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VIBRATION-ROTATION SPECTRUM OF MATRIX ISOLATED AMMONIA

by

Robert Earl Meredith

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of the requirements for the degree of
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To my wife and my mother.

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I. INTRODUCTION

Matrix isolation—the technique of embedding atoms or molecules under study in an otherwise inactive solid medium—was first used to facilitate the study of free radicals. Lewis and Lipkin[1] reported the successful isolation of a number of organic radicals dispersed in organic solvents. In their work, the radicals were formed by ultraviolet irradiation of the frozen mixture containing the parent molecules. Subsequent workers[2,3,4] developed a common practice of producing the radicals in an electrical discharge, and having the gas mixture flow out through a leak into a high vacuum where it hit and condensed on a cold surface whose temperature could be controlled. The condensate was investigated by its emission and absorption spectra.

A program[5,6] on the study of trapped radicals centered at the National Bureau of Standards from 1956 to 1960 greatly increased the knowledge and understanding of matrix isolation effects. Points relevant to the present work are summarized in the following two paragraphs.

A. PROPERTIES OF THE MATRIX

The diffusion rate of a radical in a matrix depends strongly upon the size of the radical. The diffusion rate for large radicals is determined almost completely by the ratio of the temperature to the melting point of the matrix—the diffusion becoming rapid when the temperature approached one-half the melting point temperature. Small radicals on

the other hand were found to diffuse out of the matrix even when the temperature was as low as one-tenth its melting point.[7]

X-ray diffraction studies[8] gave accurate information concerning the structure of condensed gases. Crystals deposited at various rates of speed were found to show a long range order when deposited slowly. Annealing the solid increased the ordering. In all cases it was found that solids formed by condensing gases onto a cold surface were of poor crystal quality, suffering from dislocations, holes, etc. Livingston[9] and co-workers concluded that the more imperfect the crystal (or more nearly amorphous), the larger the number of different sites at which impurities could be trapped. X-ray diffraction measurements on condensed argon by Peiser[8] indicated a surprisingly high density of dislocations. Moreover, he observed a slight orientation of the 111 plane parallel to the deposition surface.

B. SPECTRA OF TRAPPED RADICALS

The spectra studied involved electronic transitions exclusively. Usually, most of the absorption or emission lines could be correlated with the vapor phase spectrum of the radical, with only small frequency shifts arising from the perturbation of the matrix on the impurity. Large shifts were attributed to either polymeric species, or to an entirely different radical. A sizeable number of experiments showed the vibrational structure of the electronic bands. Robinson and McCarty[10] observed some 20 vibrational transitions in the absorption spectrum of

NH_2 trapped in solid argon. They observed very small matrix shifts of the vibration frequencies, and the spacings between lines were almost unaltered. These authors also investigated HNO in an argon matrix, discovering again that vibration spacings were nearly the same. These and other workers have concluded that inert gas matrices perturb the vibrational motion of trapped species only slightly.

Robinson and McCarty also interpreted the fine structure of their electronic-vibronic bands of NH_2 and NH as evidence of free rotation in argon matrices. The rotation constants attributed to this structure were identical with those of the free gas species.

Pimentel[11] initiated the study of matrix isolated stable molecules. The usual method of preparation involved spraying the gas mixture through a capillary leak onto a cold surface. Becker and Pimentel[12,13] in a detailed extension of the initial work, investigated the effect of temperature, different matrix materials and active molecules, and the ratio of the number of matrix to active species concentrations (designated by M/A). Chemical inertness, rigidity, low volatility, and transparency in the spectral region of interest were necessary properties of the matrix. Isolation was best achieved at low temperatures. The inert gases and nitrogen were found to be the most suitable matrix materials. They concluded that the matrix lattice is sufficiently rigid to produce isolation as long as the temperature is kept below particular values: 70°K for xenon, 35°K for nitrogen and 30°K for argon. The concentration of the active molecule also had a decided influence on the stability of the

deposit. In general, it was difficult to form deposits with M/A values less than 50. In addition, they found that the intensity of some absorption lines exhibited a strong dependence upon the concentration of the active molecule—varying directly as the concentration. These lines were attributed to associated active molecules, and they gave evidence of not only dimer formation, but also trimers, tetramers, and polymers.[14]

The particular work that led to the investigation here was that reported by Hexter, Milligan, and Dressler[15] at the Fourth International Symposium of Free Radical Stabilization held at the National Bureau of Standards in 1959. They had measured the absorption due to the ν_2 fundamental of NH_3 in the 10 micron region for NH_3 isolated in argon on a AgCl window held at 4°K and had found some eight lines. The large number of transitions observed seemed to be incompatible with the low temperature at which more than 99% of the molecules would be expected to be in the J = 0 level. Their interpretation, which involved the violation of the selection rule $\Delta J = -1$ while retaining the rule $\Delta J = +1$, was that the inversion doubling of the ν_2 vibration had decreased from 36.5 cm^{-1} in the free molecule to about 8 cm^{-1}, and that rotation of the molecule in the matrix was possible only for states having K = J. That is, the molecule could rotate freely about its symmetry axis, but other rotations about other axes were hindered by the matrix. The large number of transitions were explained as being Q(1), R(0), R(1), and R(2) lines. The difficulty in observing transitions from the J = 2 level of molecules at or even close to 4.2°K was not mentioned, although the absence of the correspond-

ing P branch lines were explained by assuming that K is allowed to be equal to J or very nearly equal to J.

The observed spectrum was so far at odds with what would have been anticipated that it seemed worthwhile to look into the problem further. With the spectroscopic facilities of this department several significant advantages could be realized: (a) better resolution, (b) reduction of the implied temperature differential between the sample and the dewar by placing the sample in the exit optics of the spectrometer so that it is illuminated by only the radiation in the band pass of the spectrometer, (c) the possibility of examining the absorptions due to the other fundamentals of the molecule.

Becker and Pimentel[12] had been the first to publish results of a matrix isolated NH_3 investigation. Four strong bands in the 1000 cm^{-1} region were reported for NH_3 isolated in argon. Although no assignments were made, it was concluded that some of the lines observed arose from incomplete isolation of the NH_3 molecules.

Since starting the work here, Pimentel, Bulanin, and Van Thiel[16] have observed the absorption for all four fundamental vibrations of NH_3 isolated in nitrogen. They concluded that the rotation of NH_3 was strongly hindered, and that there was no inversion doubling in ν_2. They pointed out that this and other spectroscopic evidence from other molecules indicated that nitrogen matrices trap impurities in a much more restrictive "cage" than noble gas matrices. There are some very striking qualitative similarities between the results of the present work and

that of Pimentel et al., even though the latter used nitrogen as a matrix. In particular, Pimentel observed lines which increased in intensity as the M/A ratio was increased. These lines were explained on the basis of a polymer picture, whereas, it will be seen that this work seems to indicate that more than one site may be available to NH_3.

Considerable work has been done in the interval since 1959 in other laboratories on the matrix isolation spectra of other simple molecules. Schoen[17] et al., have investigated HCl in argon matrices at 4°K and 20°K, and have interpreted their results in terms of a hindered rotation of the HCl molecule. Three absorptions were observed and labeled P(1), R(0), and R(1), in analogy with the notation used for a free rotor. The spacings of the lines were much smaller than observed for HCl in the gas phase, but for a reasonable value of their hindering potential, the spacing 4B between the P(1) and R(0) lines in the matrix can be accounted for. The spacing 2B between the R(0) and R(1) lines, however, was much smaller than the model predicted.

Glasel[18] and Redington[19] et al., have presented evidence of free rotation of water in inert gas matrices. Frequency shifts from gas phase values were measured, and the rotational spacings were found to be almost unchanged in the matrix. An interesting result of their investigations is a proof of the existence of two modifications of matrix isolated water—para and ortho. The para modification has the nuclear spins of the two identical nuclei pointing opposite one another, and the ortho has the spins parallel. It was estimated from the data that the iso-

lated water molecules were 75% ortho and 25% para. Lines which did not show rotational structure were also observed and were explained as arising from molecules trapped in interstitial sites.

The existence of matrix isolated ortho and para species has received considerable attention in recent years. Besides H_2O, matrix isolated NH_2, the methyl radical, and NH_3 have been investigated in order to see if ortho and para modifications are both contributing to the spectra. Robinson et al., have concluded that for matrix isolated NH_2, almost 100% conversion of the para nuclear species to the ortho has taken place. On the other hand, electron spin resonance measurements on matrix isolated methyl radicals indicated strongly that no such nuclear conversion is taking place. Since in the absence of a spin dependent perturbation a conversion of nuclear spins to one type cannot take place, no adequate explanation for the observed effect has been presented. K. Dressler[20] has speculated that the nitrogen atom in NH_2 has perturbed the spin functions enough to eliminate all traces of the para molecules. He observed a series of bands in the 1600 to 1900 Å region in matrix isolated NH_3 and attributed this structure to transitions of the symmetric bending vibration ν_2. The absence of alternate lines in the structure was interpreted as arising from an almost 100% conversion from para ammonia to ortho.

II. EXPERIMENTAL DETAILS

The problem faced was to determine and account for the fine structure of the vibrational absorption bands of NH_3 in rare gas matrices. NH_3 has four fundamental frequencies: two non-degenerate parallel type of species A_1, ν_1 near 3335 cm^{-1}, and ν_2 near 950 cm^{-1}, and two degenerate ones of species E, ν_3 and ν_4 near 3440 and 1625 cm^{-1} respectively. It was difficult to work in the 1600 cm^{-1} region because of low detector sensitivity and strong water vapor absorption and no observations were made there. It was thought that valuable information could be gained by also obtaining the spectrum of ND_3 whose corresponding frequencies lie at 2420, 785, 2555 and 1190 cm^{-1}—all of which were in accessible regions of the spectrum. The overtone $2\nu_4$ lies in the region of ν_1 for both molecules and complicates the situation there somewhat.

With respect to matrix materials, the rare gases were selected because of the simplicity of their structure. Of these neon is not satisfactory because of the rapid diffusion of other molecules through the matrix. Most of the deposits were made with argon, and some with krypton and xenon.

The basic components of the apparatus involved were: (1) the spectrometer, (2) the low temperature dewar, and (3) the system for preparing the samples.

1. Two spectrometers were used in the course of this work. The symmetric bending vibration ν_2 of both NH_3 and ND_3 was investigated with

a one meter focal length F-5 spectrometer built by Hardy in 1930. This instrument makes use of 8 in. paraboloidal mirrors in a Pfund type mount, and has excellent imaging properties when used in the medium infrared. It utilizes a 6 in. by 8 in. grating. A diagram of the optical components is shown in Figure 1. M_1 and M_4 are the 8 in. paraboloidal mirrors and M_2 and M_3 are 8 in. flats which are pierced so that the beam may pass through the entrance and exit slits S_1 and S_2. A 2400 line/in. grating (G) was used for all measurements made with this instrument. Radiation from a Nernst glower (S) was collected by a mirror m_1 and rendered parallel by a mirror m_2. The parallel beam passed through a KBr littrow prism (P) and then focused on the entrance slit by the mirror m_3. This arrangement supplied the desired F-5 beam to the spectrometer proper with no overlapping orders when used in the 10 to 12 micron region.

Two sets of exit optics were used for the medium infrared measurements. For spectra of crystals deposited on a copper surface (see Chapter III) it was found most convenient to use the copper substrate as one of the component mirrors. m_4 and m_5 (see Figure 2) demagnify the image by a factor of two and throw it beyond m_5 where there is enough room to place the copper "mirror," m_6. After reflecting off the copper, the beam is demagnified again by a 5:1 elliptical mirror and focused onto a thermocouple. The other set of exit optics shown in Figure 3 differed in that the beam was focused through a transparent window being demagnified by m_4 and m_5, and was focused onto a Golay cell off of a flat m_8 and an elliptical mirror, m_9. The radiation was chopped at 10 cps, and

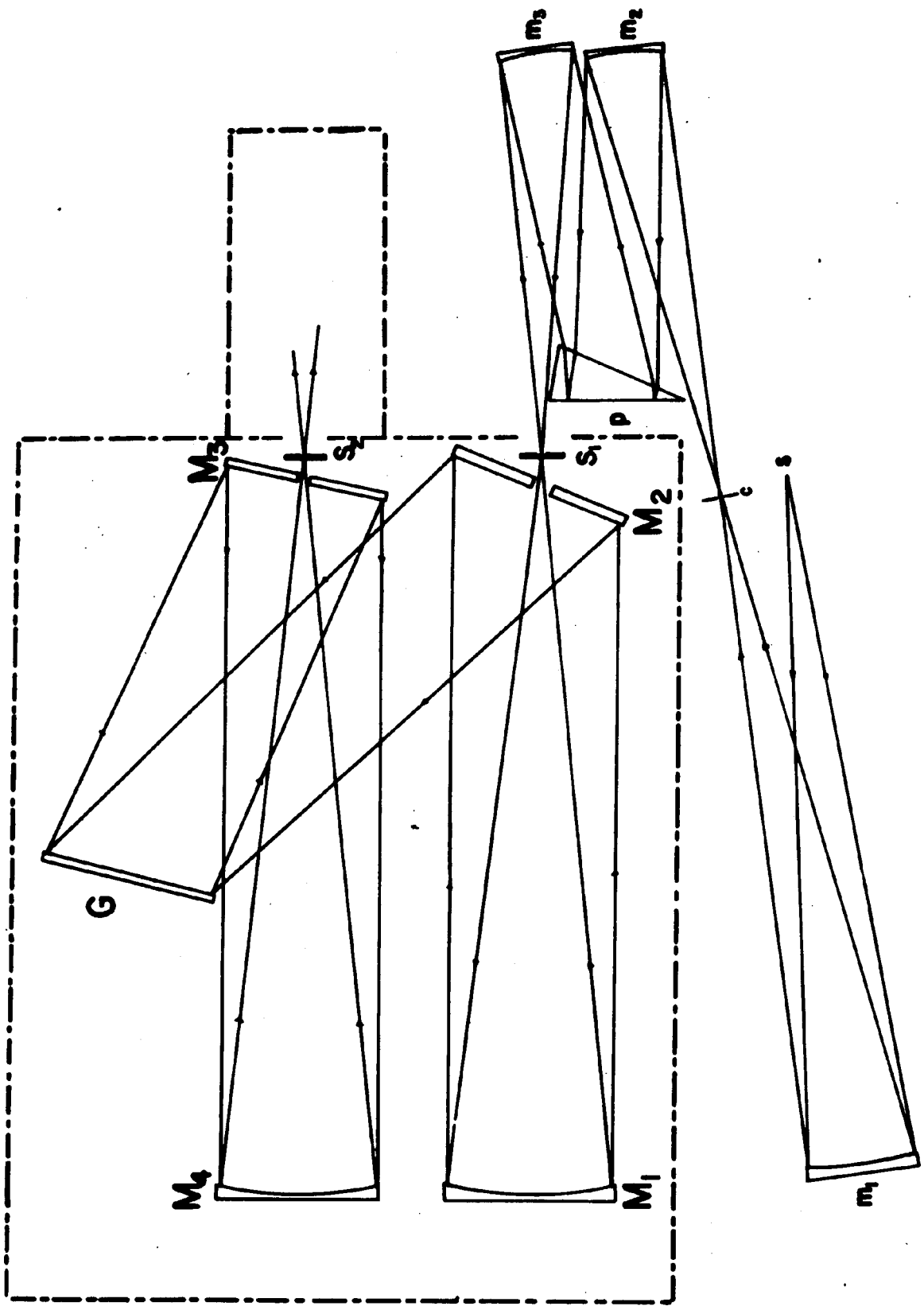


Figure 1. Diagram of medium infrared spectrometer and fore optics.

