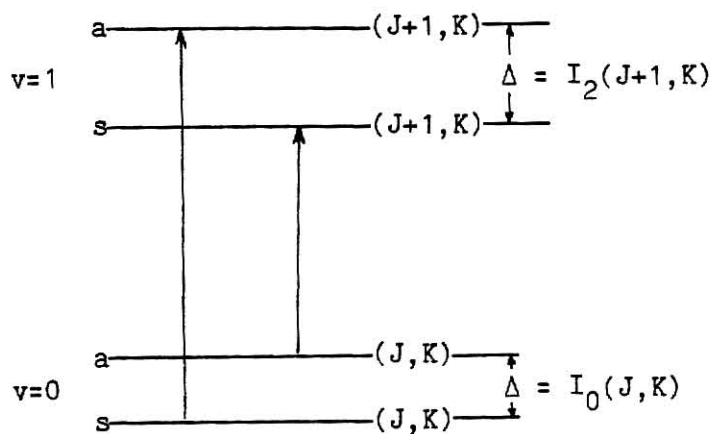


Figure 3. Schematic Diagram of Allowed Transitions between Vibrational Levels.

only in their point of origin in the ground state level (a or s)) will be the sum of the two inversion separations. For example, for  $v_2$ :

$$sR(J,K) - aR(J,K) = I_0(J,K) + I_2(J+1,K)$$

where  $I_0(J,K)$  represents the inversion splitting for the ground state vibrational level, and  $I_2(J+1,K)$  represents the inversion splitting for the  $v=1$  vibrational level. As shown below:



# NITROGEN ISOTOPIC EFFECTS ON THE INFRARED SPECTRUM OF AMMONIA

When a particular atom in a molecule is replaced by its isotope there will be neither an appreciable change in internuclear distance nor bond force constant. There is only a change in mass; and, because of the difference in the masses, the vibrational levels and the rotational levels are different for molecules of differing isotopic compositions (16). Differences in spectra due to isotopic substitution are easily resolved with modern instruments such as a Fourier transform infrared spectrometer.

Jones in 1978 pointed out that the  $^{14}\text{N}$ - $^{15}\text{N}$  isotopic shift is ( $-6.2\text{ cm}^{-1}$ ) between  $^{14}\text{ND}_3$  and  $^{15}\text{ND}_3$  in the  $\nu_2$  band (17). In 1970 F. and T. Shimizu (18) published a study of isotopic ammonia,  $^{15}\text{NH}_3$ , which gave the band origin, the rotational constants, and the inversion constant of the isotopic ammonia  $^{15}\text{NH}_3$ , as obtained from the analysis of the  $\nu_2$  band spectrum around  $1000\text{ cm}^{-1}$ .

In 1972 P. Varanasi (19) reported, with a spectral resolution of  $0.15\text{ cm}^{-1}$ , the half-width and the shapes of several rotational lines in the  $\nu_2$  band of ammonia. He also studied the effects of collision-broadening by hydrogen on the line-width and found that the broadening is independent of the quantum numbers J and K. According to his study, which was based on the line intensities, he estimated the integrated intensity of the pair of bands  $\nu_2$ "s" and  $\nu_2$ "a" to be  $600 \pm 30\text{ cm}^{-2}\text{atm}^{-1}$ .

In 1976 D. Bargues (20) reported the high resolution spectrum of ordinary and isotopic ammonia  $^{14}\text{NH}_3$ ,  $^{15}\text{NH}_3$ , and he claimed that use of a dual-grid spectrometer permitted a new analysis of the absorption  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the  $1000\text{ cm}^{-1}$  region. The spectroscopic constants were computed by least-squares method, and inversion energies were calculated

from the vibrational level (0,1,0,0). In 1981 P. Varanasi and P. Wyant (21) reported the spectral transmission measurement in the  $\nu_2$ "s" and  $\nu_2$ "a" fundamentals of ordinary and isotopic ammonia ( $^{14}\text{NH}_3$ ,  $^{15}\text{NH}_3$ ), and according to their study they got information that is valuable in the interpretation of the spectroscopic scans of Jupiter covering the thermal infrared,  $1100\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$ . Also, they found that the absorption spectra of the two species (ordinary  $^{14}\text{NH}_3$  and isotopic  $^{15}\text{NH}_3$ ) differ from each other only in the line position but not in the strenghts, widths, or shapes of the lines of the same quantum number designations.

## APPLICATION OF (FT-IR) TO THE ISOTOPIC ANALYSIS OF AMMONIA

Fourier Transform Infrared (FT-IR) spectroscopy, which is based on the use of Michelson interferometers, became a promising possibility for measurement of infrared spectra in the late 1950s and early 1960s. Today the commercial (FT-IR) systems are the standard in high performance infrared spectrometers. The most important developments in the area of high-resolution infrared spectroscopy have been the construction of instruments with improved resolution, and the exploitation of fast and low noise detectors (22).

In 1978 L. H. Jones (17) reported the  $\nu_2$  fundamentals of  $^{14}\text{ND}_3$  and  $^{15}\text{ND}_3$  with sufficient resolution making use of (FT-IR) to resolve many of the individual P, Q, and R-lines for both components of the inversion doublet. With the help of observed intensity alterations, assignments of many of the lines were made. A least-squares analysis was applied to determine the various vibration-rotation constants pertinent for these transitions. The  $^{14,15}\text{N}$ -N isotopic shift was found to be  $(-6.2\text{ cm}^{-1})$ . Soon afterward M. Carlotti, et al. (23) reported the rotation-inversion spectrum of  $^{15}\text{NH}_3$  between 280 and  $38\text{ cm}^{-1}$  with a resolution of about  $0.03\text{ cm}^{-1}$  making use of (FT-IR). They combined their results with the inversion frequencies obtained by microwave spectroscopy and got the main rotational and centrifugal distortion constants.

Making use of a 10 cm path length cell in conjunction with an FT-IR spectrometer at the telescope, Tokunaga, et al. (24) reported the spectra of the central region of Jupiter in the  $980$  to  $744\text{ cm}^{-1}$  spectral range at  $0.5$  and  $0.28\text{ cm}^{-1}$  resolution. They were able to detect the gases  $^{14}\text{NH}_3$  and



$^{15}\text{NH}_3$  in the spectra. A synthetic spectrum was compared with their observations, and they concluded the following:

- 1) "The  $^{14}\text{NH}_3$  line profiles are best fitted with the  $^{14}\text{NH}_3$  density in the Jovian troposphere which is 0.5 times the saturated vapor pressure level ( $T=140\text{K}$ )."
- 2) "The best-fit  $^{15}\text{NH}_3/^{14}\text{NH}_3$  ratio is 0.006 (but may be consistent with terrestrial ratio within model uncertainties)."

## QUANTITATIVE DETERMINATION OF AMMONIA BY INFRARED SPECTROSCOPY

Ammonia is a pollutant in the aquatic environment as well as in the air. For natural waters, ammonia exerts a stress in several ways. Among these ways we can mention its contribution to blue-green algae growth causing eutrophication and accompanying toxicity to fish and aquatic life. Also it causes corrosion of certain metals of construction and reduces the amount of dissolved oxygen in receiving waters due to the occurrence of nitrification. Finally, it inhibits the water and food intake for both mammals and plants. Excessive amounts of ammonia and ammonium salts decrease the pH in human blood and cause acidosis which can be monitored by the increase of ammonia in the urine (25).

The well-known and the most popular colorimetric method of ammonia determination was first proposed by Julius Nessler in 1856 (26). The Nessler method is not truly a colorimetric method because of the colloidal character of the colored species formed by the Nessler reagent,  $\text{KHgI}_4$ . Temperature, alkalinity, purity of chemicals used for the reagent, and the condition of the reagent are the factors affecting the color intensity. Among the other well-established techniques for ammonia determination is the Berthelot method which is based on the blue color formed by reaction of phenol and sodium hypochlorite with ammonia. But the most significant one among the novel techniques for the determination of ammonia is the use of ammonia selective electrodes (27).

Infrared spectroscopy, on the other hand, has been commonly used for only qualitative purposes. But with the advent of on-line computers, the quantitative power of infrared spectroscopy has gained new dimensions, along with new qualitative conveniences (28). The application of FT-IR as

a dedicated signal gas monitor is an interesting example. For trace sampling, extremely small concentrations can be determined by FT-IR methods using very long path lengths and using very large scale expansions to detect weak absorption (29).

O. Y. Ataman, et al. (25) investigated a technique of quantitative determination of ammonia, in ammonium ion form, based on preconcentration on zeolite followed by quantitative infrared analysis of the sample and zeolite matrix in a KBr pellet. Mark G. Rockley, et al. (30) have shown that the Fourier Transform Infrared Photoacoustic Spectroscopy (FT-IR-PAS) is a technique which is useful for quantitative analysis of nitrogen.

Finally, analysis of nitrogen isotopes has been done in solid  $\text{KNO}_3$  (30). The method used was photoacoustic which is not directly related to my work.

## EXPERIMENTAL METHODS

### Ammonia Samples of Known $^{15}\text{N}/^{14}\text{N}$ Content

- 1)  $^{15}\text{N}$ -enriched ammonia was prepared in this laboratory from  $^{15}\text{N}$ -ammonium sulfate. The latter was kindly supplied by Dr. R. V. Olson of the Agronomy Department
- 2)  $^{14}\text{N}$ -ammonia was obtained from either a lecture bottle (Matheson Co. Inc.) or from  $^{14}\text{N}$ -ammonium sulfate (analytical reagent grade, AR).

### Absorption Cell

The absorption cell used in this study was constructed of Pyrex glass. The cell had a path length of 24.8 cm and a diameter of 4.5 cm (volume  $\approx 400\text{ cm}^3$ ) and was fitted with sodium chloride windows.

### Pressure Measurements

Since all spectra were obtained at a pressure of around 6 torr, a U-tube mercury monometer was found to be sufficiently accurate for pressure measurements.

### Measurement of the Spectra

Absorption spectra of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  in the  $\nu_2$  band between  $1000\text{--}800\text{ cm}^{-1}$  and  $885\text{--}860\text{ cm}^{-1}$  were obtained with a commercial Fourier transform infrared spectrometer. The spectrometer was an IBM instrument

model 98 interferometer of Genzel type, with a regular glowbar as a source and a MCT liquid nitrogen cooled detector.

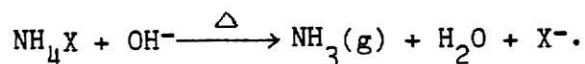
### Selection of the Working Spectral Range

Based upon both literature reports and some preliminary spectra obtained with the (FT-IR) spectrometer, I chose to study the P-branch of the  $\nu_2$  band of ammonia which occurs in the region between  $1000-800\text{ cm}^{-1}$ . In my study, I focused my attention on the region between  $885$  and  $860\text{ cm}^{-1}$  as a working region for the following reasons:

- 1) Both sP(J,K) and aP(J,K) transition lines for  $^{15}\text{NH}_3$  and  $^{14}\text{NH}_3$  occur in this region which makes possible a study of each in the presence of the other.
- 2) Water vapor does not absorb radiation in this region and thus did not interfere.
- 3) The instrument was equipped with a MCT detector with capabilities of working well in this region.

### Method of Preparation of Ammonia

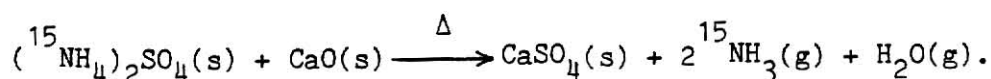
Ammonia is a colorless, pungent gas with a normal b.p. of  $-33.35^\circ\text{C}$ . The natural abundance of  $^{15}\text{N}$  in ammonia is 0.36% (31). The laboratory preparation of ammonia is based on the displacement reaction between an ammonium salt like  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{SO}_4$  and a strong base like  $\text{CaO}$  or  $\text{KOH}$  (32).



However, the laboratory preparation of natural ammonia from ammonium salts should seldom be required since pure ammonia is commercially available in steel cylinders.

### Preparation of $^{15}\text{N}$ -Labeled Ammonia

$^{15}\text{N}$ -Ammonia is stable, but at the same time it is expensive; therefore, the  $^{15}\text{N}$ -ammonia has been prepared in this research from stock ammonium sulfate both at 40%  $^{15}\text{N}$  and 99.71%  $^{15}\text{N}$ . Samples were prepared from the reaction between  $^{15}\text{N}$ -ammonium sulfate and calcium oxide in an apparatus especially suitable for small quantities (Fig. 4). A known weight of  $^{15}\text{N}$ -ammonium sulfate was introduced into the reaction vessel, and the vessel was placed in the oven for a few hours to achieve complete dryness. Then an excess amount of calcium oxide was introduced into the reaction vessel. After thorough mixing, the reaction flask was attached to the vacuum system and evacuated. The solid mixture was then heated to release the ammonia.



The evolved gases were passed through a long tube filled with KOH pellets to absorb the water vapor. One can achieve further purification of the ammonia by condensing the gas and dissolving some sodium metal in the condensate, but this was found unnecessary for this study because of the absence of infrared absorption by water in the region between 1000-800  $\text{cm}^{-1}$ .