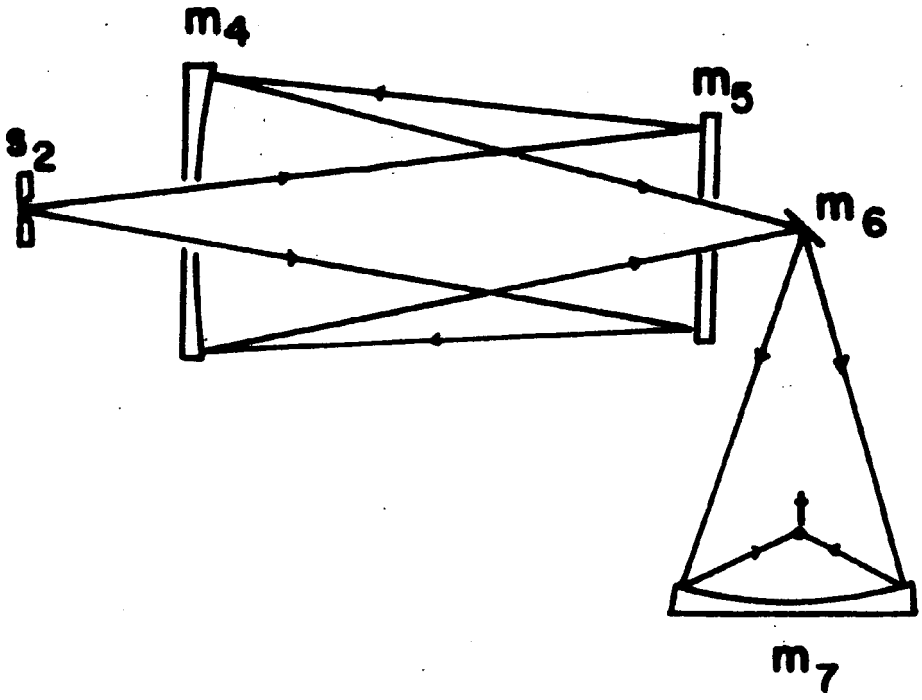


Figure 2. Diagram of exit optics used with the thermocouple detector.

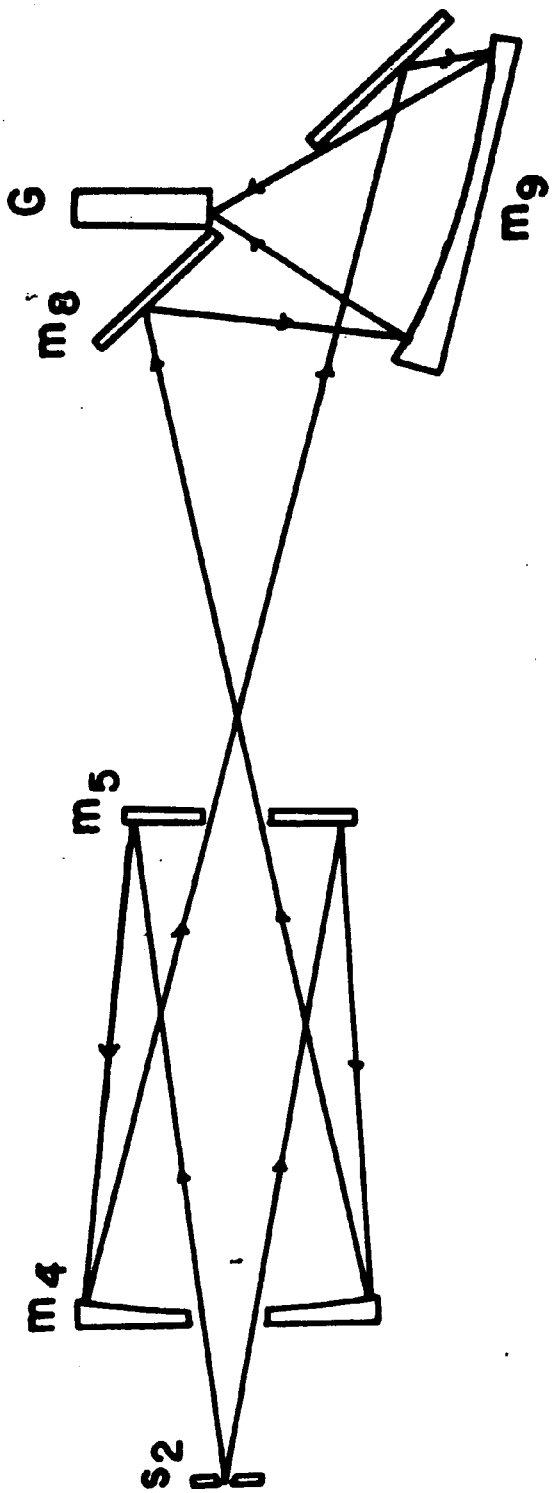


Figure 3. Diagram of exit optics used with the Golay detector.

the signal from the detector was amplified, synchronously rectified and recorded.

The measurements of the ν_1, ν_3, and $2\nu_4$ bands were carried out with a 3 meter focal length f/15 ebert vacuum spectrometer designed by H. W. Marshall. Its spectral band pass is customarily less than 0.1 cm^{-1} in the near infrared where photoconductive detectors are available. A 6-in. by 8-in. 300 line/mm grating was used in first order in scanning the NH_3 spectra, and a 180 line/mm grating of the same size was used for the ND_3 spectra. In all cases appropriate interference filters were used to remove higher spectra order radiations. A Nernst glower was used as source, and a simple set of condensing optics was used in order to supply the spectrometer with an f/15 beam and 2 cm high image. Auxiliary optics in the main spectrometer tank throw an image out far enough to permit passage through a transparent substrate. The beam is then demagnified by a five to one elliptical mirror onto a photoconductive detector placed at the tip of a glass dewar that could be cooled to liquid nitrogen temperature in order to achieve maximum detector sensitivity. The NH_3 spectra were scanned using a p-type lead sulfide detector, and the ND_3 spectra were scanned using an R-type lead selenide detector, both made by the Eastman Kodak Co. The entire optical path is enclosed in a vacuum housing, and strong atmospheric absorption in the $2\nu_4$ and ν_1 region of ND_3 made it necessary to pump out the entire system except for the source housing, which was flushed with dry nitrogen.

The infrared beam was modulated by a three bladed chopper driven

by an 1800 rpm synchronous-motor and the signal produced in the detector was amplified by an amplifier tuned to 90 cps. The chopper was also used to modulate a light beam incident on a phototube, thus generating a synchronizing signal. This signal was used to synchronously rectify the infrared signal for display on a chart recorder.

2. The low temperature dewar used for the preparation of the matrix isolated samples except in one case was a typical metal double dewar designed to hold approximately 1.2 liters of liquid helium in the inner container. The machine work was carried out in the Physics Department instrument shop, and the parts were soldered together in the Chemistry shop. The inner containers were made of 1/32 in. brass and were suspended from the outer housing by 1/64 in. stainless steel tubing. A dewar tip in which the cold window was mounted projected downward from the helium pot. One-sixteenth in. copper shields were attached to the liquid nitrogen container so that the inner container was completely protected from the room temperature except for a very narrow slit through which the infrared beam and the depositing ammonia-noble gas mixture passed. The inner containers were also polished and chrome plated to minimize radiation loss. The dewar was evacuated before each run by an oil diffusion pump. Through the course of the experiment, it was found that the dewar was capable of holding liquid helium for as long as 12 hr. In as much as most deposits were sprayed on very slowly, it was important that the dewar be at least this efficient.

The crystals were deposited by leaking the gas mixture through a

10 mil I.D. stainless steel tube which was pointed through the outer dewar housing toward the cold window. The window (sapphire for all near infrared measurements) was forced firmly against the dewar tip in order to be in good thermal contact. The dewar tip was of a somewhat special design, and is shown in Figure 4. It was felt to be of importance that the temperature be close to 4.2°K, so the copper tip was made to be hollow all around the window, permitting liquid helium to completely surround it at all times. The window was made flush by recessing the tip, and a snugly fitting collar was fitted against it to hold it in place. Several checks were made of the thermal contact between the window and copper surfaces. The contact was first coated with a thin layer of vacuum grease, then again with a mixture of vacuum grease with fine copper fillings, and finally with nothing at all. No differences were observed in the spectra of NH_3 isolated in argon for the three cases, and it was felt that only a good clean contact was needed.

3. The ammonia and noble gases were mixed in a manometer system shown schematically in Figure 5. The mixing took place in a one liter glass bulb. A mercury manometer attached to the bulb was used to read the pressure of the mixture, and a smaller differential manometer was used to assist in arriving at the desired ratio. The mixing was carried out in the following way: the differential manometer stopcock was turned to the "open" position and the bulb was pumped out. The stopcock was then closed and ammonia was slowly leaked into the system. The difference between the two columns of the differential manometer accurately

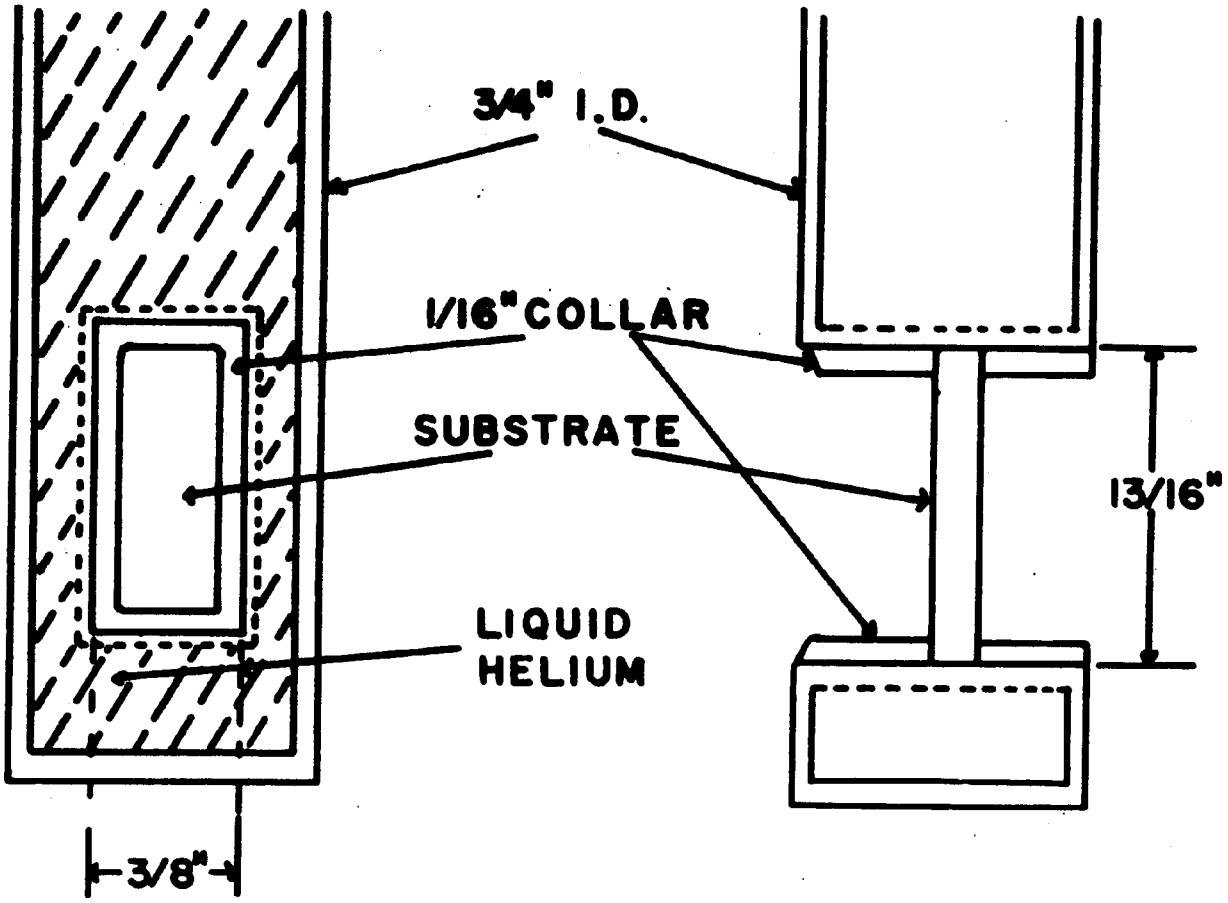


Figure 4. Diagram of dewar tip.

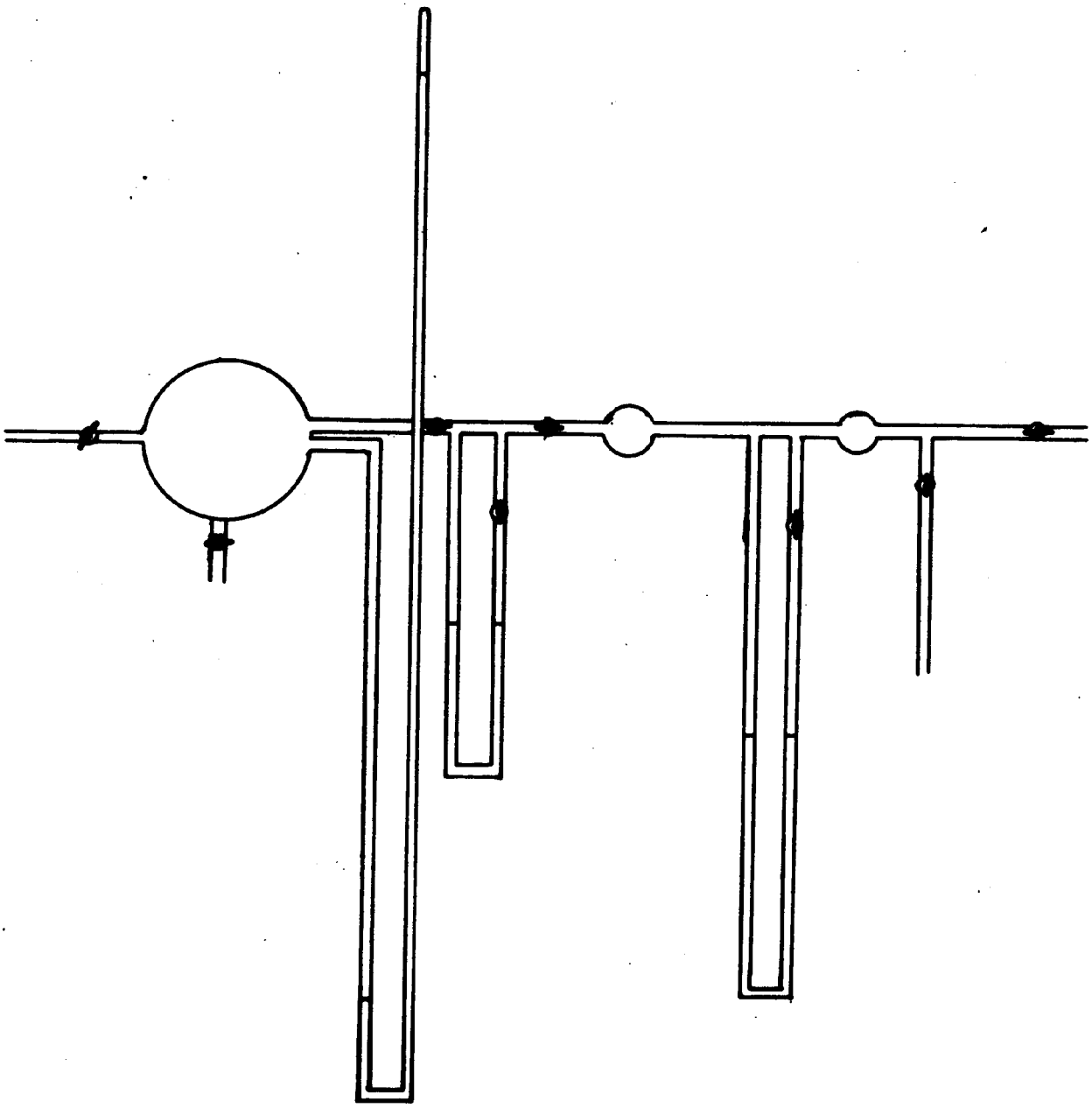


Figure 5. Diagram of manometer system used for mixing and spraying gases onto the cold finger.

measured the pressure of the ammonia let into the bulb. The stopcock was then turned back to the "open" position, and the desired amount of inert gas was leaked in as measured by the mercury manometer. The liquid used in the differential manometer was chosen to be octoil-s because of its low specific gravity. This made the measurements of ammonia to noble gas ratios much more accurate than could be obtained using only the mercury column.

The second section of the manometer system consisted of a smaller bulb and another differential oil manometer. This part served as a let down valve so that a uniform rate of deposition could be established. By first evacuating this section and turning its manometer to the off position and then cracking the stopcock leading to the large bulb, it was possible to maintain a constant pressure of gas mixture entering the low temperature dewar. After a little practice, it was possible to let the mixture leak out of the bulb at a constant rate for several hours.

The "let down section" entered into a glass tube leading to the low temperature dewar. The 10 mil stainless steel tube mentioned earlier was fused into the glass tube completing the path from the mixing bulb to the cold window. The hole in the dewar through which the stainless steel tube was aimed was placed as close to the outer window as possible and was approximately 1-1/4 in. from the cold window. The direction of the gas as it sprayed onto the window was not perfect at first, but after several adjustments of the tube the spray seemed to be quite well centered on the window.

A spectrum of matrix isolated NH_3 was obtained also of a sample deposited on a copper substrate. The dewar used in this case was made of glass and had only one inner container, and had a copper container at its tip. One side of the container was a highly polished flat piece of copper. Ammonia was successfully isolated on this surface, and although the dewar was capable of holding helium for only 2 hr, it was used to observe the first spectra. This copper substrate is of course the copper "mirror" mentioned in the discussion of the exit optics for the medium infrared instrument.

III. RESULTS OF THE EXPERIMENT

The work of Hexter et al., on the ν_2 band of NH_3 in argon and nitrogen had just been reported, the results of which were surprising enough to warrant an investigation using higher dispersion. The glass dewar referred to in the previous chapter was modified for this use, and a spectrum of NH_3 isolated in argon at a dilution of M/A = 500 was scanned. This spectrum is shown in Figure 6, and the line positions are indicated in Table 1. When compared with the spectrum of Hexter et al., several differences were noted. First, Hexter observed a line at 961 cm^{-1} and did not observe one at 1032 cm^{-1}. The present investigation does not indicate an absorption at 961 cm^{-1} but does find one at 1032 cm^{-1}. Also, the three lines near 975 cm^{-1} are much better resolved than those in the earlier work. The spectral slit width at which the spectrum in Figure 6 was scanned was approximately 0.2 cm^{-1}, so it is felt that the half widths listed in Table 1 are accurate measurements of the natural widths of the lines. A number of attempts were made to bring out a line at 961 cm^{-1}, but with no success.

In general, however, Hexter's observations were substantiated, and no light was shed on the perplexing problem of how so many transitions could arise from NH_3 molecules that must certainly have been in the ground state at liquid helium temperature. It was decided to examine the other fundamental vibrations of NH_3 accessible in the near infrared, ν_1 and ν_3, which would exhibit a much different inversion splitting, if

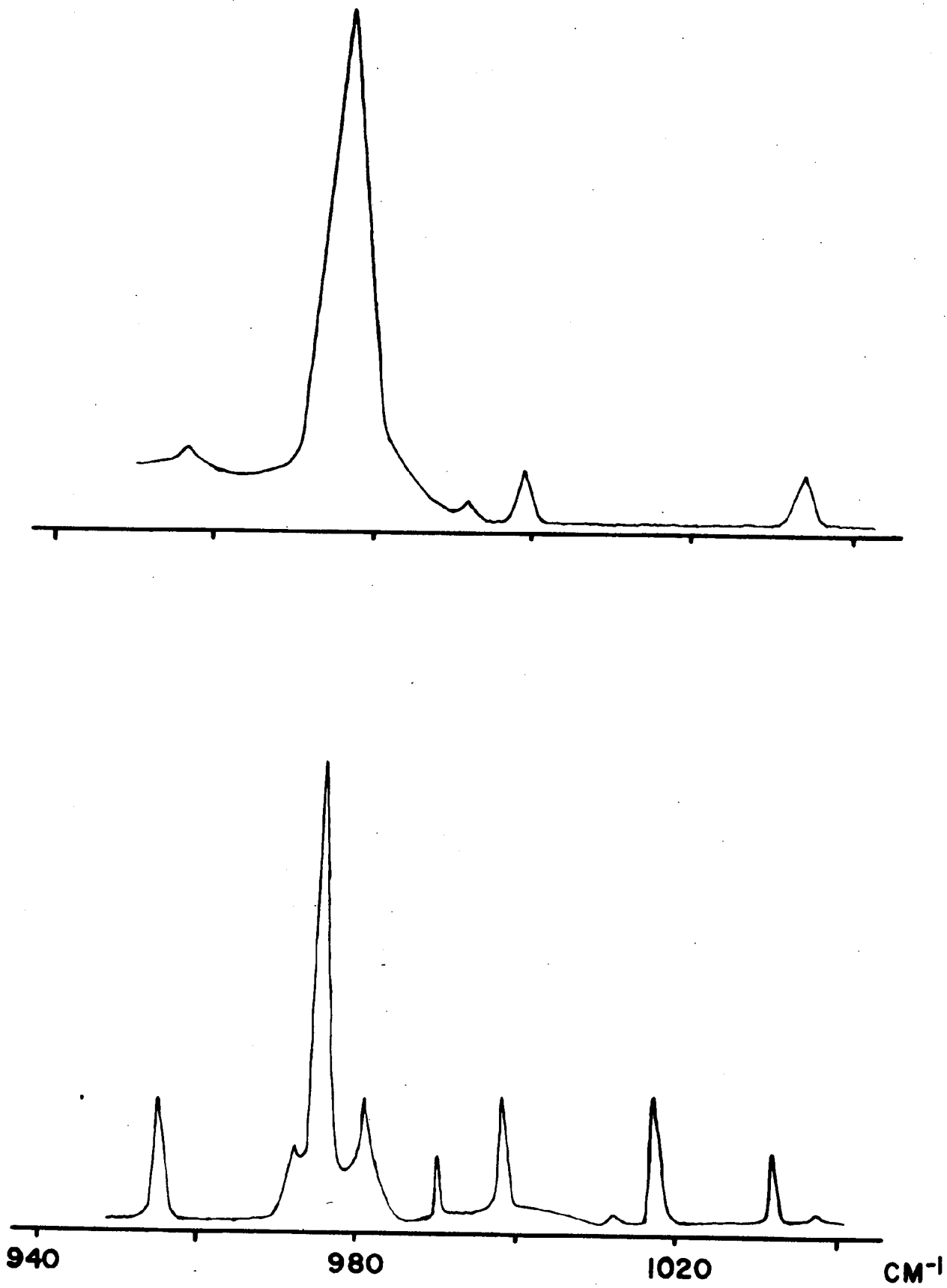


Figure 6. Spectrum of NH_3 isolated in argon with M/A equal to 500 using KCl (above) and Cu. as substrate.

TABLE 1

LINE POSITIONS FOR NH_3 ISOLATED IN ARGON USING A COPPER SUBSTRATE

Frequency, cm^{-1}	Assignment	Half Width, cm^{-1}
955	Q(1)	1.4
972	Polymer	---
975	R(0)	2.2
981	Site	1.1
990	Q(1)	1.2
998	R(1)	1.6
1012	Weak	---
1017	Site	1.7
1032	R(1)	1.6
1037	Weak	---

nothing else. The new metal dewar was used with the three meter spectrometer to obtain transmission spectra in this region of NH_3 isolated in argon.

The first measurements were made primarily to ascertain the dependence of the spectra on concentration. Sample spectra of NH_3 isolated in argon are shown in Figure 7 at ratios M/A = 200 and M/A = 20 respectively. The lines which differ in dilute mixtures are attributed to polymeric species, and they are indicated in Table 2 as type p. Other lines are attributed to monomeric NH_3, and are designated by type m. Table 2 also gives the half widths of the sharper lines, along with the most reasonable vibrational assignment. The spectral slit width used in these scans was approximately .2 cm^{-1}, even though the instrument is capable of a resolution of .03 cm^{-1} in this region. It was found that the argon deposit scattered the infrared radiation quite severely, and the loss of

TABLE 2

LINE POSITIONS FOR THE NEAR INFRARED SPECTRUM OF NH_3 ISOLATED IN ARGON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)	Half Width, cm^{-1}
3211.6	$2\nu_4$	m	---
3234.9	$2\nu_4$	p	---
3242.9	$2\nu_4$	m	1.40
3305.5	ν_1	p	---
3310.2	ν_1	m	2.24
3324.?	ν_1	p	---
3326.2	ν_1	m	---
3345.7	ν_1	p	---
3391.5	ν_3	p	---
3398.7	ν_3	m	2.8
3433.0	ν_3	m	Broad
3436.0	ν_3	m	Broad
3445.0	ν_3	p	Broad

energy necessitated opening the slits considerably. The region was scanned with the slits set at approximately .1 cm^{-1} and again at .2 cm^{-1}, but no broadening of any lines were observed. From this it was concluded that the resolution was quite sufficient to assure the measurement of natural line widths.

The rate of deposition of the gas mixture was also varied. There was no noticeable difference in the spectra of films grown both slowly and very quickly from the standpoint of line position or strength. It was quite apparent that scattering from the crystals grown very slowly was not as severe as from those grown very rapidly. It was anticipated that if light scattering were to become a problem in subsequent experiments, crystals would have to be grown very slowly. It was also possible

to shine a flashlight onto the deposit and view it directly. The only obvious difference in the physical appearance of solids grown at different rates of speed was their transparency. Solids grown very quickly had a white milky appearance, whereas solids grown slowly for several hours had the appearance of a film of ice.

NH_3 isolated in krypton and xenon was investigated next. The spectrum of NH_3 in krypton for M/A = 200 and NH_3 in xenon at M/A = 200 is shown in Figure 8. The line positions and designations as to type are given in Tables 3 and 4. All the gross features of the NH_3 spectra in argon, krypton, and xenon are the same, as should be expected. A substantial shift of the line positions toward lower frequencies is evident in going from argon to krypton and to xenon, and the separation between groups of lines is approximately the same. A narrowing and splitting of the broadest argon absorption occur in the krypton and xenon spectra, but this just indicates that the absorptions in question consist of a number of relatively broad lines.