### Preparation of a Set of Different Concentrations of $^{15}\text{N}$ -Ammonia

In order to study the variation of peak heights as a function of concentration, a set of different concentrations of  $^{15}\text{N}$ -ammonia was prepared as follows: Mixtures of known weights of  $^{15}\text{N}$ -ammonium sulfate with differing weights of natural ammonium sulfate were prepared. This method was not hard to follow since both  $^{15}\text{N}$  and  $^{14}\text{N}$ -ammonium sulfate

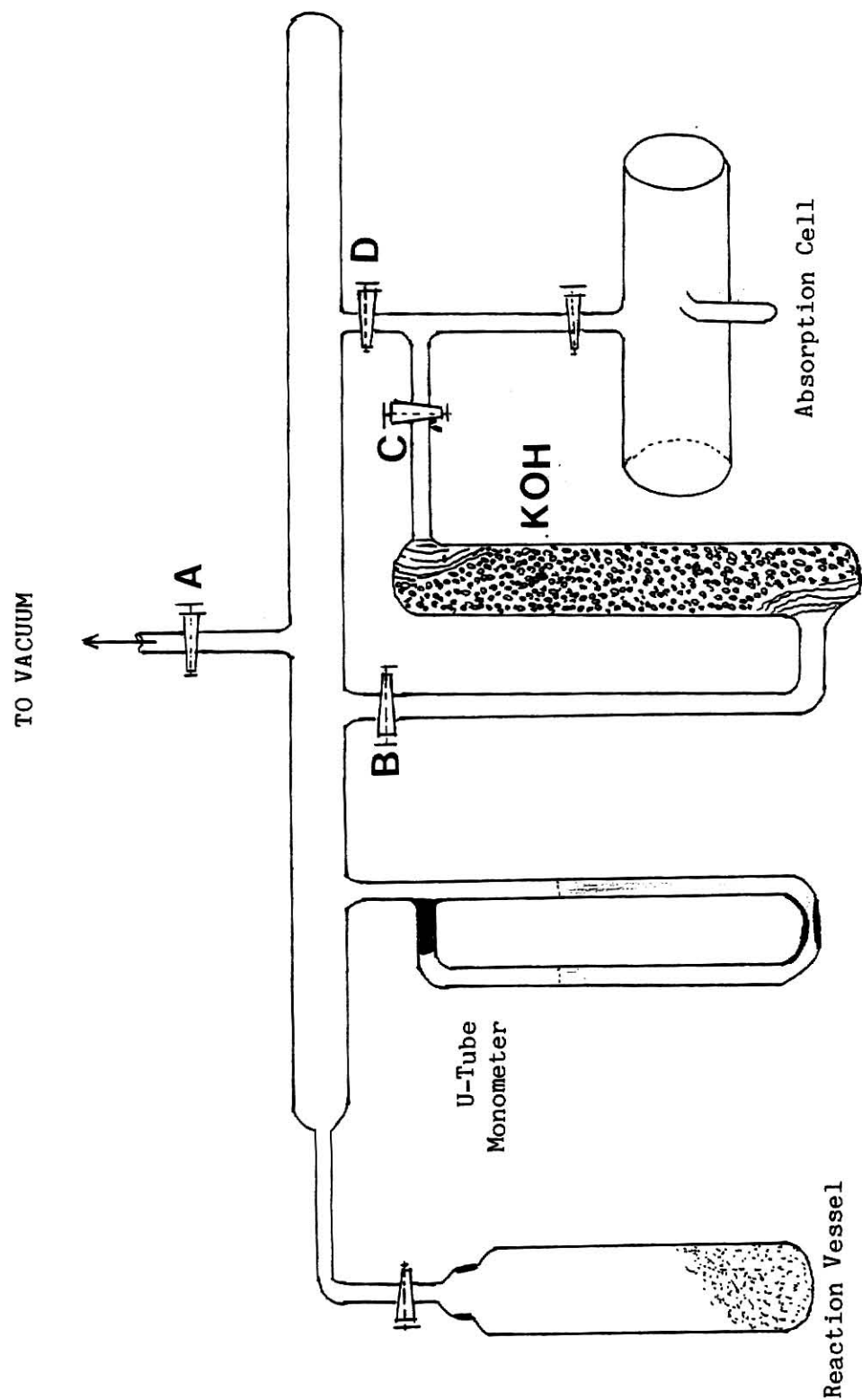


Figure 4. Apparatus for Preparation of Ammonia Samples.

were available. In order to prepare a set of different concentrations of  $^{15}\text{N}$ -ammonia starting with 0.250 gram of 58.44 WT%  $^{14}\text{N}$  and 41.56 WT%  $^{15}\text{N}$ , the following equation may be used:

$$\%^{15}\text{N} = \frac{0.00150 + 0.0000545\text{M}}{0.003761 + 0.015134\text{M}} 100,$$

where (M) is the weight of natural ammonium sulfate that is mixed with 0.250 gram of stock sample to give the desired  $^{15}\text{N}\%$ . Table 1 shows the weights of natural ammonium sulfate that were added to give the desired percentage of  $^{15}\text{N}$ . (See Appendix A for a derivation of this relationship.)

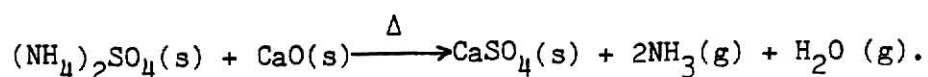


Table I. Weights, M, of Natural Ammonium Sulfate that Were Mixed with 0.2500 g of 39.91%  $^{15}\text{N}$ -Ammonium Sulfate to Give the Desired Percentage of  $^{15}\text{N}$ .

$^{15}\text{N}\%$	(M) Weight of $(\text{NH}_4)_2\text{SO}_4$ Added (grams)
39.91	0.0000
37.00	0.0196
35.00	0.0350
33.00	0.5241
30.00	0.0829
28.53	0.1002
25.00	0.1501
20.00	0.2516
15.00	0.4224
10.00	0.7704
9.51	0.8249
6.00	1.4930
5.00	1.8683
2.85	3.6915
2.00	5.7409

## EXPERIMENTAL PROCEDURES

Depending on the desired percentage of  $^{15}\text{N}$ -ammonia, a known weight of natural ammonium sulfate (M) that had been placed in the oven for few hours at  $100^{\circ}\text{C}$  was mixed with a known weight of 39.91%  $^{15}\text{N}$ -ammonium sulfate which also had been dried, and both samples were introduced into a reaction vessel. In order to improve the mixing of both weights, a small amount of water was added to the reaction vessel to dissolve the ammonium sulfate. Then the reaction vessel was placed in the oven for overnight at  $100^{\circ}\text{C}$ . Next, the sample in the reaction vessel was well mixed with an excess weight of calcium oxide (CaO). The reaction vessel and the absorption cell were then attached to the vacuum system to pump out all of the air as shown in Fig. 4. Stopcocks (A) and (D) were closed, and the reaction vessel was heated with an electrically heated blower to force the following reaction to proceed:



When the pressure inside the vacuum line started to rise, stopcock (B) was opened to let all of the reaction products pass over potassium hydroxide (KOH) pellets inside the tube that leads to the absorption cell. The latter absorbed the water produced during the reaction. Once the pressure inside the vacuum line reached 6.0 torr, the absorption cell was closed, removed from the vacuum line and placed in the instrument sample chamber. The instrument was adjusted, and both the sample and the reference was

scanned for at least 64 scans with a resolution of  $0.5\text{ cm}^{-1}$  between  $1000\text{--}800\text{ cm}^{-1}$ . Spectra were plotted with a digital plotter. Absorbances were determined by employing the base line method (see Appendix B).

## EXPERIMENTAL RESULTS

As part of the investigation of the infrared isotopic analysis of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$ , the  $\nu_2$  fundamental band has been studied in the region between  $1000\text{--}800\text{ cm}^{-1}$  under a resolution of  $0.5\text{ cm}^{-1}$ . The transmittance spectra for both species ( $^{14}\text{NH}_3$ ,  $^{15}\text{NH}_3$ ) are shown in Fig. 5, 6, and 7. The infrared spectrum of water in the region between  $1600\text{--}800\text{ cm}^{-1}$  under the same resolution is shown in Fig. 8. Figure 9 is spectrum of 25%  $^{15}\text{N}$ -ammonia between  $885\text{--}860\text{ cm}^{-1}$  under a resolution of  $0.5\text{ cm}^{-1}$ .

### EXPERIMENT 1

#### THE ABSORPTION SPECTRUM OF $^{15}\text{N}$ -AMMONIA BETWEEN $1000\text{--}800\text{ cm}^{-1}$

Three ml containing 30 mg of 99.71%  $^{15}\text{N}$ -ammonium sulfate solution was introduced into the reaction vessel and placed in the oven for overnight at  $100^\circ\text{C}$ . About 0.10 gram of calcium oxide was well mixed with the sample, and the reaction vessel was attached to the vacuum system and heated. Reaction was continued until 6.0 torr of the produced gases were transferred into the absorption cell. The spectrum was then measured (Fig. 5).

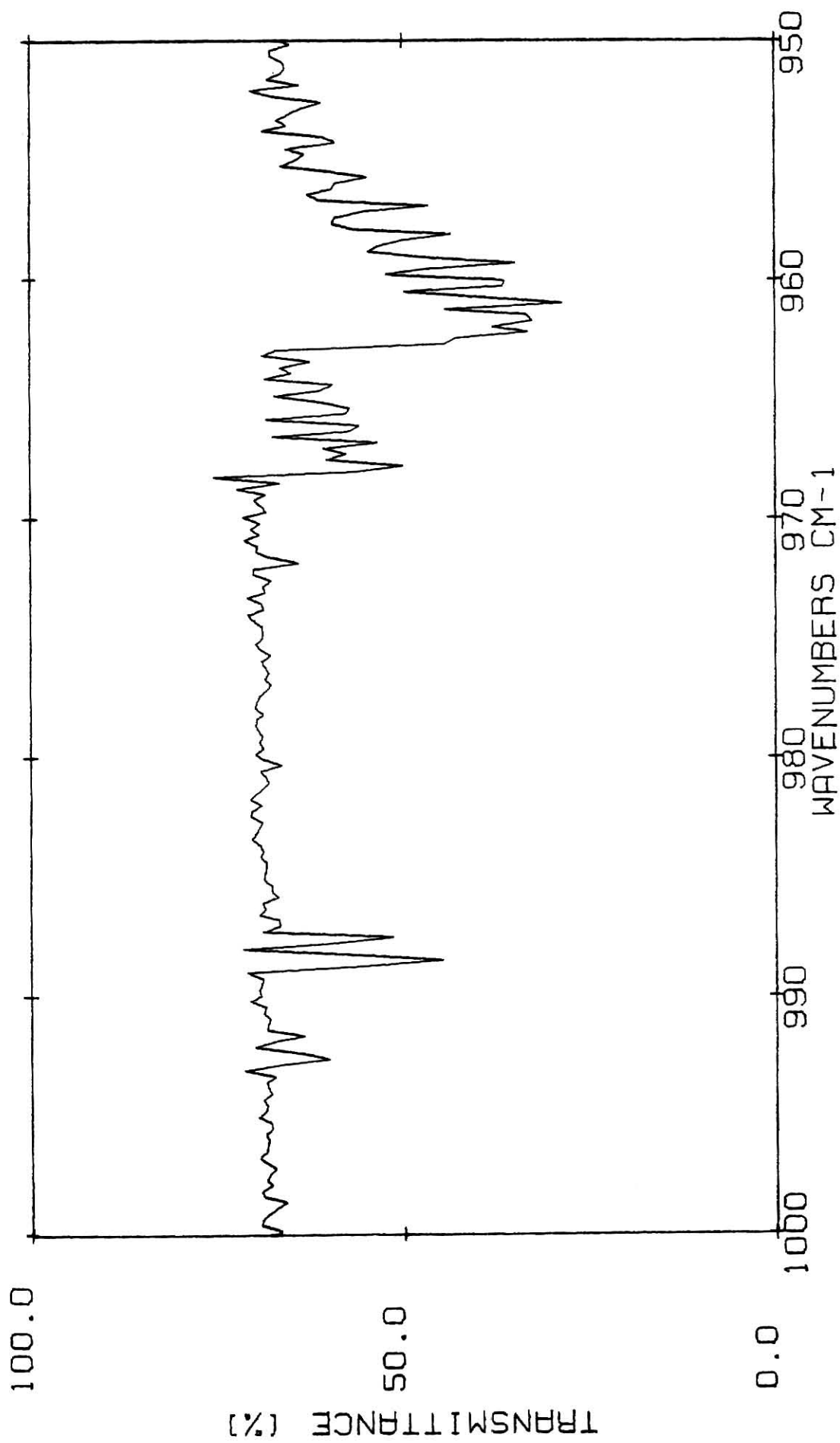


Figure 5. Infrared Spectrum of  $^{15}\text{N}$ -ammonia between 1000-8000  $\text{cm}^{-1}$ .

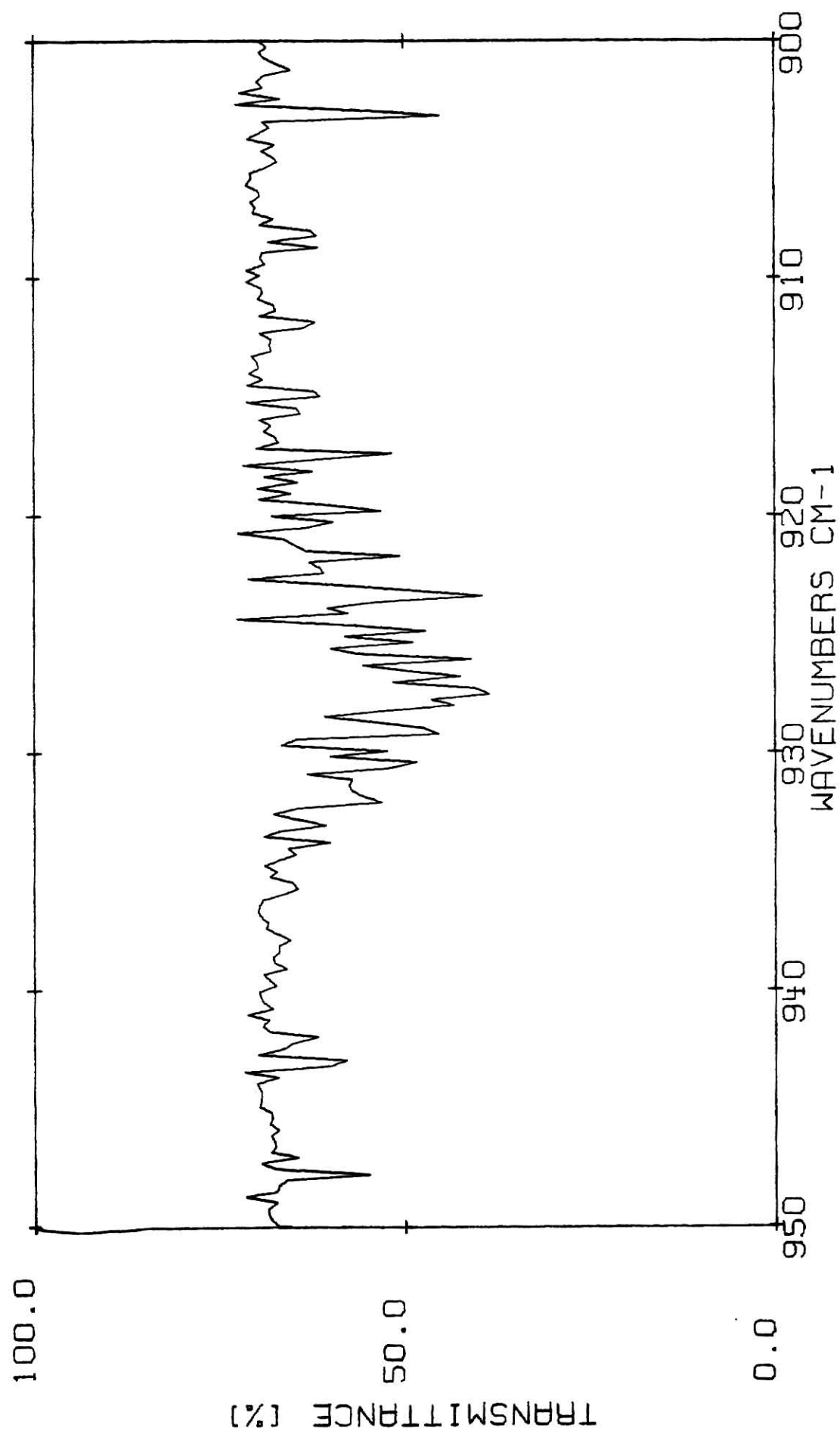


Figure 5 (continued).

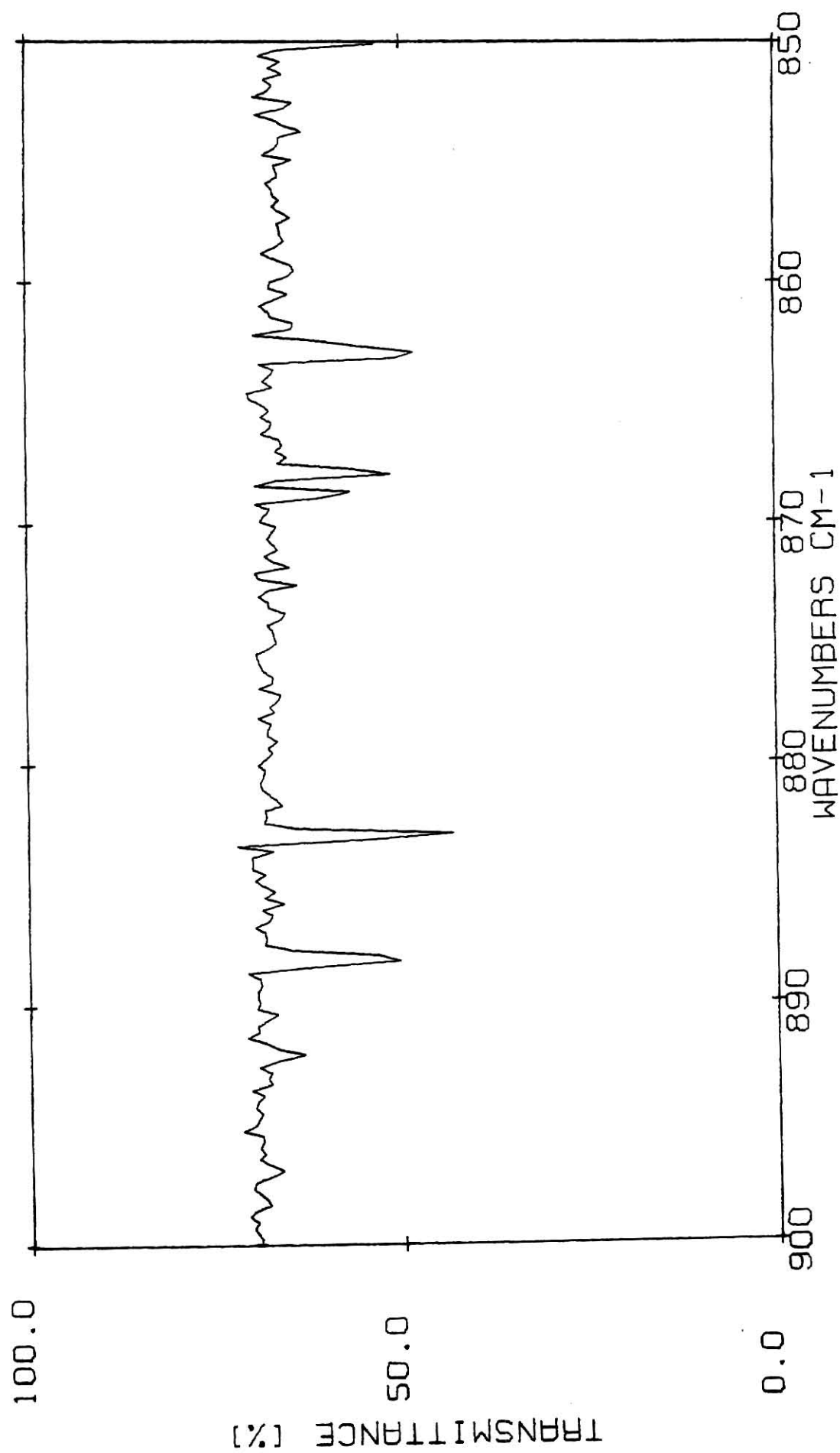


Figure 5 (continued).

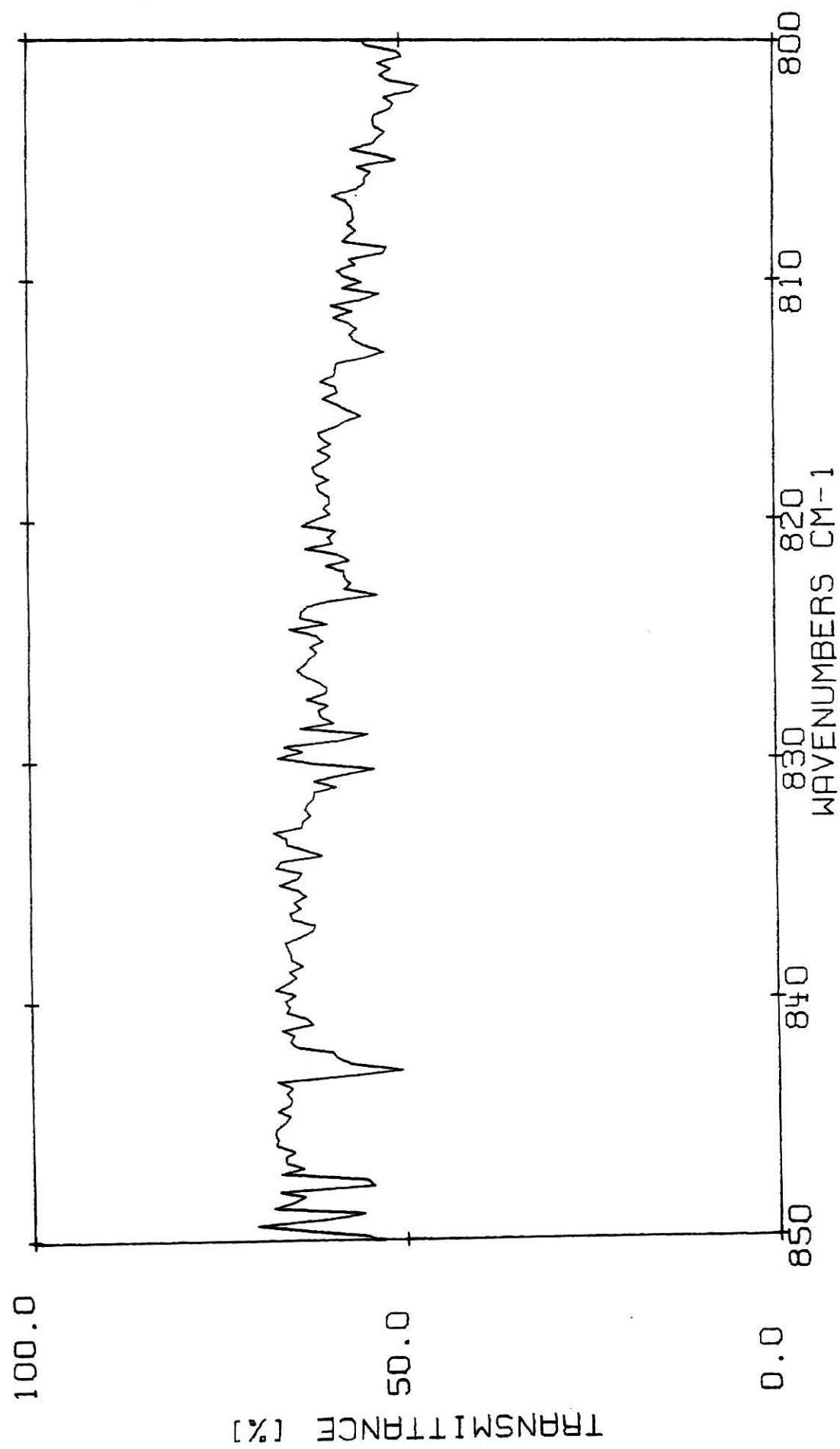


Figure 5 (continued).



## EXPERIMENT 2

THE ABSORPTION SPECTRUM OF  $^{14}\text{N}$ -AMMONIA BETWEEN  $1000\text{--}800\text{ cm}^{-1}$ 

Ammonia gas from a lecture bottle was transferred into the absorption cell until the pressure reached 6.0 torr, and then the spectrum was measured (Fig. 6).

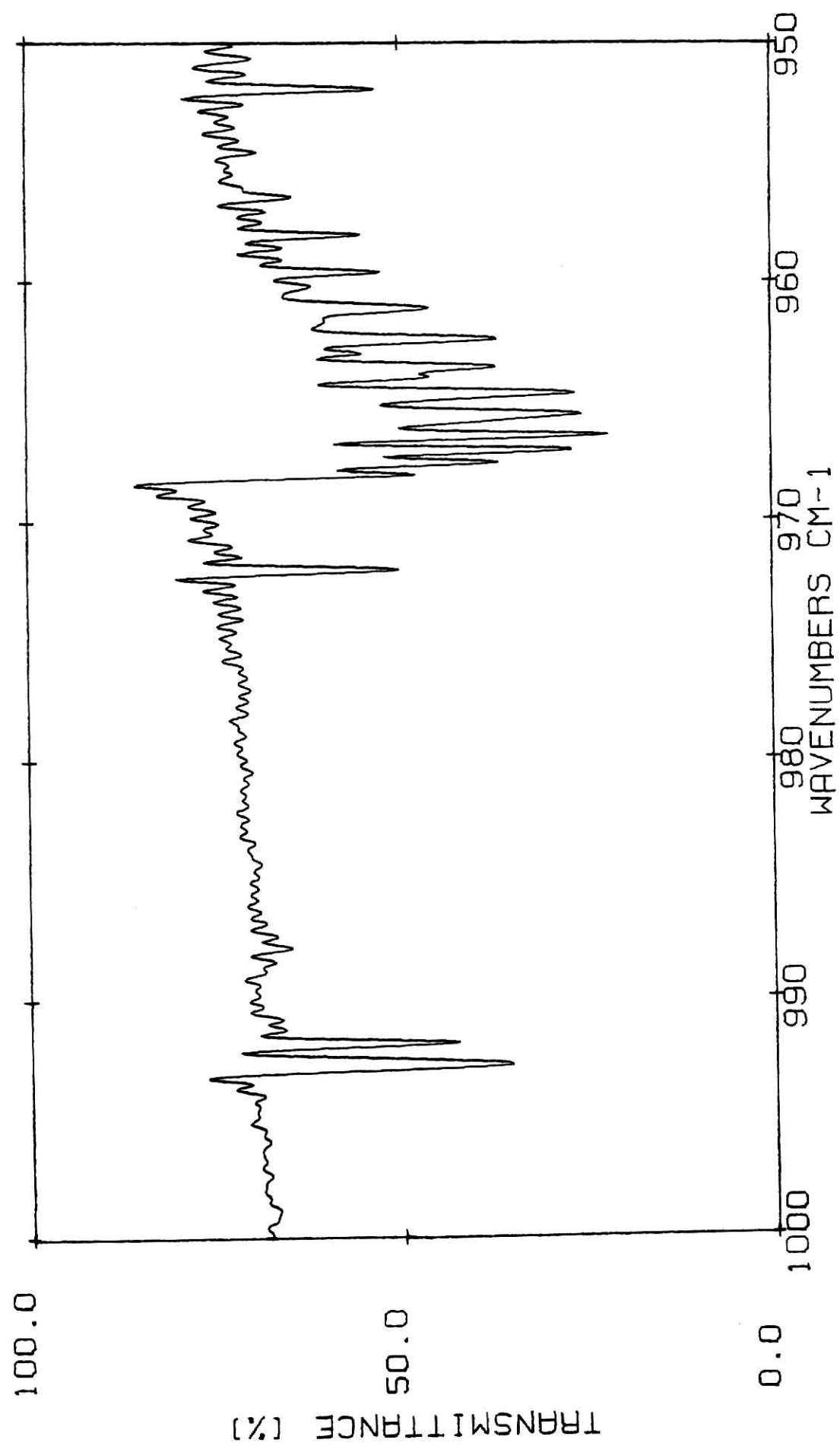


Figure 6. Infrared Spectrum of  $^{14}\text{N}$ -ammonia between  $1000\text{--}800\text{ cm}^{-1}$ .