Perhaps the most interesting comparison between the three sets of data is the relative strengths of the absorption lines. The apparent weakening of the lines in krypton and xenon as seen in Figure 8 is a real effect. When the number of absorbing molecules on the cold window are taken into account, it turns out that the line strengths of NH_3 isolated in xenon are more than an order of magnitude weaker than for NH_3 isolated in argon. To make matters worse experimentally, the scattering loss is also much greater for krypton and xenon matrices. In

TABLE 3

LINE POSITIONS FOR THE NEAR INFRARED SPECTRUM OF NH_3 ISOLATED IN KRYPTON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)
3206.8	$2\nu_4$	m
3231.2	$2\nu_4$	p
3236.6	$2\nu_4$	m
3298.8	ν_1	p
3302.5	ν_1	m
3313.9	ν_1	p
3317.3	ν_1	m
3334.2	ν_1	p
3384.4	ν_3	p
3392.7	ν_3	m
3430.7	ν_3	m
3436.0	ν_3	p
3444.0	ν_3	p

TABLE 4

LINE POSITIONS FOR THE NEAR INFRARED SPECTRUM OF NH_3 ISOLATED IN XENON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)
3202.2	$2\nu_4$	m
3228.4	$2\nu_4$	p
3231.6	$2\nu_4$	m
3294.0	ν_1	p
3297.0	ν_1	m
3304.6	ν_1	p
3306.8	ν_1	m
3323.8	ν_1	p
3380.3	ν_3	p
3388.8	ν_3	m
3413.6	ν_3	m
3424.6	ν_3	p

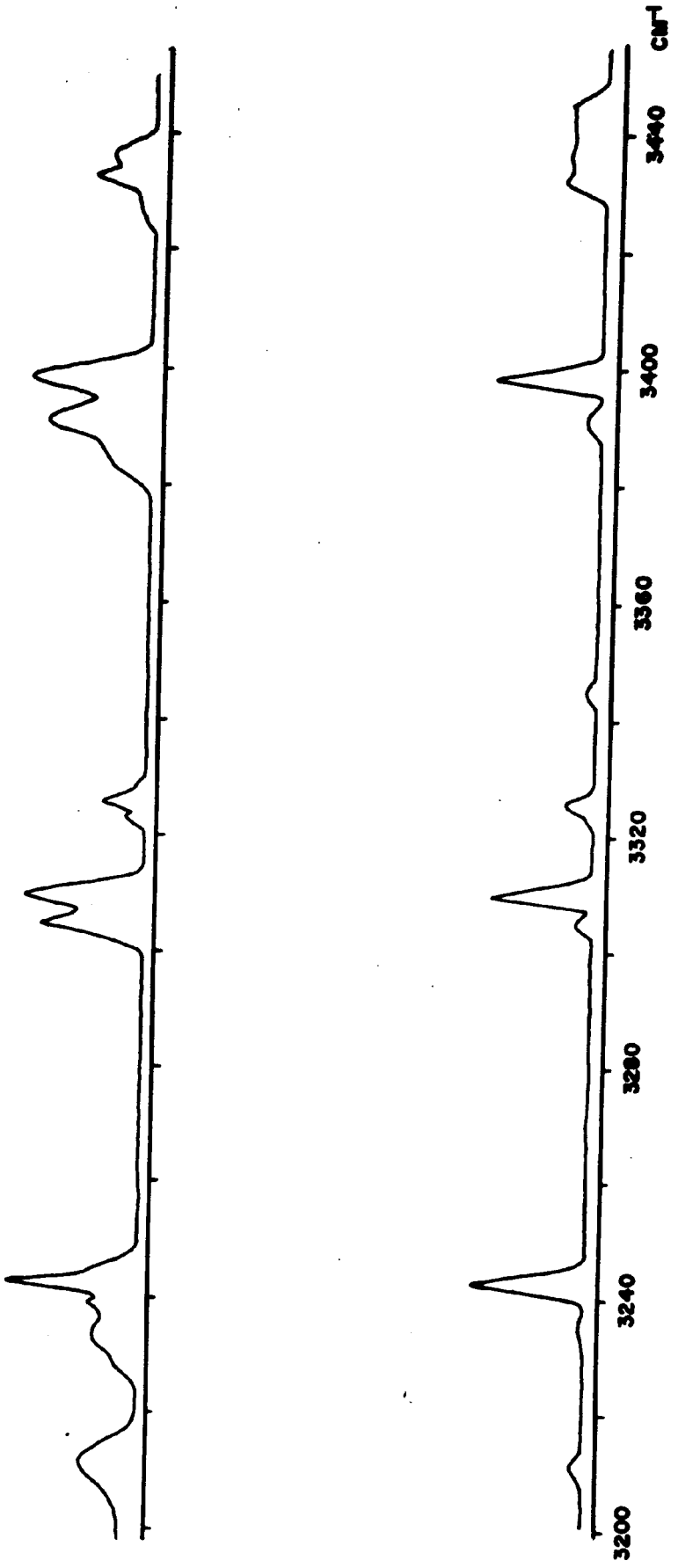


Figure 7. Near infrared spectrum of NH_3 isolated in argon for an M/A value of 20 (above) and 200.

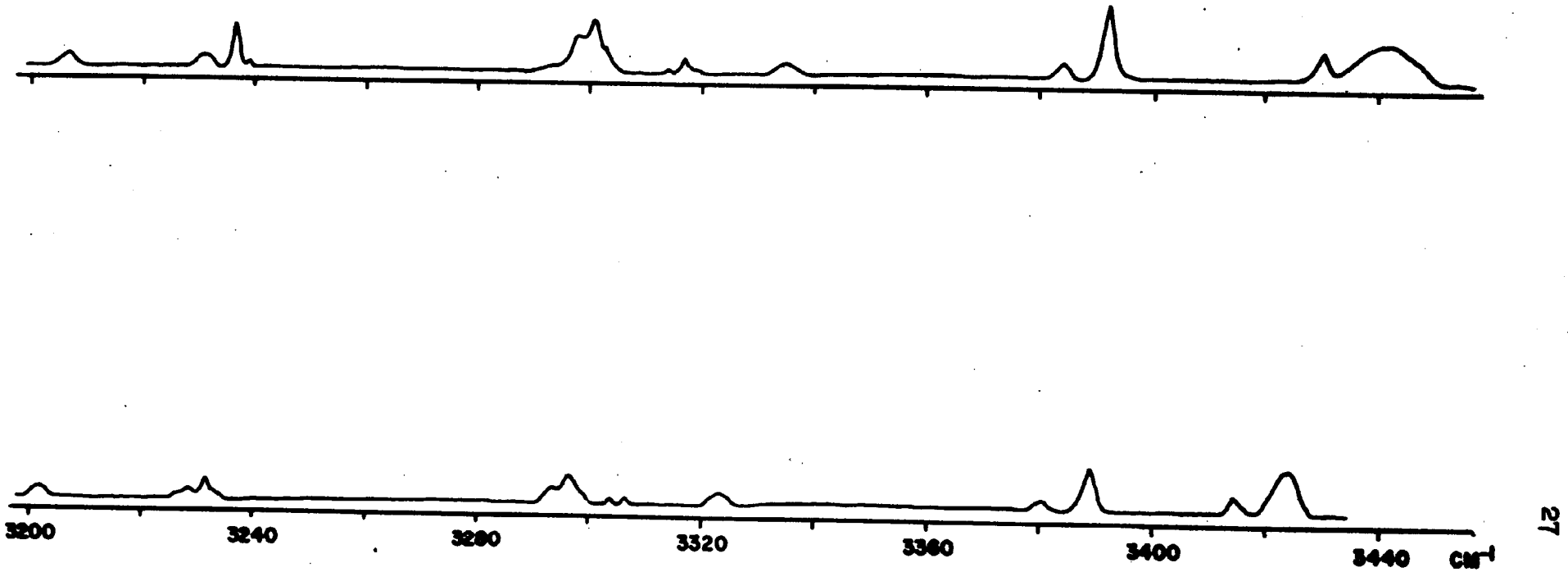


Figure 8. Near infrared spectrum of NH_3 isolated krypton (above) and xenon for an M/A value of 200.

order to bring out the krypton and xenon lines as shown in Figure 8, it was necessary to grow the crystals for approximately 15 hr. This was accomplished by transferring liquid helium twice before taking down the final scans. The spectral slit width of the instrument during these scans was approximately .5 cm^{-1}. Energy seemed to be scattering so badly that the two pass alignment was taken out, and the slits were opened almost as far as they would go. A mixture of nitrogen and NH_3 was also prepared and sprayed onto the sapphire window held at 4.2°K. In a very short time compared to that taken for NH_3-argon mixtures, strong absorptions were observed in the vicinity of 3300 cm^{-1} and 3400 cm^{-1}. There did not seem to be any direct correlation between the NH_3-argon spectra and that of the NH_3-nitrogen mixture, but there seemed to be only a negligible loss of energy due to scattering in the latter case. It seemed clear also why the spectrum of NH_3 in the 10 micron region is so readily obtained. In the first place scattering of 10 micron radiation should be much less severe than for 3 micron radiation, and even more important, the symmetric bending motion has a much stronger dipole change than the other fundamentals. The spectrum of NH_3 isolated in nitrogen was the same as that of Pimentel et al., so it was not felt necessary to include it here.

In general, the spectra of ν_1 and ν_3 were in marked contrast to that of ν_2, having only a few components and showing some broad band absorption. These spectra of the high frequency fundamentals could also not be interpreted in terms of the free molecule energy levels, nor was there

a recognizable correlation between the spectra of ν_1 and ν_3.

A study of the isotopically substituted molecule ND_3 was undertaken in an attempt to examine the dependence of the spectra on the mass and moment of inertia of the molecule. Much more difficulty was encountered in obtaining the near infrared ND_3 spectra. Not only was the lead selenide detector less sensitive than the lead sulfide, but it was not possible to open the slits wider than approximately 400 microns. It was possible to obtain spectra of ND_3 in argon and krypton at several concentrations in the ν_3 region, but the detector sensitivity fell off so rapidly below 2500 cm^{-1} that the $2\nu_4$ and ν_1 bands were scanned only for an argon to ND_3 ratio of 30. This was not considered a serious matter inasmuch as the extensive NH_3 data had shown a very definite pattern as regards the identity of the "monomer" and "polymer" spectra. It is quite evident that for ν_1, ν_3, and $2\nu_4$, a single narrow "monomer" line always has a single narrow "polymer" line approximately 5 wave numbers toward lower frequencies. This is verified also for ν_3 of ND_3 in argon in Figure 9. For ν_1 and $2\nu_4$ of ND_3 it is natural to designate the low frequency components of the two pairs of lines as "polymer" lines. The spectrum is shown in Figure 10, and the line positions and designations are given in Tables 5 and 6.

It was decided next to scan the ν_2 band of ND_3. This was done with the one meter infrared instrument. The deposit was formed on a KCl window. The spectrum of the ν_2 band of ND_3 in argon for M/A = 500 is shown in Figure 11, and the line positions are given in Table 7. The

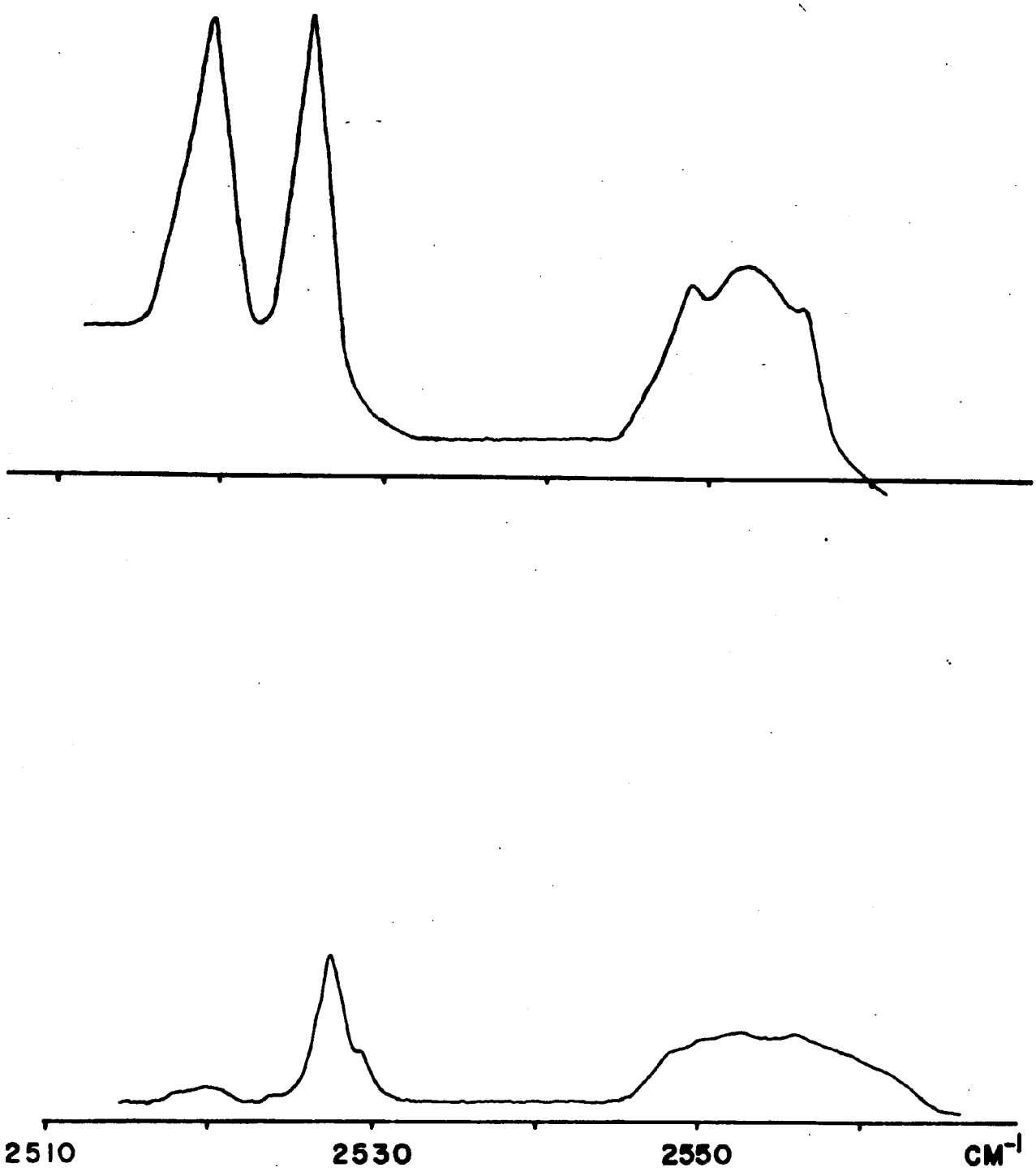


Figure 9. Spectrum of ν_3 of ND_3 isolated in argon for M/A equal to 30 (above) and 200.

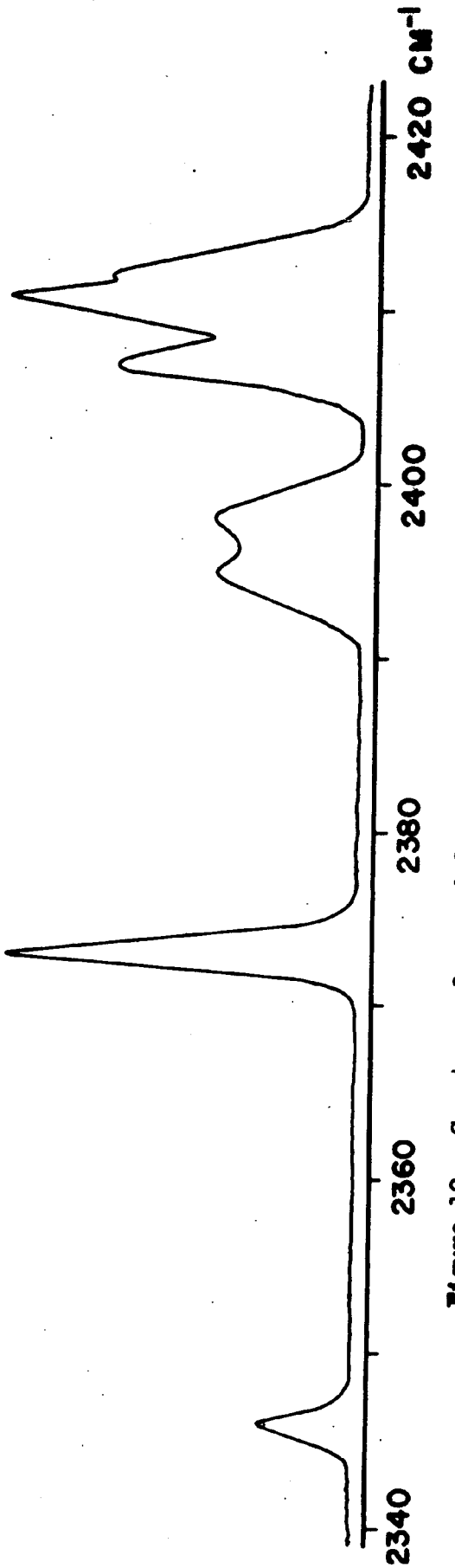


Figure 10. Spectrum of ν_1 and $2\nu_4$ of ND_3 isolated in argon for M/A = 30

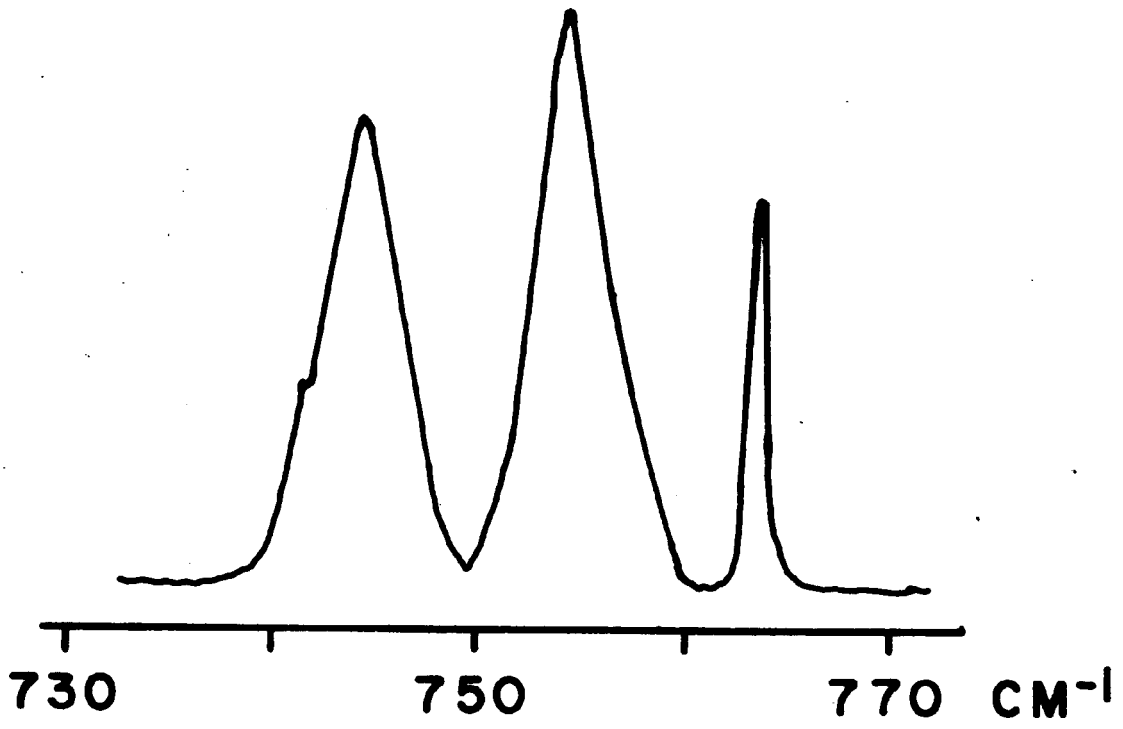


Figure 11. Spectrum of ν_2 of ND_3 isolated in argon for M/A = 500.

TABLE 5

LINE POSITIONS FOR THE NEAR INFRARED SPECTRUM OF ND_3 ISOLATED IN ARGON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)
2519.3	ν_3	p
2527.3	ν_3	m
2548.8	ν_3	m
2552.2	ν_3	m
2555.7	ν_3	p
2346.0	$2\nu_4$	m
2373.0	$2\nu_4$	m
2395.0	ν_1	p
2398.0	ν_1	m
2407.0	ν_1	p
2411.0	ν_1	m

TABLE 6

LINE POSITIONS FOR THE NEAR INFRARED SPECTRUM OF ND_3 ISOLATED IN KRYPTON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)
2515.8	ν_3	p
2523.0	ν_3	m
2543.1	ν_3	m
2549.0	ν_3	m

TABLE 7

LINE POSITIONS FOR THE ν_2 FUNDAMENTAL OF ND_3 ISOLATED IN ARGON

Frequency, cm^{-1}	Assignment	Species (Monomer or Polymer)
744.0	Q(1)	m
753.9	R(0)	m
763.7	R(1)	m

TABLE 8

LINE POSITIONS FOR THE ν_2 FUNDAMENTAL OF NH_3 ISOLATED IN ARGON USING A KCl SUBSTRATE

Frequency, cm^{-1}	Assignment	Half Width, cm^{-1}
957.1	Q(1)	---
976.4	R(0)	7.5
992.0	Q(1)	---
999.0	R(1)	---
1034.1	R(1)	---

spectral slit width used for the measurements was 1/3 cm^{-1}.

The simple three-line spectrum for ν_2 of ND_3 was completely different from that mentioned earlier for ν_2 of NH_3. A rerun of ν_2 of NH_3 was then tried with the same KCl window as for ND_3. This spectrum for an argon to NH_3 ratio of 500 is shown in Figure 6, so that a comparison with the spectrum taken earlier can be most conveniently made. Some very striking differences in the two spectra are apparent, and this will be discussed further in Chapter IV. It is evident that the deposition process and/or the substrate used has a very important effect upon the spectra of matrix isolated ammonia.

IV. INTERPRETATION OF THE OBSERVED SPECTRA

A. SOME PROPERTIES OF THE ENERGY LEVELS OF FREE AMMONIA MOLECULES

The interpretation of the spectra of molecules freely rotating or nearly rotating as an isolated impurity in a matrix at low temperatures requires a detailed knowledge of the energy levels and wave functions of the unperturbed molecule. In the case of NH_3 and ND_3 it is of value to review the following items: (a) The symmetry properties of the rotational levels; (b) The influence of nuclear spin and statistics on these levels; and (c) The sizable doubling of the energy levels of ν_2 of NH_3 caused by the relatively low barrier to inversion of the nitrogen atom through the plane of the three hydrogen atoms.

1. The energy of vibration and rotation of a symmetric top molecule for a nondegenerate vibration is:

$$E = G(v_1,v_2,\ldots) + BJ(J+1) + (A-B)K^2$$

where $G(v_1,v_2,\ldots)$ is the vibrational contribution and is given by Herzberg v. II, p. 400.

The energy of vibration and rotation of a symmetric top molecule for which one degenerate vibration is excited is given by

$$E = G(v_1,v_2,\ldots) + BJ(J+1) + (A-B)K^2 \mp 2A\zeta_i K$$

where the term $\mp 2A\zeta_i K$ is a correction arising from the interaction of the

angular momentum due to the ith degenerate vibration with that which is due to rotation about the symmetric top axis. ζ_i has values $0 \leq |\zeta_i| \leq 1$. The values of ζ_i for NH_3 and ND_3 are:

NH_3	ζ_3	= .06	ζ_4	= -0.26
ND_3	ζ_3	= .02	ζ_4	= - .36

The ground state rotational constants are:

NH_3	B	= 9.94 cm^{-1}	A	= 6.3 cm^{-1}
ND_3	B	= 5.1 cm^{-1}	A	= 3.15 cm^{-1}

The rotational energy levels for NH_3 and ND_3 for both parallel (non-degenerate) vibration-rotation and perpendicular (degenerate) vibration-rotation levels are given in Figures 12 and 13. With the exception of the $\mp 2A\zeta_i K$ correction to the degenerate vibration-rotation levels, the spacings are drawn to scale.

Since the symmetry of NH_3 and ND_3 is C_{3v}, the rotational subgroup is C_3, with irreducible representations A and E. The symmetries of the levels shown are the symmetry of the total wave function excluding nuclear spin

$$\psi = \psi_e \psi_v \psi_r$$

The ground electronic state of an NH_3 molecule is totally symmetric. The symmetry of ψ is thus the product of the vibrational and rotational symmetries. For ψ_v totally symmetric, the levels have symmetry A or E,

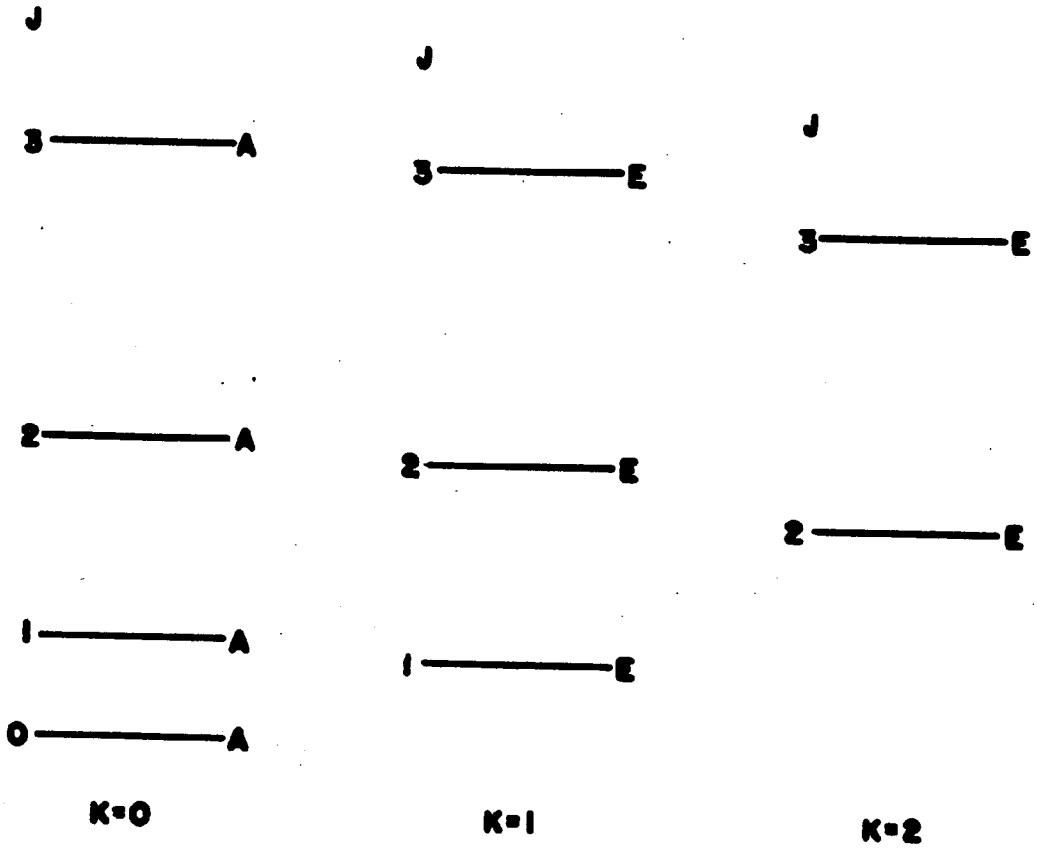


Figure 12. The lower lying rotational levels of NH_3 in a totally symmetric vibrational state.

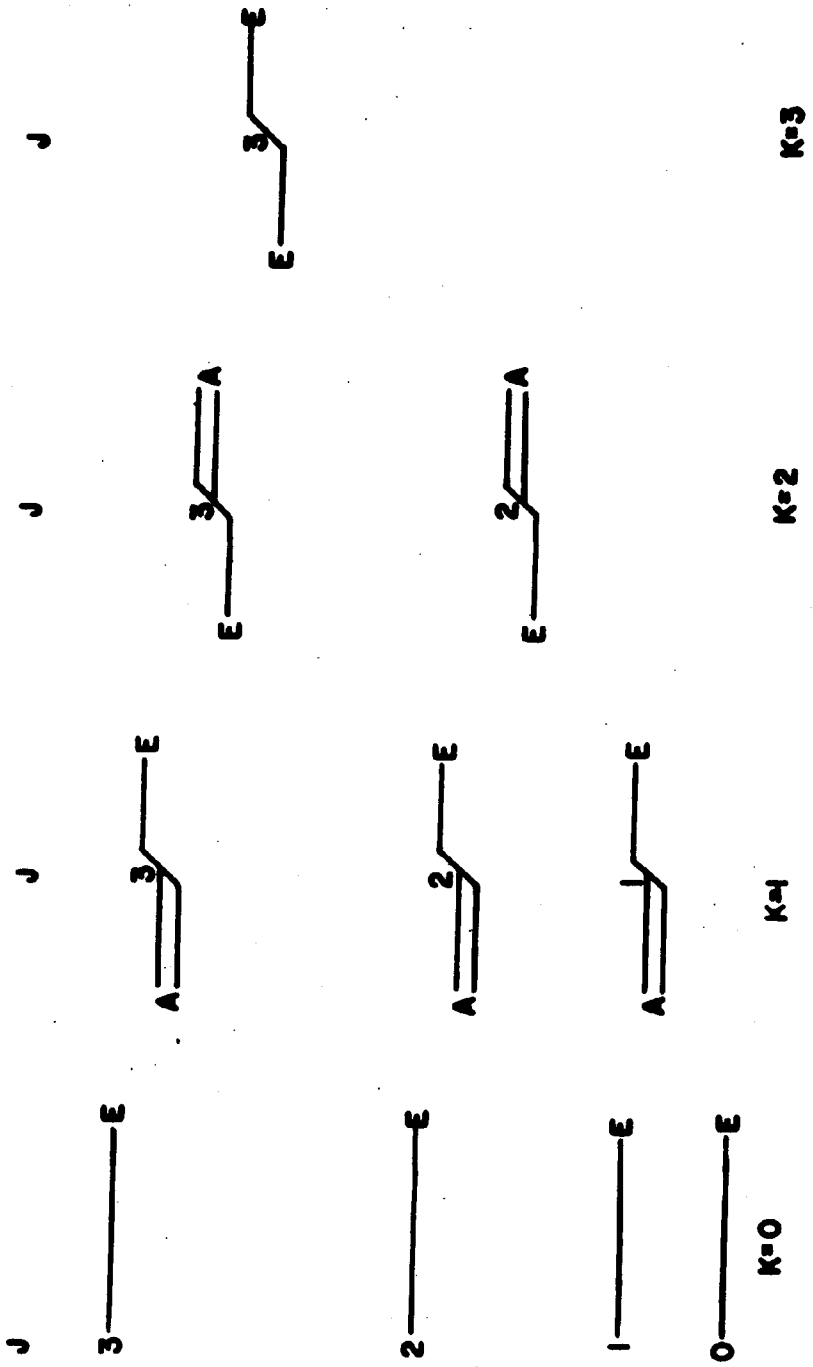


Figure 13. The lowest lying rotational levels of NH_3 in a doubly degenerate vibrational state.

depending on whether the rotational wave function has symmetry A or E. Since

$$\psi_r = \Theta_{JKM}(\theta)e^{iM\bar{\psi}}e^{\pm K\phi}$$

ψ_r is of type A for $K = 3q$, $(q = 0,1,2,\ldots)$ and type E for $K = 3q\pm1$ as shown in Figure 12.