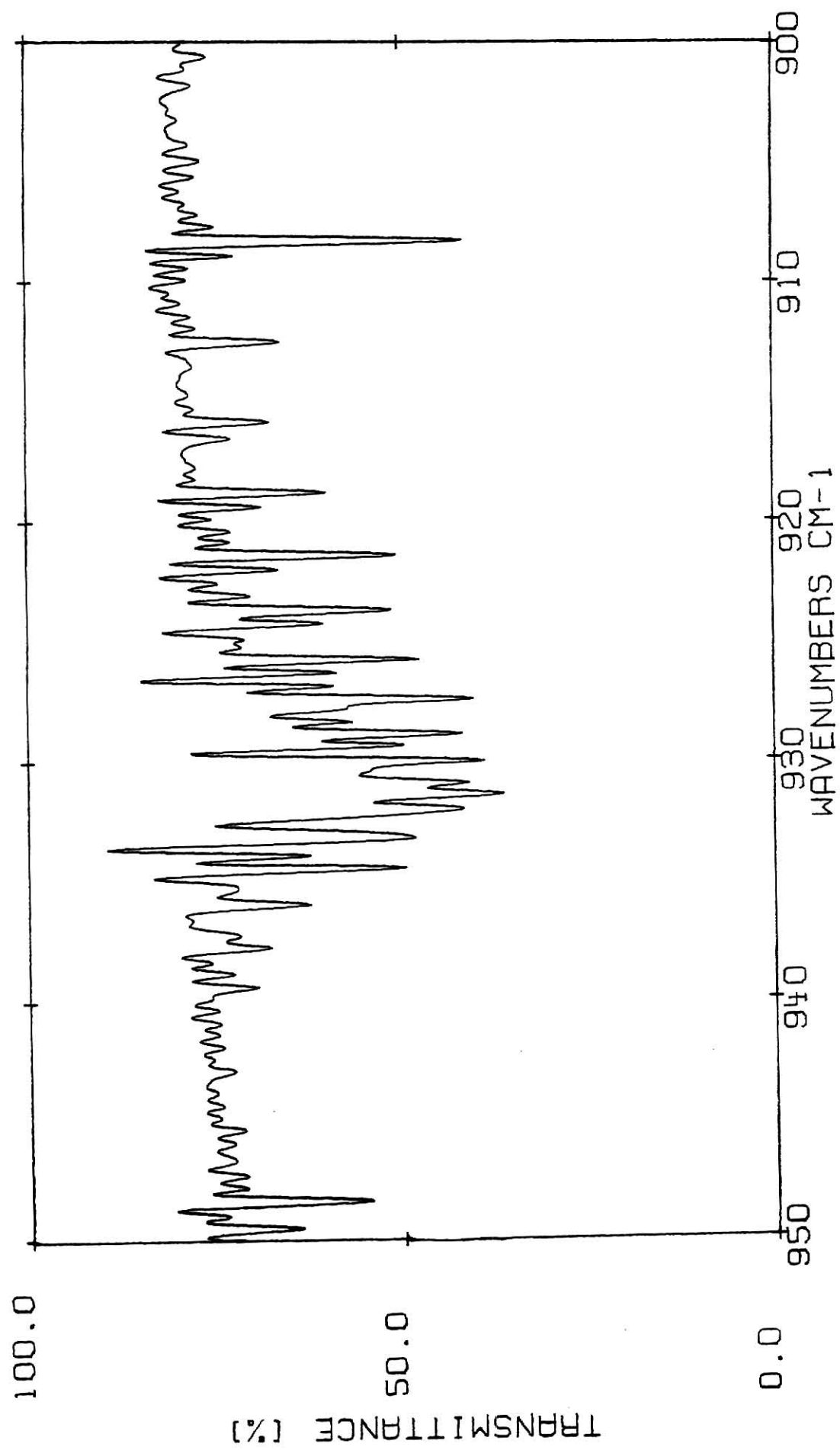


Figure 6 (continued).

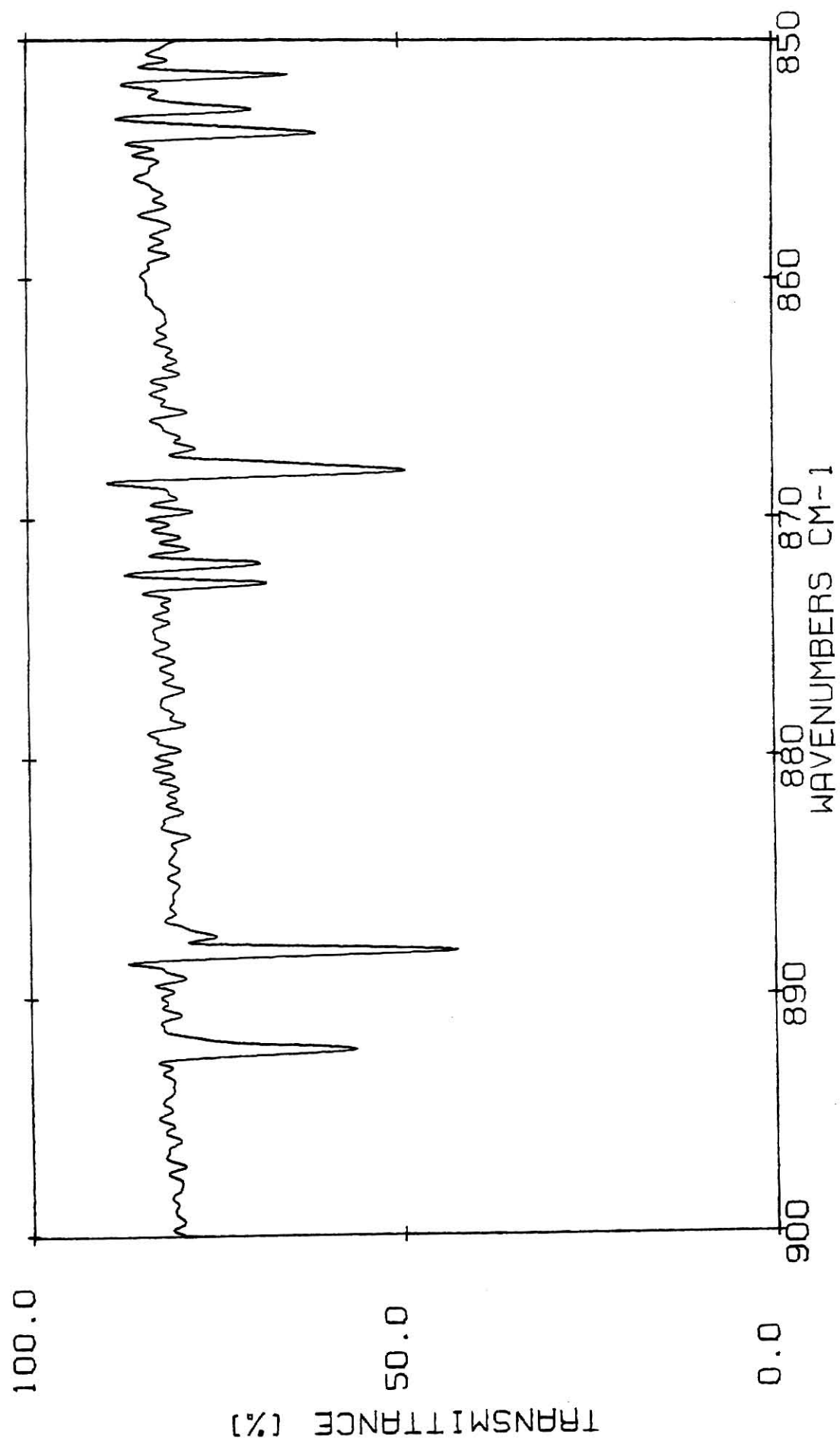


Figure 6 (continued).

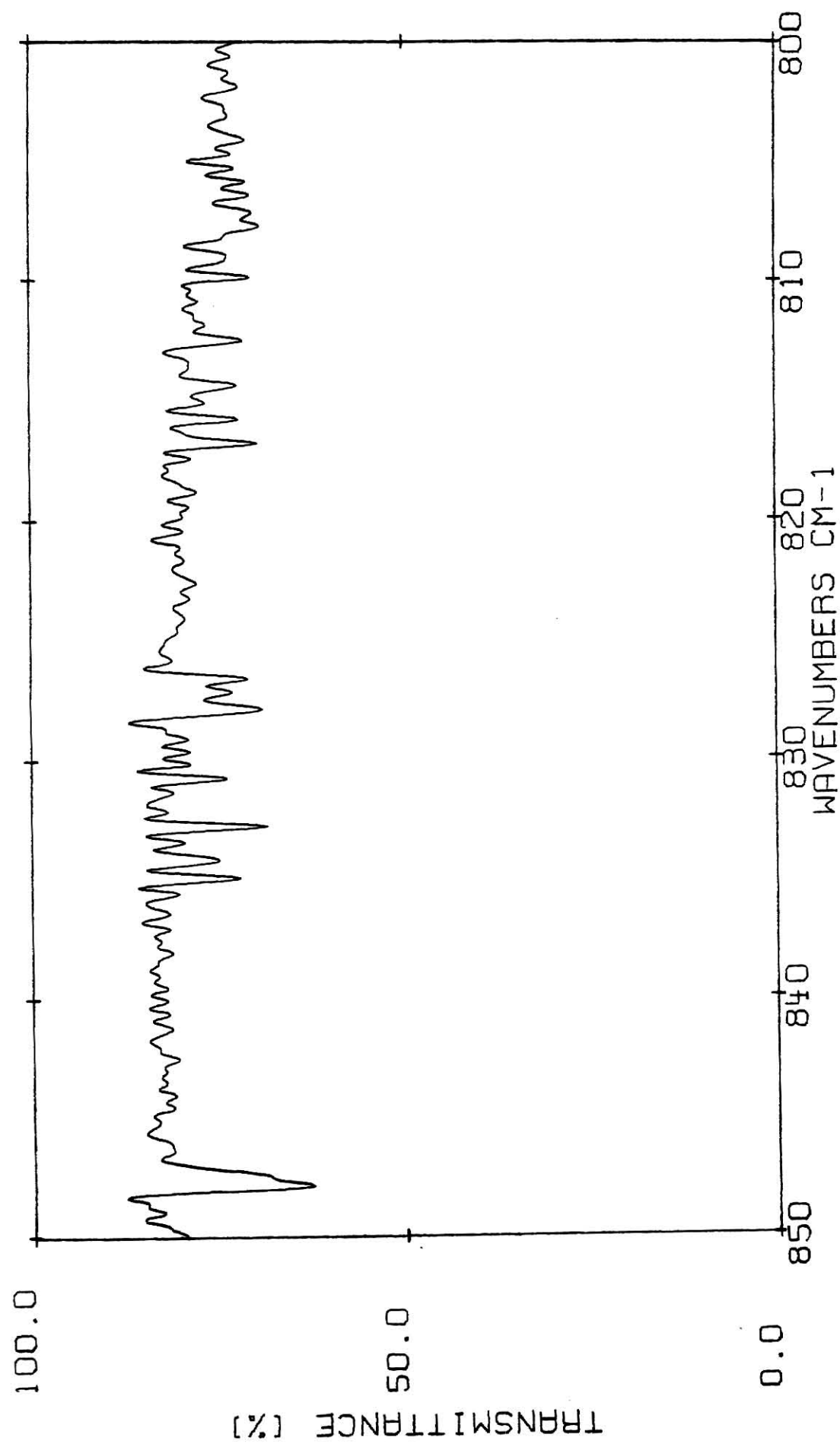


Figure 6 (continued).