If ψ_r is of type E, ψ must be of type $E \times A = E$ for $K = 3q$ or $E \times E = E+2A$ for $K = 3q\pm1$. For the case $K = 3q$, there are two levels of type E (except for $K = 0$) for each J, and for the case $K = 3q\pm1$ there are two of type A and one of type E, as in Figure 13.

2. For NH_3 and ND_3 and other molecules having identical nuclei of nonzero nuclear spin I there is a nuclear spin wave function ψ_N that must be included in the total wave function, i.e.,

$$\psi = \psi_e\psi_v\psi_r\psi_N$$

The symmetry of ψ is thus not given by the product $\psi_v\psi_r$, as in Figures 12 and 13, but by $\psi_v\psi_r\psi_N$. In the case of NH_3, I is 1/2, and as a consequence there are four nuclear spin wave functions of symmetry A and two of symmetry E. The symmetry of ψ is then 4A or 2E in the case of $\psi_v\psi_r = A$, or the symmetry of ψ is 4E or 2E+4A in the case of $\psi_v\psi_r = E$.

It can be seen now that the E rotational levels and the A rotational levels have the same statistical weight. This is true because there are only two E type spin functions, and because only A type ψ

are permitted for molecules whether they obey Fermi or Bose statistics. It follows for nondegenerate vibrations that for $K > 0$, if K doubling is not resolved, the rotation levels for $K = 3q$ have double the statistical weight of those for $K = 3q \pm 1$.

In the case of ND_3 the identical nuclei have $I = 1$, and the results of reasoning similar to the above is that all rotational levels occur, but with $K = 3q$ levels with a weight of 11 and $K = 3q \pm 1$ with a weight of 8.

3. An important property of the wave functions corresponding to the rotational levels discussed above is the effect on them of inversion of the molecular coordinates through the center of mass. It can be shown that the inversion operator i commutes with the Hamiltonian, H, for a symmetric top and therefore the eigenfunctions of H are simultaneously eigenfunctions of i. This is true also for i^2 so the eigenvalues of i must be +1 or -1. All energy levels of nonlinear and nonplanar polyatomic molecules must therefore be doubled, and are generally labeled + or -; and all levels in Figures 12 and 13 are actually doubly degenerate. This degeneracy can be removed if the barrier to inversion is small enough. In the case of the symmetric vibration ν_2 this barrier is so low that the overall symmetry of the molecule must be regarded as D_3 instead of C_{3v}, and the rotational subgroup consists of species E, A_1, and A_2. The rotational levels for ν_2 of NH_3, taking into account this removal of the inversion degeneracy are given in Figure 1 . The splitting is only .66 cm^{-1} in the ground state, but it is 35.84 cm^{-1} in

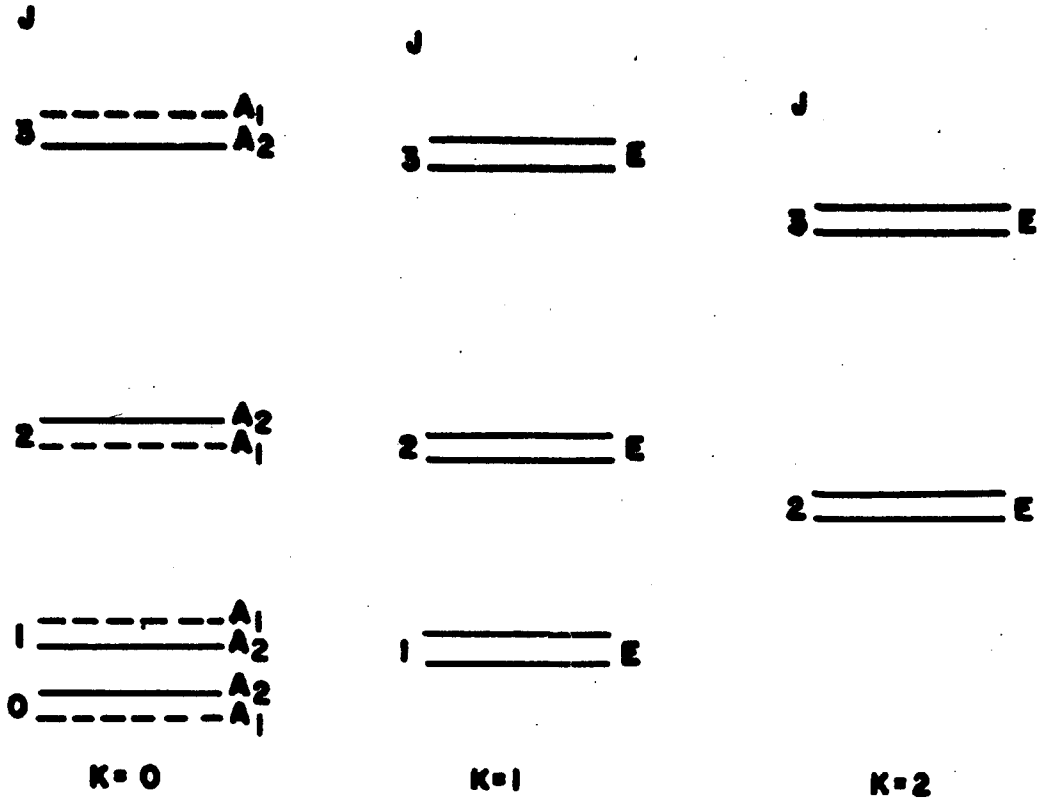


Figure 14. Rotational levels of ν_2 of NH_3 showing the effect of inversion doubling.

the first excited vibrational level; therefore, two Q branches separated by 36.5 cm^{-1} are observed for ν_2 for gas phase molecules. For ND_3 the separation of the Q branches of ν_2 is only .4 cm^{-1}. It is seen that not only are there levels of types E, A_1 and A_2, but the + and - levels no longer coincide. When the effects of nuclear spin and statistics are taken into account now, the A_1 rotational levels for NH_3 are no longer permitted (since neither $A_1 \times A_1$ nor $A_1 \times E$ has the symmetry A_2 demanded by the Fermi statistics). This is indicated by drawing all A_1 levels as dotted lines.

B. INTERPRETATION OF THE ν_2 BAND OF MATRIX ISOLATED AMMONIA

The interpretation of spectra of molecules isolated in matrices at low temperatures has relied to a large extent upon models ranging from free rotation to a severely hindered motion of the impurity in its "cage."[15,17,19] Irregularities in the spectra have often been attributed to the possibility of molecules being trapped in more than one site and to the possibility of interactions between nearest neighbor molecules—i.e., the formation of polymers.[14,16]

Since dimer or polymer formation should be strongly concentration dependent, it was imperative that wherever possible spectra be taken for a variety of molecule to inert gas atom ratios (see Chapter III). It was thus possible to pick out lines that were not concentration dependent, and to attribute the transitions giving rise to them to molecules completely isolated in the matrix. All spectra referred to in

the following paragraphs will be this "monomer" spectra.

Some very striking similarities are apparent between the observed spectra of NH_3 and ND_3 trapped in the inert gases and the spectra predicted on the basis of a free rotation model. If the molecules are freely rotating, it must be the case that all selection rules and energy level positions are relatively unchanged. In the case of ν_2 of NH_3, one would expect that several very important features be present: (a) A "two molecule" spectrum, consisting of a nuclear spin "E" NH_3 and a nuclear spin "A" NH_3. This is an anlaogy with the ortho and para type H_2O mentioned in Chapter I; and (b) Removal of the inversion degeneracy.

All spectra were taken at or very close to 4.2°K. Therefore, only two rotational levels should be appreciably populated. The J = 0, K = 0, $\bar{+}$ level should be the only K = 0 level populated, since at 4.2° the number of molecules in the J = 1, K = 0 level relative to the lowest level is proportional to $e^{-20/kT} \approx e^{-7}$. Molecules occupying this level will be called "A type" ammonia.

The J = 1, K = 1 levels should be populated appreciably if there are no spin dependent perturbations present. This is true because these two levels exist only for E type NH_3, and in the absence of a spin dependent perturbation, the E type NH_3 cannot pass over into the A type even though the J = 1, K = 1 level is 16.5 cm^{-1} above the ground state.

A free rotation model therefore predicts a superposition of the A and E type NH_3 spectra, giving a total of five lines. These five transitions are shown in Figure 15. Since all rotational levels of symmetry

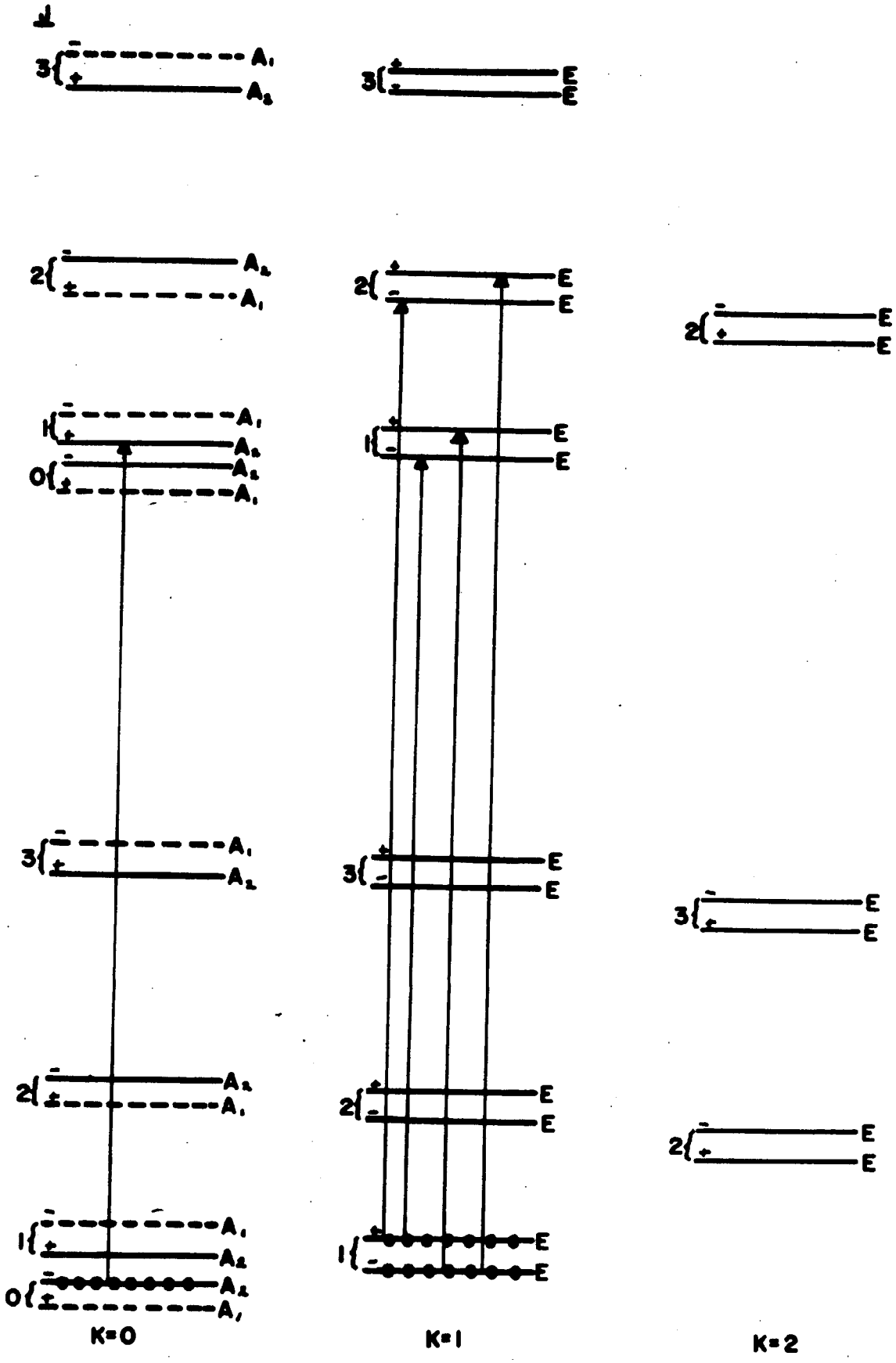


Figure 15. Transitions predicted for ν_2 of NH_3.

A_1 do not exist in nature, the A type spectrum should not show the doubling feature, and in fact should only consist of one line. The E type spectrum should consist of four lines, all allowed by the usual selection rules $\Delta K = 0$, $\Delta J = \pm 1, 0$. These are the two Q(1) and the two R(1) lines. This is shown in Figure 16a, b and c. Figure 16d shows the lines observed for NH_3 isolated in argon and deposited on the KCl window.

Experiment seems to indicate, then, that the separation between the Q branches has changed to 34.9 cm^{-1} in the matrix as compared with 36.5 cm^{-1} in the free molecule, and that the separation between the $J = 1$, $K = 1$ and $J = 2$, $K = 1$ levels has been changed from approximately 40 cm^{-1} to approximately 42 cm^{-1}. It is possible to rationalize shifts of this size using the results of recent investigations of pressure induced line shifts. Rank[21] et al., have investigated shifts in vibration-rotation lines in pure HCl and hydrogen at low pressures, and in mixtures of these molecules with inert gases. Frequency shifts on the order of a few hundredths of a wave number were observed. May[22] et al., have made Raman measurements on pure hydrogen and hydrogen-noble gas mixtures at very high pressures (up to 1940 atmospheres) in an attempt to measure and explain pressure induced shifts in the vibration-rotation bands. Quite large shifts, amounting to 1.86 cm^{-1} in the case of the S(1) line of hydrogen mixed with helium, were observed. These shifts were explained as arising from a perturbation on the rotational constant caused by Van der Waals forces.