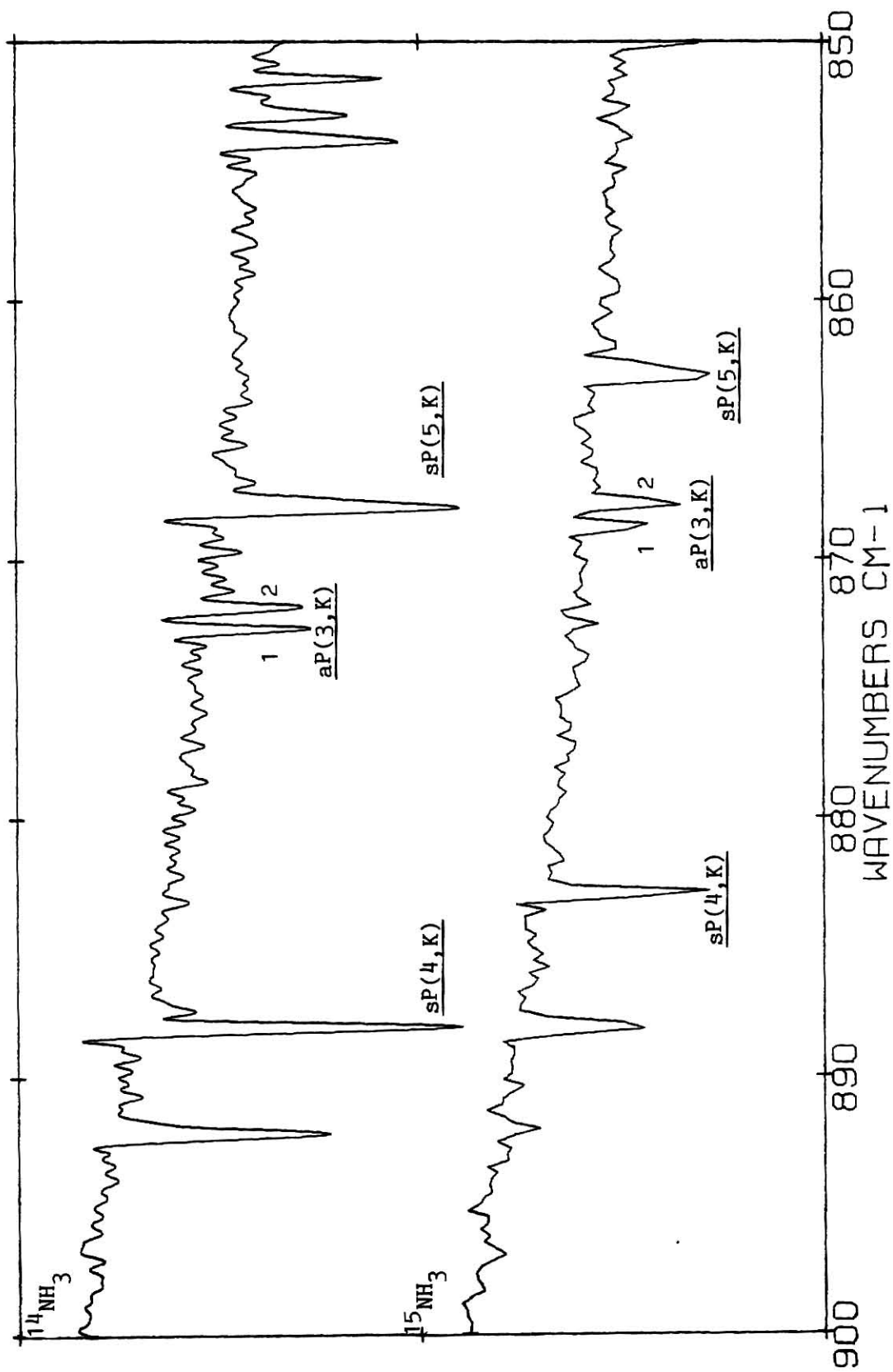


Figure 7. Single-beam Spectra of Both Species  $^{14}\text{N}$ ,  $^{15}\text{N}$ -ammonia between 900-850  $\text{cm}^{-1}$ .

## EXPERIMENT 3

THE ABSORPTION SPECTRUM OF WATER BETWEEN  $1600\text{--}800\text{ cm}^{-1}$ 

About 6 drops of distilled water were placed in the reaction vessel which was then immersed in a liquid nitrogen trap. The reaction vessel was attached to the vacuum line and evacuated. Then the liquid nitrogen trap was removed and water vapor was transferred into the absorption cell until the pressure reached 6.0 torr. The spectrum is shown in Fig. 8(a) and Fig. 8(b).

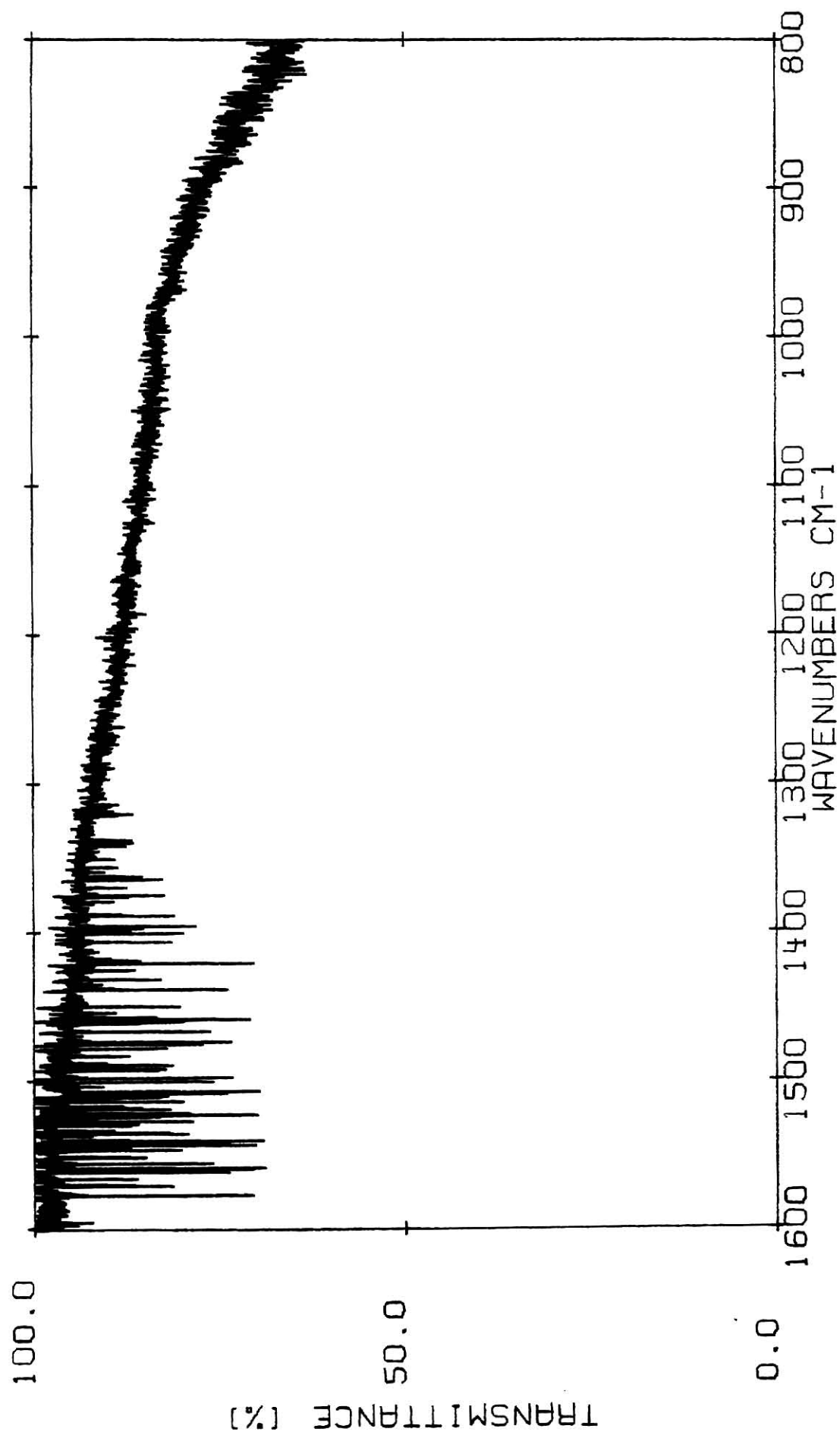


Figure 8(a). The Infrared Spectrum of Water between 1600-800  $\text{cm}^{-1}$ .



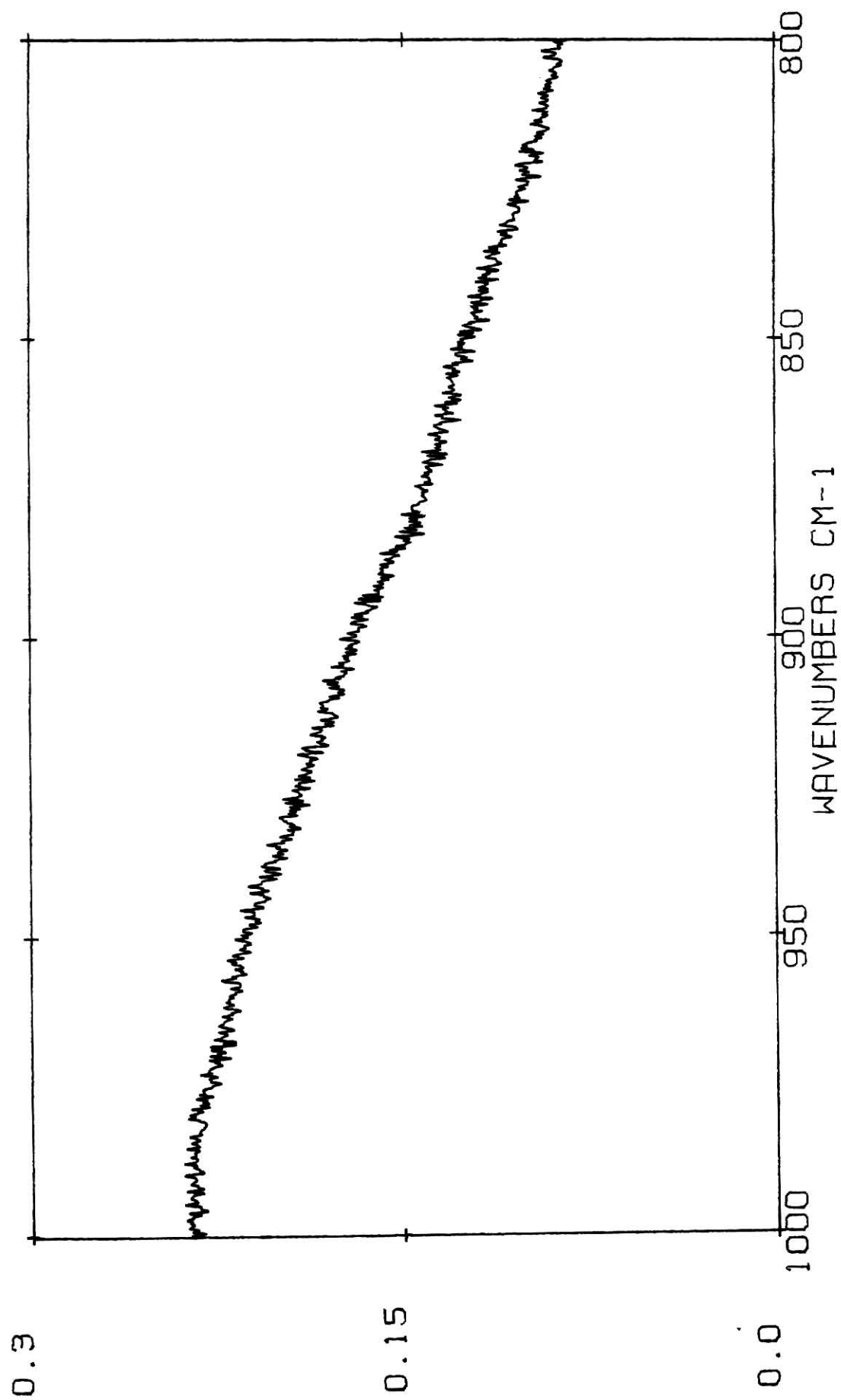


Figure 8(b). Single-beam Spectrum of Water between 1000-800  $\text{cm}^{-1}$ .

## EXPERIMENT 4

THE ABSORPTION SPECTRUM OF A MIXTURE OF  $^{14}\text{NH}_3$  AND  $^{15}\text{NH}_3$   
BETWEEN  $1000\text{--}800\text{ cm}^{-1}$ 

Exactly 0.4001 gram of 25%  $^{15}\text{N}$ -ammonium sulfate powder was introduced into the reaction vessel and placed in the oven for a few hours at  $100^\circ\text{C}$ . About 0.50 gram of calcium oxide was well mixed with the sample, and the reaction vessel was attached to the vacuum system and heated. Reaction was continued until 6.0 torr of the produced gases were transferred into the absorption cell. The spectrum was then measured between  $885\text{--}865\text{ cm}^{-1}$  (Fig. 9).

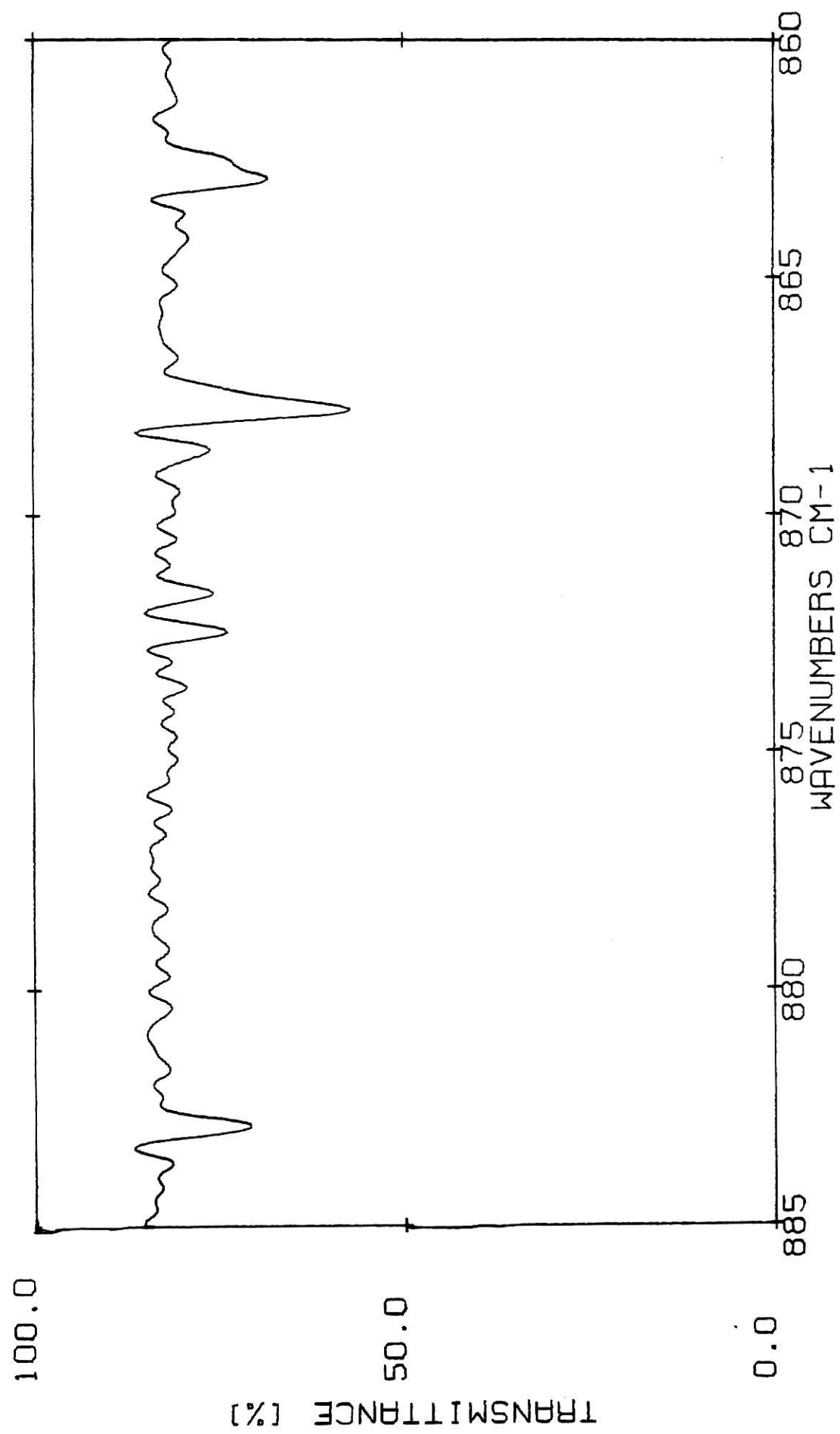


Figure 9. The Infrared Spectrum of 25% <sup>15</sup>N-ammonia between 885-860 cm<sup>-1</sup>.

Table II. Concentration and Absorbance Ratios:  $aP(3,1)^{15}\text{N}$   
and  $aP(3,1)^{14}\text{N}$  Absorption Lines.

Concentration Ratio $^{15}\text{N}/^{14}\text{N}$	Absorbance Ratio: $\frac{\log aP(3,1)^{15}\text{N}}{\log aP(3,1)^{14}\text{N}}$
0.0294	0.307
0.0526	0.280
0.1050	0.403
0.1765	0.570
0.2500	0.665
0.3333	0.815
0.4286	0.912
0.4925	1.05
0.5385	1.06
0.5873	1.12
0.6642	1.21

Slope: 1.49

Intercept: 0.266

Correlation Coefficient: 0.994

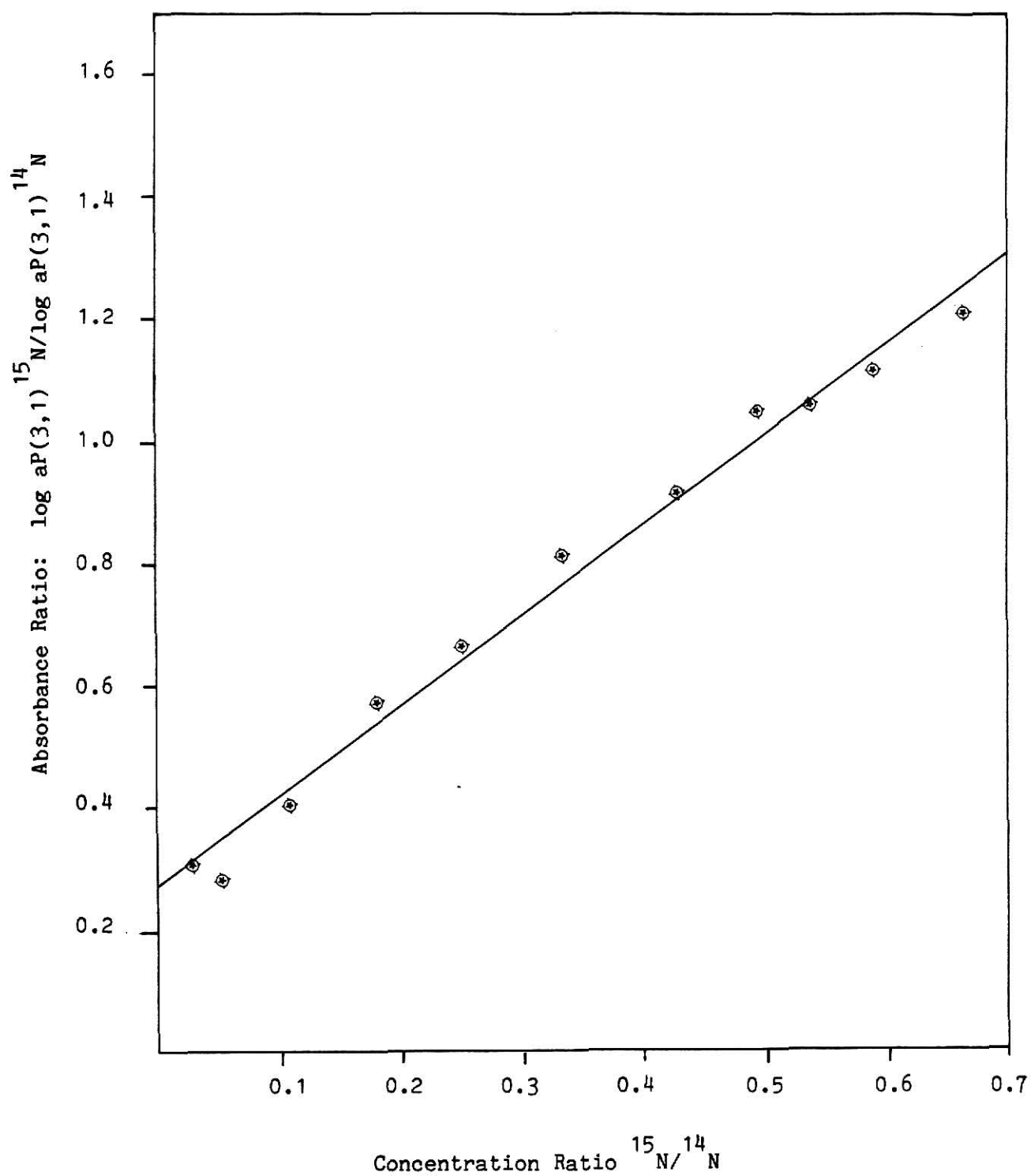


Figure 10. Plot of Ratio of Absorbance versus Ratio of Concentration:  
 $aP(3,1)^{15}\text{N}$  and  $aP(3,1)^{14}\text{N}$  Absorption Lines

Table III. Concentration and Absorbance Ratios:  $sP(4,K)^{15}N$   
and  $aP(3,1)^{14}N$  Absorption Lines.

Concentration Ratio $^{15}N/^{14}N$	Absorbance Ratio: $\frac{\log sP(4,K)^{15}N}{\log aP(3,1)^{14}N}$
0.0294	0.278
0.0526	0.380
0.0638	0.448
0.1050	0.532
0.1765	0.589
0.2500	0.888
0.3991	1.35
0.4925	1.64
0.5385	1.67
0.6642	1.93

Slope: 2.68

Intercept: 0.229

Correlation Coefficient: 0.995

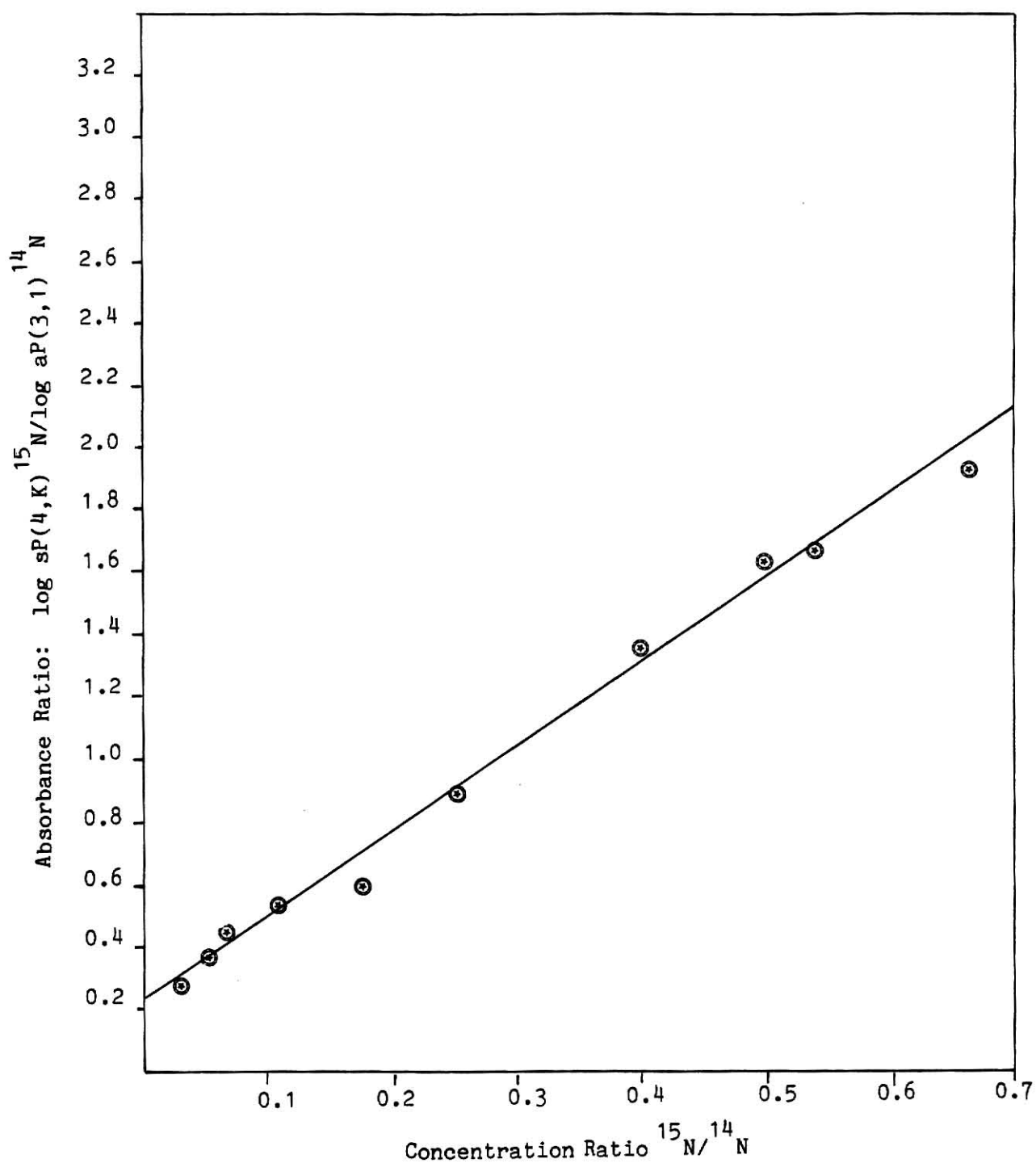


Figure 11. Plot of Ratio of Absorbance versus Ratio of Concentration:  
 $sP(4,K) ^{15}\text{N}$  and  $aP(3,1) ^{14}\text{N}$  Absorption Lines.

Table IV. Concentration and Absorbance Ratios:  $sP(5,K)^{15}N$   
and  $aP(3,1)^{14}N$  Absorption Lines.