It is suggested here that the matrix "cavity" in which the NH_3

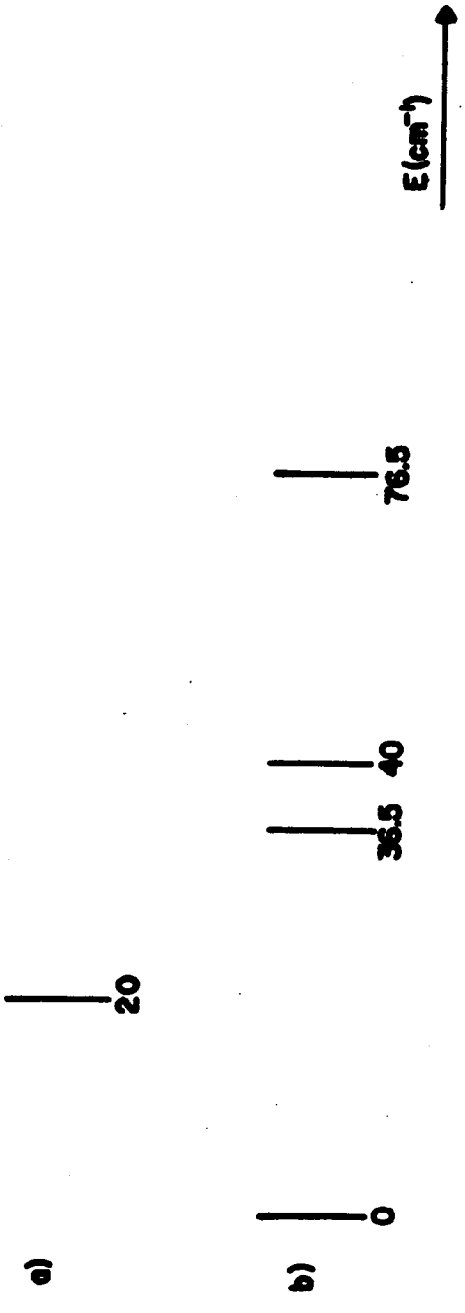


Figure 16. (a) Predicted gas phase spectrum of "A type" NH_3, (b) predicted gas phase spectrum of "E type" NH_3, (c) composit "A" and "E type" spectra predicted, (d) lines observed in the ν_2 region for NH_3 isolated in argon using a KCl substrate.

molecule is trapped exerts an effective "pressure" which alters the value of the rotational constant. The work of May et al., lends support to this notion in that the shifts observed in the present work are in the same direction, and in that they show up for the transitions ending at the $J = 2$ level.

As was mentioned earlier, the spectrum of ν_2 of NH_3 was taken using copper as the deposition surface in one case, and KCl in the other. At first glance the two spectra appear quite different. The line widths measured from the KCl deposit are noticeably wider, indicating that the temperature of the sample might be considerably higher. If this were the case, P branch lines ought to be present, and the R(1) lines ought to be stronger relative to the main R(0) transition. Since this is not the case it is concluded that the difference in the two spectra are due primarily to the effect of the substrate on the matrix. One can also see that the KCl deposited spectrum has fewer lines than that obtained on copper—just the opposite of what one would expect at a higher temperature. It is noteworthy that all absorptions on KCl have their counterpart in the copper spectrum, and that all these lines offer a reasonable fit to the explanation given above—i.e., that the molecule is nearly freely rotating, vibrating and inverting, as though in almost complete isolation.

No explanation has been made as of yet of the four unassigned lines appearing in the NH_3 on copper spectrum. Two of these transitions are quite weak—absorbing only several per cent of the radiation. The other

two are as strong as the "E" type lines discussed above. These four lines are listed in Table 1, but in the interest of clarity it is best to state their positions here in terms of their separation from the lowest frequency Q(1) line. The weak lines are 57 cm^{-1} and 82 cm^{-1} from Q(1), and the stronger lines are 26 cm^{-1} and 62 cm^{-1} from Q(1).

It is proposed that the two stronger lines arise from molecules trapped in sites not present in crystals grown on KCl. Two reasons may be advanced in explanation of this. First, the KCl window was a good single crystal, whereas the copper "mirror" was not. It is not only reasonable to expect that different substrates should result in crystals of different quality, but work carried out at other laboratories have proved it (see Chapter I). It is proposed then, that argon films grown on the KCl window has a more ordered structure and has fewer dislocations and/or fewer available interstitial sites. Moreover, according to Zwanzig,[23] the deposition process is a function of the substrate. In the language of Zwanzig, it can be said that if in the case in question the condensing gas has different sticking probabilities, then crystals of different quality may be grown.

The two weaker lines may be explained in the same way, of course. There is a possibility however, that the one of lower frequency arises from a breakdown in selection rule. This would be the transition $J = 0 \rightarrow J = 2$. If this is actually the case, only a very small mixing of the wave functions is indicated, since the transition is very weak,

and no other selection rule breakdown has been observed.

Robinson and McCarty[24] have used the notion of multiple trapping sites to explain a complicated spectrum of sodium isolated in argon, and very recently Leroi[25] and co-workers have explained a spectrum of CO in argon in the same manner. The CO spectrum was scanned at various dilutions, window temperatures and deposition rates, the conclusion being reached that CO was not rotating in the matrix, and that the observed structure was due to different trapping sites. Leroi also resorted to heating the gaseous CO-argon mixture to a temperature well above room temperature before spraying it on a cold surface. This resulted in a narrowing of the lines and a slight difference in relative intensities. No reasons were proposed for this change, other than the well established fact that annealing a matrix seems to give more order to the structure. In view of the obvious importance of the deposition process when conducting these experiments, and in view of the widely accepted theory that atoms and molecules sprayed onto very cold surfaces wander about briefly before condensing, the idea that substantially different quality crystals with different trapping sites is not completely out of the question.

In concluding the discussion of the ν_2 band of NH_3 it should be emphasized once again that the fact that the separation between the Q branches in the matrix is so nearly the same as that for the free molecule serves as very strong evidence that the matrix isolated ammonia does indeed rotate with nearly complete freedom, and it is difficult to con-

ceive of the molecule being hindered appreciably and still have so little change in the inversion barrier and rotation constant. Also, the discussion of the ν_2 band of ND_3 to be given below completely substantiates this interpretation. Of course it can be said that one should not be surprised to observe free rotation, since ammonia is a small molecule, and the argon matrix is inert; indeed, these are the primary reasons for choosing the ammonia-noble gas mixture to investigate. It must be remembered, though, that the previous investigations of ammonia in argon matrices had not been extensive enough to permit a satisfactory interpretation.

As mentioned above, the spectrum of ν_2 and ND_3 in argon also substantiates the free rotation model. This does not mean to say that the ND_3 spectrum has the same appearance as that of NH_3. The free molecule inversion doubling of ν_2 for ND_3 is expected to be completely obscured by the widths of the lines, thus reducing the complexity of the spectrum. Only three lines should be observed, corresponding to transitions $J = 1, K = 1 \rightarrow J = 1, K = 1$; $J = 0, K = 0 \rightarrow J = 1, K = 0$ and $J = 1, K = 1 \rightarrow J = 2, K = 1$. Moreover, the spacing between them should be approximately 10 cm^{-1}. This is exactly what is observed for ν_2 of ND_3 in argon, as in Figure 11.

An interesting feature of the ν_2 lines is their relative intensities. In the case of NH_3, one line, R(0), is much more intense that the others. This is the one transition corresponding to A type ammonia. This indicates that there is actually more A type NH_3 relative to the E type than

one would expect on the basis of statistical weights. Now counting the 2J+1 factor, the levels should have the weight factors 4 for K = 0 and 4 for K = 1. It would appear that there has been a substantial amount of conversion of E type NH_3 to A type, although this should not be the case in the absence of a spin dependent perturbation. The amount of conversion (if indeed this has taken place) is quite large, since the per cent absorption of the stronger line is above 80%, in a range where the absorption is highly nonlinear so that the relative intensity difference of the A and E spectra should be even more drastic than it appears to be. Although difficult to explain, a similar phenomenon has been observed by other workers. Robinson and McCarty have reported substantial evidence for free rotation of NH_2 isolated in a matrix. Their spectrum indicated that a very large amount of nuclear conversion has taken place, permitting a near thermal equilibrium to take place at low temperatures. No mechanism was proposed which permits this conversion to take place. K. Dressler[20] has carried out absorption experiments in the 1800Å region on NH_3 isolated in argon interpreting his data as proof of free rotation and almost 100% conversion from nuclear spin species E to A.

The relative intensities measured from the three lines observed in the ν_2 region of ND_3 in the present work are more consistent with the assumption of E and A type ND_3. The statistical weights of the K = 0 and K = 1 levels should be in the ratio of 11 to 16 whereas the observed intensities are nearly equal. It should be remembered of course, that

the "E type" molecules are trapped at an energy well above the Boltzman energy corresponding to 4.2°K.

C. INTERPRETATION OF THE ν_3 BAND

It is most convenient for the discussion of the ν_3 band of NH_3 in the 3400 cm^{-1}—3450 cm^{-1} region to proceed in the same manner as was done with ν_2. In doing so however, several major differences are expected to be present. These are:

1. Being a prependicular band, ν_3 has the K selection rule $\Delta K = \pm 1$ instead of $\Delta K = 0$ for the parallel vibration ν_2. Therefore, rotational transitions in this band must undergo a change in the component of angular momentum along the symmetry axis of the molecule, a feature not present in ν_2.

2. Experiment (see Chapter III) has indicated that the near infrared bands are extremely weak compared to ν_2. This implies at the onset that the very weak lines (the "E type" spectrum) should be difficult or impossible to observe.

3. Inversion doubling of the ν_2 band is completely negligible, with the result that fewer lines should be observed.

Figure 17 shows the transitions expected if both "A" type and "E" type spectra are observed. The expected lines are compared with the observed lines in Figure 18. The lines are measured relative to the vibrational frequency of the free molecule and the position selected for the observed spectrum in the lower half of the figure is the only one

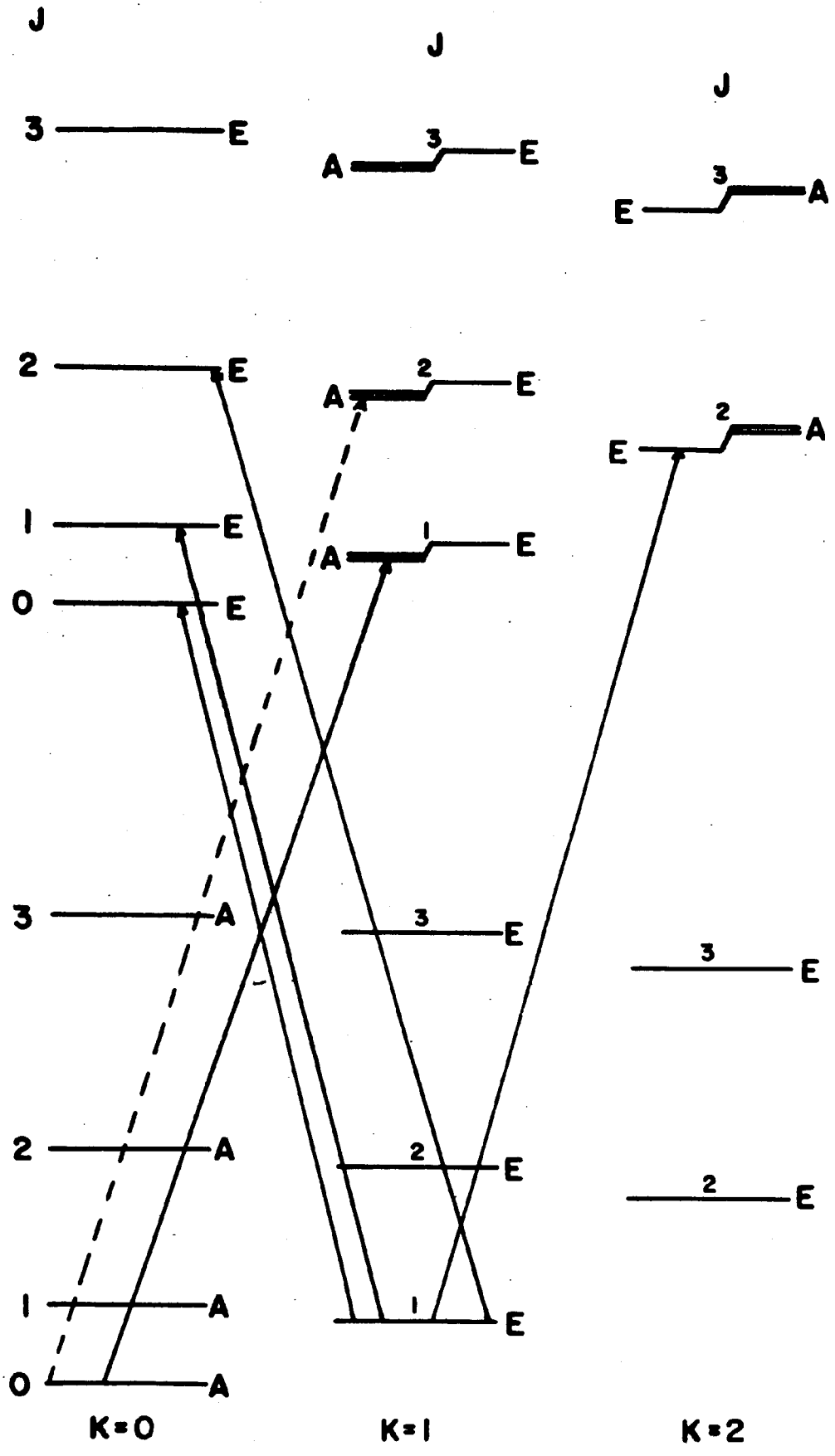


Figure 17. Transitions expected for the V_3 band of NH_3.