Concentration Ratio $^{15}N/^{14}N$	Absorbance Ratio: $\frac{\log sP(5,K)^{15}N}{\log aP(3,1)^{14}N}$
0.0294	0.369
0.0526	0.508
0.0638	0.648
0.1765	0.872
0.2500	1.25
0.3333	1.68
0.3991	2.09
0.4286	1.85
0.5873	2.69
0.6642	3.11

Slope: 4.18

Intercept: 0.260

Correlation Coefficient: 0.993



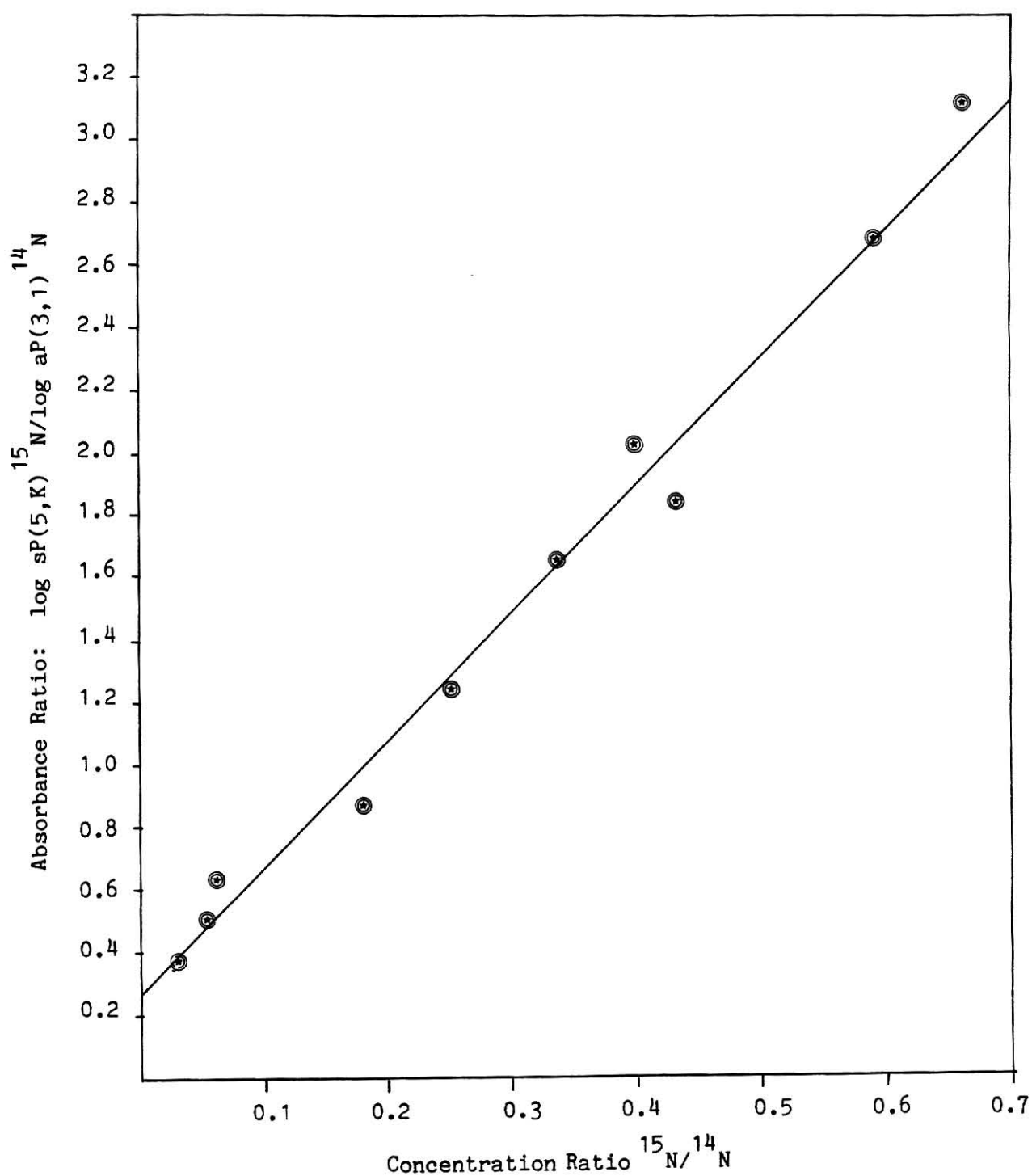


Figure 12. Plot of Ratio of Absorbance versus Ratio of Concentration:  
 $sP(5,K)^{15}N$  and  $aP(3,1)^{14}N$  Absorption Lines.

Table V. Mean Value for the Three Absorbance Ratios  
at Various  $^{15}\text{N}/^{14}\text{N}$  Ratios.

Concentration Ratio $^{15}\text{N}/^{14}\text{N}$	Mean Value for the Three Absorbance Ratios (Y)
0.0294	0.318
0.0526	0.389
0.1050	0.468
0.1765	0.677
0.2500	0.934
0.4286	1.381
0.5873	1.905
0.6642	2.080

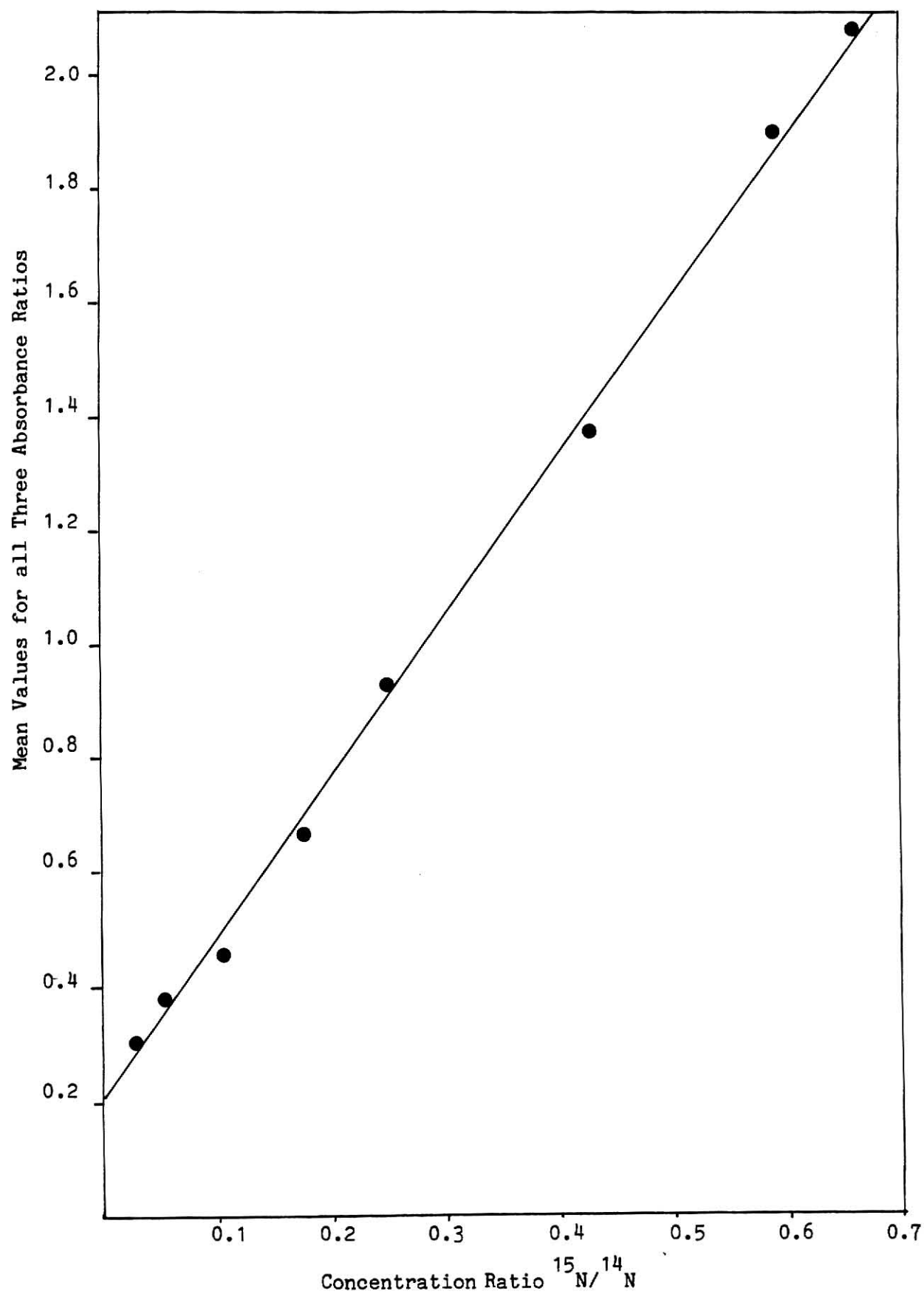


Figure 13. Plot of the Mean Values of the Three Absorbance Ratios versus the Concentration Ratio,  $^{15}\text{N}/^{14}\text{N}$ .

Ratios of absorbances of  $^{15}\text{NH}_3/^{14}\text{NH}_3$  and the ratios of concentrations in mole percent are shown in Tables 2, 3, and 4. Most of the values were obtained from the average of 2 or 3 spectra. A plot of the ratio of the absorbance associated with the aP(3,1) peak of  $^{15}\text{N}$ -ammonia at  $868.750\text{ cm}^{-1}$  to that of the aP(3,1) peak of  $^{14}\text{N}$ -ammonia at  $872.5647\text{ cm}^{-1}$  versus the  $^{15}\text{N}/^{14}\text{N}$  ratio is shown in Fig. 10. A linear relationship was obtained, and a least-squares fit of the data gave a slope of 1.49, intercept of 0.266, and a correlation coefficient of 0.994 (Fig. 10). The line has been drawn according to the least squares results.

Figure 11 is a similar plot making use of the sP(4,K) multiple peak of  $^{15}\text{N}$ -ammonia between  $882.856$  and  $883.022\text{ cm}^{-1}$  and aP(3,1) peak of  $^{14}\text{N}$ -ammonia at  $872.5647\text{ cm}^{-1}$ . A least squares fit of the data gave a slope of 2.68, intercept of 0.229, and correlation coefficient of 0.995.

Figure 12 is a plot making use of the sP(5,K) multiple peak of  $^{15}\text{N}$ -ammonia between  $862.543$  and  $863.220\text{ cm}^{-1}$  and aP(3,1) peak for  $^{14}\text{N}$ -ammonia at  $872.5647\text{ cm}^{-1}$ . A least squares fit of the data gave a slope of 4.18, intercept of 0.260 and correlation coefficient of 0.993.

Figure 13 is a plot making use of the average of the sum of the absorbance ratios versus the concentration ratios. A least squares fit of the data gave a slope of 2.82, intercept of 0.210 and correlation coefficient of 0.999.

## DISCUSSION

The applications of infrared spectroscopy as a quantitative analytical tool vary widely from one laboratory to another. The availability of high-resolution instruments materially increases the scope and reliability of quantitative infrared work.

Up to the present time, the isotopic analysis of nitrogen has been primarily by mass spectrometry, but there has been some work with emission spectra as well. Both methods are based on the measurement of intensity ratios and are therefore similar to the FT-IR method. Sample preparation is simpler in the FI-IR method than in the emission spectra method where nitrogen gas at controlled pressure is sealed in quartz tubes. And in the mass spectrometry method there is the requirement of a specially designed instrument to measure accurately the ion current ratios.

In this study I have made use of FT-IR for the isotopic analysis of ammonia. The results are presented in Figures 5 through 13 and Tables II through VII. From these results the following conclusions may be stated:

- 1) The spectra of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$  are resolved effectively as shown in Figures 5 and 6. Figure 7 shows spectra of both species of ammonia on the same plot and shows agreement between this study and other published results. Also there is not any water interference in the working region between  $1000\text{--}800\text{ cm}^{-1}$  which makes this method easy to use.

- 2) Preparation of samples is neither time consuming nor difficult, and the starting chemical form of nitrogen is the ammonium ion which is the chemical form produced in the Kjeldahl procedure. Also, the amount of sample needed to do the analysis is very small being of the order of 0.0014 gram of nitrogen.
- 3) Three linear relationships were obtained between ratios of absorbances and ratios of concentrations of the nitrogen isotopes (Figures 10, 11, and 12). Comparisons between these graphs show that they have different slopes due to different molar absorptivities. Since the  $aP(3,1)$  line for  $^{15}\text{NH}_3$  and the  $aP(3,1)$  line for  $^{14}\text{NH}_3$  are associated with transitions from the same quantum state, the graphical representation shows a better agreement with the relationship  $Y = b + mx$  than do those involving transitions from different states.
- 4) The practical lower limit of the  $^{15}\text{N}/^{14}\text{N}$  ratio under present experimental conditions is 0.02 because of signal to noise limitations below this value.
- 5) The length of time to do the analysis by this method is no longer than 30 minutes exclusive of drying time.

# QUANTITATIVE EVALUATION AS A METHOD OF ANALYSIS OF NITROGEN ISOTOPES

The methods that employ peak-height data will probably continue to be the principal routines of quantitative infrared analysis because of the great convenience with which the peak heights are measured and their relative insensitivity to a lack of precision of the base line determination.

By looking at the scatter in the diagrams of ratio of absorbance against the ratio of concentration, it seems clear that the ratio of absorbance may be adequately described as a linear function of the concentration ratio. The average deviation,  $\Delta x$ , of individual experimental points from the calibration line (which was determined by a least-squares analysis) is

$$\Delta x = \frac{\sum |Y - PY|}{N} = 0.031.$$

This means that the percent error according to the relationships

$$(Y = b + mx, \Delta Y = \Delta x \text{ or } \frac{\Delta Y}{Y} = \frac{\Delta x}{x})$$

is 10.1% at a ratio of 0.029 and 2.6% at a ratio of 0.66 (see Table VI). It is clear then that the smaller the ratio is, the harder it is to get an accurate ratio and the larger the percent error. Better advantage of the data can be made by making use of the mean value for the combination of all three calibration schemes as a function of the concentration ratio. These data are given in Table VII and plotted in Figure 13. In this case the percent error is 8.8% at a ratio of 0.029 and 1.4% at a ratio of 0.66.

Another evaluation of the precision may be made in terms of the standard deviation,  $s$  (33).

$$s = \sqrt{\frac{x_1^2 + x_2^2 + \cdots + x_n^2}{N-1}}$$

Table VI. Deviations between Estimated and Observed Absorbance Ratios.

Observation	Concentration Ratio X	Absorbance Ratio Y	Estimated Absorbance Ratio PY	Deviation
1	0.0294	0.307	0.310	-0.003
2	0.0526	0.280	0.345	-0.065
3	0.1050	0.402	0.423	-0.020
4	0.1765	0.570	0.530	0.040
5	0.2500	0.665	0.640	0.025
6	0.3333	0.815	0.764	0.051
7	0.4286	0.912	0.906	0.006
8	0.4925	1.05	1.00	0.050
9	0.5385	1.06	1.07	-0.010
10	0.5873	1.12	1.14	-0.020
11	0.6642	1.21	1.26	-0.050



Table VII. Error Analysis for the Mean Value of the Three Absorbance Ratios as a Function of the  $^{15}\text{N}/^{14}\text{N}$  Ratio.

Concentration Ratio $^{15}\text{N}/^{14}\text{N}$	Mean Value for the Three Absorbance Ratios (Y)	Estimated Mean Value for the Three Absorbance Ratios (PY)	Residuals
0.0294	0.318	0.293	0.025
0.0526	0.389	0.358	0.031
0.1050	0.468	0.506	-0.038
0.1765	0.677	0.708	-0.031
0.2500	0.934	0.915	0.019
0.4286	1.381	1.420	-0.039
0.5873	1.905	1.868	0.037
0.6642	2.080	2.085	-0.005

where  $x_i = X_i - \bar{X}$  and  $N$  is the number of observations. From a set of measurement on the 39.91%  $^{15}\text{N}$ , the observed values of  $Y$  are 1.15, 1.19, 1.28, and 1.21. This means that  $\bar{X} = 1.21$  and the standard deviation  $s = 0.056$ . Let us assume that we want a 70% confidence interval. From the  $t$  table, the  $t$ -value of 1.25 is found in the row of sample size of 4 and in the column of 70% confidence level. The precision for single value is  $\mu \pm ts$  or  $1.21 \pm (1.25)(0.056) = 1.21 \pm 0.070$ . There is a 70% probability that any  $Y$  value picked at random has a value that lies within 0.070 of the average. The precision of the mean is given by  $1.21 \pm (1.25) \frac{0.056}{4} = 1.21 \pm 0.0175$ . This means that for a series of 4 measurements and the specified confidence level, the true value of  $Y$  will lie in the interval  $1.21 \pm 0.0175$ .

Thus a  $^{15}\text{N}/^{14}\text{N}$  ratio determined from an experimental measurement of  $Y$  should be expected to be within 2.9% of the true value, if the ratio of concentration were in the region of 0.66.

## POSSIBLE IMPROVEMENTS

This method like any method employing curves is empirical. Its inherent errors are negligible, and the ultimate accuracy is limited chiefly by the accuracy of the calibration data (working curves). As noted by Griffiths and Block (34), detection limits achievable in practice by FT-IR are frequently determined by factors other than inherent performance limitations of FT-IR instrumentation.

The major limitation is not being able to measure  $^{15}\text{N}/^{14}\text{N}$  ratios below 0.02. Possible improvements might be achieved by the following:

- 1) Use of a long path cell: In the analysis of gases, a common path length is 10 cm. When this is too short to measure the spectra of minor components or substances encountered in trace analysis, a variable path cell of 1.5-120 meters might be used. A unique optical arrangement has been devised by which the infrared beam is made to traverse a cell several times. Even though the amount of gas needed to fill this kind of cell is larger, the signal to noise ratio is much improved by using this kind of cell. Obtaining spectra of samples containing  $^{15}\text{N}$  at the natural abundance level (0.36%) should be possible with a long path cell.
- 2) Increasing the number of scans: Further gains in sensitivity can be realized by increasing the number of scans which decreases the noise and makes it possible to detect the low signals.
- 3) Using a different detector: Sensitivity might be improved by changing from one detector to another keeping in mind the useful range of each detector. Since the (MCT) liquid nitrogen cooled detector is the best kind available to date, changing the detector offers little promise of improvement at the present time.

## APPENDIX A

### DERIVATION OF THE EQUATION USED FOR PREPARATION OF A SET OF AMMONIUM SULFATE SAMPLES CONTAINING DIFFERENT CONCENTRATIONS OF $^{15}\text{N}$ -AMMONIUM SULFATE

In order to prepare a set of different concentrations of  $^{15}\text{N}$ -ammonium sulfate, a known weight of stock sample which contained 58.44 WT%  $^{14}\text{N}$  and 41.56 WT%  $^{15}\text{N}$  was mixed with different weights of natural  $^{14}\text{N}$ -ammonium sulfate. In each gram of nitrogen contained in the stock sample there are 0.5844 gram of  $^{14}\text{N}$  and 0.4156 gram of  $^{15}\text{N}$ , and the number of  $^{14}\text{N}$  atoms is:

$$\frac{0.5844 \text{ gram} \cdot N_A \text{ mol.}^{-1}}{14.00307 \text{ gram mol.}^{-1}} = 0.04173 N_A,$$

where  $N_A$  is Avogadro's number.

The number of  $^{15}\text{N}$  atoms in 1.0 gram of nitrogen contained in the stock sample is:

$$\frac{0.4156 \text{ gram} N_A \text{ mol.}^{-1}}{15.00011 \text{ gram mol.}^{-1}} = 0.02771 N_A.$$

The atomic percent  $^{15}\text{N}$  in the stock sample is:

$$\frac{0.02771}{0.04173 + 0.02771} \cdot 100 = 39.905\%$$

Thus the atomic percent  $^{14}\text{N}$  is:

$$100 - 39.905 = 60.095\%.$$

The average atomic weight of nitrogen in the stock sample has to be known so that one can tell what number of  $^{15}\text{N}$  atoms (or  $^{14}\text{N}$  atoms) there would be in a certain mass of enriched ammonium sulfate. The average atomic mass of nitrogen in the stock sample is equal to the fractional abundance of  $^{15}\text{N}$  times the mass of  $^{15}\text{N}$  plus the fractional abundance of  $^{14}\text{N}$  times the mass of  $^{14}\text{N}$ :

$$^{15}\text{N}: (0.39905)(15.00011) = 5.9860 \text{ amu}$$

$$^{14}\text{N}: (1.0 - 0.39905)(14.00307) = \underline{8.4151 \text{ amu}}$$

$$\text{average atomic mass} \quad 14.4011 \text{ amu.}$$

Using the average atomic mass of nitrogen derived above, the molar weight of the stock sample of  $(\text{NH}_4)_2\text{SO}_4$  is found to be 132.9276 gram. The molar weight of natural ammonium sulfate is 132.14 gram, which contains 0.35 atomic percent  $^{15}\text{N}$  and 99.64 atomic percent  $^{14}\text{N}$ .

Experimental samples covering a range of  $^{15}\text{N}$  were prepared by combining a fixed quantity of stock sample (0.250 gram) with various amounts of natural ammonium sulfate. Let M be the mass of natural ammonium sulfate that is mixed with 0.250 gram of stock sample. The number of moles of  $^{15}\text{N}$  from 0.250 gram stock sample is:

$$\frac{(0.250)(2)(0.39905)}{132.9276} = 0.001501 \text{ mol.}$$

The number of moles of  $^{15}\text{N}$  from M gram of natural  $(\text{NH}_4)_2\text{SO}_4$  is:

$$\frac{M(2)(0.0036)}{132.14} = 0.0000545 M \text{ mol.}$$

The number of moles of  $^{14}\text{N}$  from M gram of natural sample  $(\text{NH}_4)_2\text{SO}_4$  is:

$$\frac{M(2)(0.9964)}{132.13} = 0.01508 M \text{ mol.}$$

The atomic percent  $^{15}\text{N}$  in a sample is:

$$\text{percent } ^{15}\text{N} = \frac{\text{mol. } ^{15}\text{N}}{\text{mol. } ^{15}\text{N} + \text{mol. } ^{14}\text{N}} \times 100.$$

Thus the atomic percent  $^{15}\text{N}$  in a sample prepared by combining 0.250 gram of stock sample with M gram of natural  $(\text{NH}_4)_2\text{SO}_4$  is:

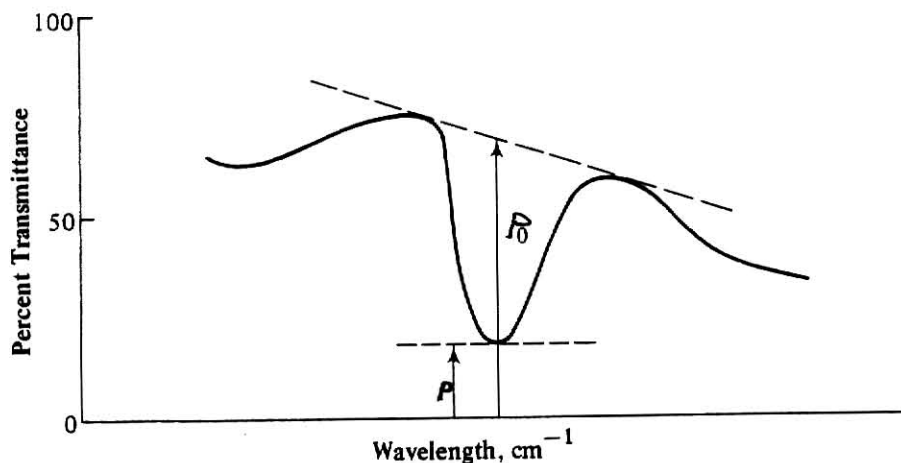
$$\text{percent } ^{15}\text{N} = \frac{0.001501 + 0.0000545 \text{ M}}{0.001501 + 0.0000545 \text{ M} + 0.00266 + 0.01508 \text{ M}} \times 100,$$

$$\text{or percent } ^{15}\text{N} = \frac{0.001501 + 0.0000545 \text{ M}}{0.003761 + 0.015134 \text{ M}} \times 100.$$

## APPENDIX B

## THE BASE LINE METHOD OF DETERMINING ABSORBANCE

The base line method involves selection of an absorption band of the substance under analysis which is separated from the bands of the other components. A base line is drawn across the shoulders of the band; the lengths  $P_0$  and  $P$  can then be measured as shown in the figure, and the absorbance calculated from  $\log(P_0/P)$ .



For quantitative analysis the base line method is an empirical method that is generally used to establish a calibration curve, i.e.  $\log(P_0/P)$  versus concentration ( $C$ ). This method of determining ( $P_0$ ) is at best approximate, but is easy to carry out, is fairly reproducible, and has wide applicability.

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ISOTOPIC ANALYSIS OF NITROGEN IN AMMONIA BY  
FOURIER TRANSFORM INFRARED SPECTROSCOPY

by

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AN ABSTRACT OF A MASTER'S THESIS

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## ABSTRACT

This work was undertaken to study the isotopic analysis of nitrogen in ammonia by Fourier transform infrared spectroscopy (FT-IR). Use was made of highly resolved spectra associated with rotational lines in the bending vibrational fundamental mode  $\nu_2$  of the ammonia molecule. Measurements of peak heights in the resolved spectra were used as a basis for the quantitative analysis of  $^{15}\text{N}/^{14}\text{N}$  ratios in ammonia samples.

Gaseous ammonia samples of known isotopic composition were prepared by heating solid mixtures of  $^{15}\text{N}$ -enriched ammonium sulfate and calcium oxide. The resulting mixtures of ammonia and water vapor were passed through a column packed with potassium hydroxide pellets into a glass cell. The cell had an optical path length of 24.8 cm and was equipped with sodium chloride windows. Infrared spectra in the 1000 to 800  $\text{cm}^{-1}$  range were obtained with the cell containing ammonia at a pressure of 6.0 torr. The region between 885 and 860  $\text{cm}^{-1}$  was used as the working range without any interference from water vapor.

For isotopic analyses, the intensities of the absorptions of sP(5,K) band, aP(3,1) line and sP(4,K) band for  $^{15}\text{N}$ -ammonia and the aP(3,1) line for  $^{14}\text{N}$ -ammonia were used. Plots of the ratios of absorbance versus the isotopic ratios were linear and served as workable calibration curves for isotopic analysis of gaseous ammonia samples having  $^{15}\text{N}/^{14}\text{N}$  ratios larger than 0.02.