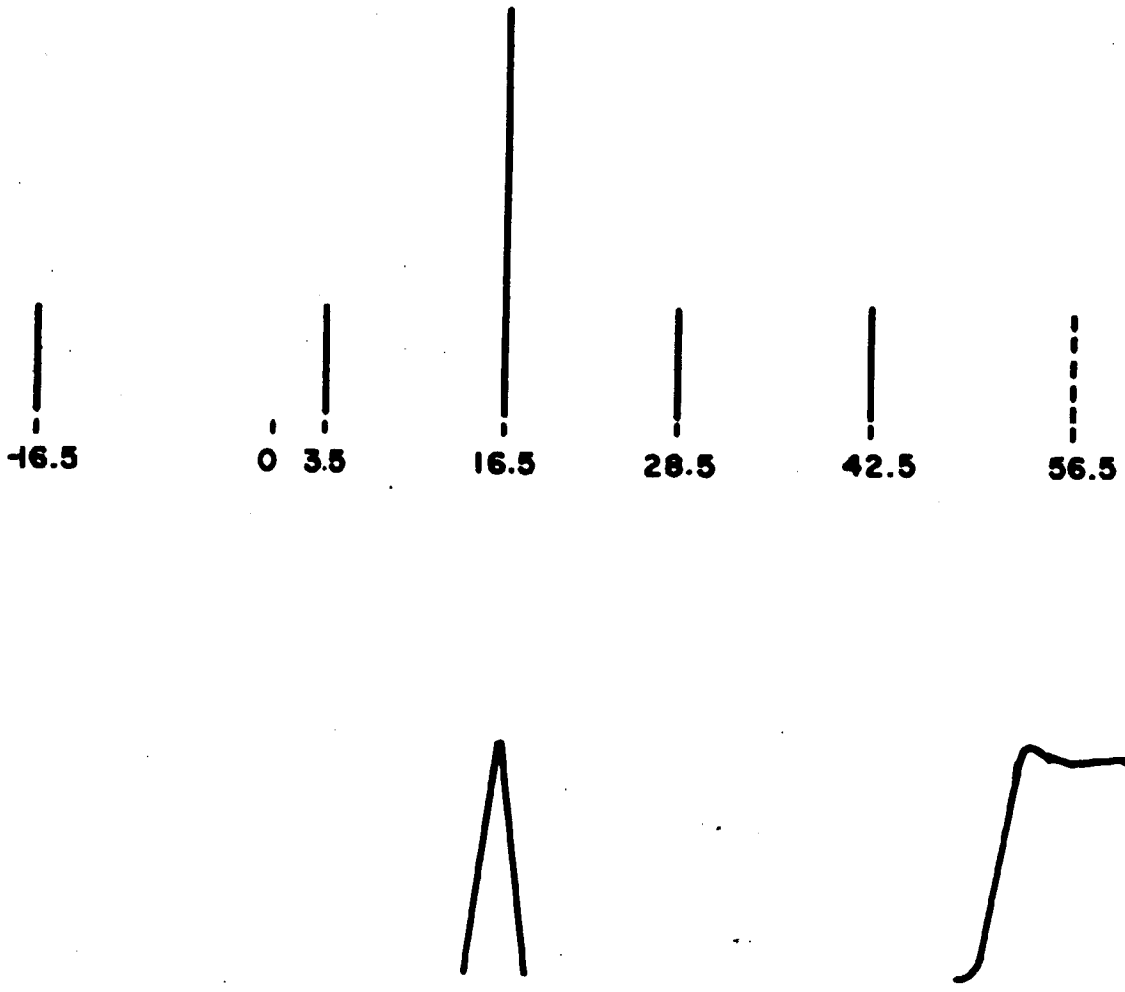


Figure 18. (a) Predicted lines for the ν_3 band of NH_3, (b) observed lines for the ν_3 band of NH_3.

which fits the upper half. As was expected, only the "A type" spectrum is observed, and the broad absorption seems to correspond to the transition $J = 0, K = 0 \rightarrow J = 2, K = 1$.

At this point enough information has been obtained to permit some qualitative remarks about the nature of the electric field surrounding the trapped ammonia molecule. First, it must be relatively weak since the molecule evidently is undergoing free rotation. "Weak" as used here does not necessarily mean weak from the standpoint of Stark fields ordinarily applied to a molecule. It means weak in the sense that barriers to free rotation are small. Second, since all evidence points to a strong adherence to the $+ \langle\!\!\longrightarrow\!\!\rangle -$, $+ \langle\!\!-\!\!/\!\!-\!\!\rangle +$, $- \langle\!\!-\!\!/\!\!-\!\!\rangle -$, selection rules, the field must be invariant under the inversion operator. In other words, it appears that the molecule is located in a site of cubic symmetry, as should be expected for solid argon.

The spectrum of ν_3 of ND_3 agrees with that of NH_3. There is no evidence of E type ND_3, and the separation between the two absorptions is close to that predicted for a free molecule. The higher frequency ν_3 absorption begins approximately 21 cm^{-1} from the narrow one, whereas the separation between the two transitions in the gas phase are more like 17.5 cm^{-1}. This is a difference similar to that observed in the ν_2 band of NH_3 for the $J = 1, K = 1 \rightarrow J = 2, K = 1$ transition. It is difficult to justify the frequency difference in this case, unless it is connected in some manner with the angular momentum change $\Delta K = +1$.

D. THE ν_1 BAND

If both "E" and "A" type transitions are present in the spectrum one expects to see three lines separated by 20 cm^{-1} corresponding to a Q(1) line, R(0) line, and an R(1) line, since this is a parallel band. This is shown in Figure 7 in the 3300 cm^{-1} region. Since no "E type" spectrum was observed in the ν_3 band and only small traces of it were observed in the strong ν_2 band, it is not expected to be present in the ν_1 region. This means that only the one "A type" line should be seen (i.e., the J = 0, K = 0 → J = 1, K = 0 transition). Actually, two monomer lines are observed, as shown in the figure. The stronger, lower frequency line is assigned to the J = 0, K = 0 → J = 1, K = 0 transition, since this is the one that should be strongest. The weaker line 15 cm^{-1} away from the R(0) line does not fit the predicted spectrum at all. This points out the difficulty in trying to interpret a spectrum which is predicted from the start to have only one line present. There is just not enough information to form a basis for comparison. The only reasonable explanation that can be given to the weaker line is that it arises from a different site. That this is a real possibility was pointed out in the discussion of the ν_2 band, where much more information was available. It must be admitted, of course, that such an explanation in this case is not very desirable.

The same situation holds for ν_1 of ND_3. Whereas only one strong transition is expected, two are observed, but spaced by approximately 12 cm^{-1}. Once again, there is not enough information available to as-

sign transitions with certainty.

There is, of course, a more fundamental reason why the interpretation of the ν_1 data should be more difficult. It is expected that a strong Fermi resonance should exist between the symmetric component of $2\nu_4$ and the fundamental ν_1. Since ν_4 of ND_3 is approximately 1191 cm^{-1}, $2\nu_4$ should be at approximately 2382 cm^{-1}. This is very close to ν_1, which is at 2419 cm^{-1}. To enhance this effect the matrix shifts are such that ν_1 decreases in frequency. The effect of this resonance on the vibration-rotation spacings has not been carried out as of yet even in the gas phase, so it should not be surprising to find anomalies in the spectrum of ν_1.

E. THE CONCENTRATION DEPENDENT LINES

The foregoing explanation of the observed spectra tacitly omitted reference to all concentration dependent lines. Whereas it is safe to conclude that lines independent of concentration arise from single isolated molecules—that is, monomers—the origin of the concentration dependent lines is open to speculation. Two kinds of dependence on concentration have been observed; the one is a decrease in intensity with increasing dilution of the sample, and the other is an increase in intensity with increasing dilution.

A definite pattern has been observed in connection with the former type line. In every case, these lines appear within 8 cm^{-1} or so on the low frequency side of a "monomer" line. The absolute position of these

lines does not depend on the dilution, so it can be said that the environment of the molecules giving rise to them does not suffer a change as the ratio M/A is changed. Moreover, it is indicated that only one type of environment is giving rise to them. That is to say, since the notion of dimer, trimer, tetramer, etc., complexes imply one, two, three or more lines for a given "monomer" line, it can be concluded that these particular lines do not arise from a bunching together of various numbers of molecules. This contention is supported by the fact that no absorptions for high concentrations of NH_3 in argon appeared in the region of strong absorption characteristic of solid NH_3. It can be concluded from these considerations that the solids with a high concentration of NH_3 have two kinds of short range crystal structure; the one having NH_3 molecules effectively shielded from any other NH_3 molecules and the other having a unit cell consisting of some preferred arrangment of argon atoms and NH_3 molecules. As the ratio of NH_3 to argon decreases, then, more isolated molecules appear at the expense of the more highly concentrated regions.

The other kind of concentration dependence appears in two places; one 35 cm^{-1} to the high frequency side of ν_1 and the other 45 cm^{-1} to the high frequency side of ν_3. These lines are broader than the "monomer" lines, and grow progressively stronger as the matrix is changed from argon to krypton to xenon. In as much as these absorptions become pronounced with increased dilution, they must surely arise from isolated molecules. That is, even though they are concentration dependent,

they must be classified as "monomer" lines. The most reasonable explanation of them, then, is that they arise from molecules trapped in a site different than those giving rise to the spectra discussed in the previous sections. This is in keeping with the belief that several sites (substitutional, interstitial, etc.) are available to the molecules, some being more easily accessible than others. It is also consistent with the model suggested above for the origin of the other type concentration dependent lines, since larger regions of "monomer" type crystal exist at higher dilutions, and more molecules are available to them. This explanation also gains support from the fact that the absorptions in question are broad and that their strength varies with matrix. This is exactly what one should expect since the more unaccessible site should assert a stronger perturbation than the others, and since this accessibility should be strongly dependent upon the quantitative features of the site itself.

V. ALTERNATIVE EXPLANATIONS

In view of the modest amount of data on which some of the foregoing arguments were based it is worthwhile to compare the experimental results with models other than that of free rotation. The first of these to be discussed is the librator model. In this model the rotational degrees of freedom are restricted in such a manner that a potential energy of the form $V = 1/2k\theta^2$ is assumed. The Schroedinger equation with this potential is identical to that of a two dimensional harmonic oscillator. The energy levels are:

$$E = (n+1)\left[\hbar\omega + \frac{2B^2}{\hbar\omega}\left(\frac{M^2}{15} - \frac{1}{60}\right) + \ldots\right]$$

where n is the librational quantum number, and $B = \hbar^2/2I$ and $\omega = \sqrt{k/I}$ and where $n = 0,1,2,\ldots$ and $|M| = n, n-2, n-4, \ldots$.

The energy level diagram for the libration levels is shown in Figure 19.

The splitting due to the M dependence is small and can be ignored for qualitative discussions of the predicted spectrum. The selection rules for parallel transitions are:

$$\Delta n = 0, \pm 2, \pm 4 \quad \text{(Decreasing in intensity)}$$

$$\Delta M = 0$$

and for perpendicular librations:

$$\Delta n = \pm 1, \pm 3, \pm 5, \ldots$$

$$\Delta M = \pm 1 \quad .$$

Two features which are immediately predicted for a vibration-libration band are the following: first, the line spacings must be equal, and second, the spacings must be proportional to $1/\sqrt{I}$, where I is the moment of inertia of the librator.

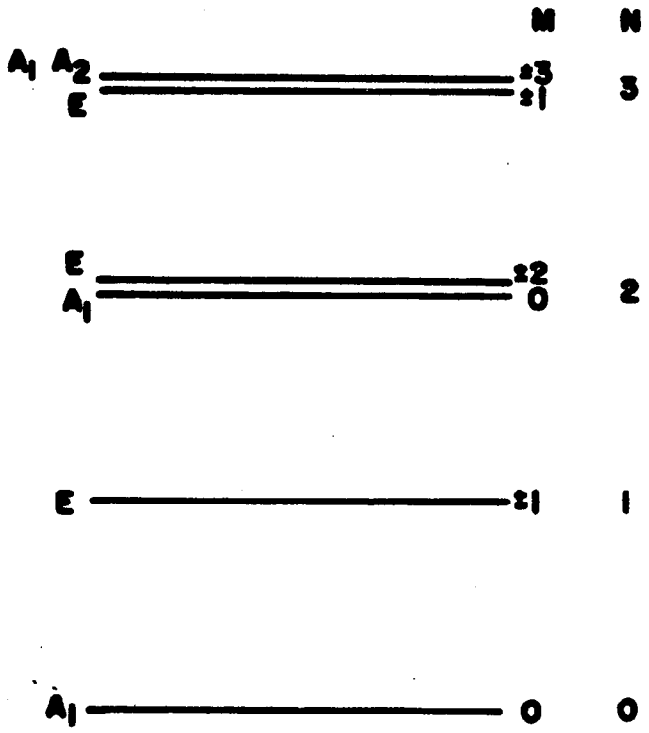


Figure 19. Energy levels for a harmonic librator.

Whether NH_3 is inverting or not, the observed spectrum does not seem to fit this scheme. In the first place, the observed spacing of approximately 10 cm^{-1} for ν_2 of ND_3 requires that the equal spacing of the corresponding NH_3 lines be approximately 14 cm^{-1}. The only regular

spacing of the stronger NH_3 lines are 20 cm^{-1}—which is more like 2x10 cm^{-1}. Also, it is predicted for a librator that the $\Delta n = 0$ transition (that of lowest frequency) should be the stronger. This is obviously not the case for ν_2 for either NH_3 or ND_3. If NH_3 is not inverting while librating, as is most likely the case, this explanation becomes even worse, since no regular spacing is at all apparent.

The same is true for the other parallel band ν_1. In this case, there are two lines, separated by 15 cm^{-1}. The spacing between the two observed lines in ν_1 of ND_3 is about 12, denying a $1/\sqrt{2}$ dependence of the energy levels. The only attractive feature is the relative intensities of the two lines is the NH_3 spectrum.

The only experimental evidence that comes close to supporting the libration picture is ν_3 in both NH_3 and ND_3. Both bands consist of two absorptions, and the ratio of their separations gives a value between 1/2 and $1/\sqrt{2}$. This is what is expected if the actual motion is not completely free, but hindered to some extent. It is safe to say, at any rate, that the librational model does not fit any of the experimental evidence.

Another model which can be quickly rejected is the harmonic oscillator model. The molecule is pictured as a three dimensional harmonic oscillator, fastened to the lattice by springs. The energy dependence of the harmonic motion must be proportional to $1/\sqrt{M}$, where M is the total mass of the molecule. As was done with the librator model, it can

be quickly seen that the line separations and the ratios of the NH_3 and ND_3 spacings do not satisfy the required $1/\sqrt{(17/20)}$ relationship.

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