THE INFRARED ABSORPTION
OF SOME
HYDRAZINE MONOHALIDES

by

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INTRODUCTION

The infrared spectrum of a substance is characteristic of the structure of the individual molecules. In particular, the near infrared spectrum, between 2.5 and 25 microns, is characteristic of the molecular vibrations and, to some extent, of the molecular rotations. The study of such spectra has led to a detailed and quantitative knowledge of the molecular structure of many substances.

The compounds studied here are hydrazine monochloride and hydrazine monobromide. These are colorless crystalline solids with melting points at about 89°C and 80°C, respectively (10, pp.323-324). The crystal structure of N₂H₅Cl has been found (13) to be orthorhombic with \( a = 21.99 \), \( b = 12.60 \), \( c = 4.44 \ \text{Å} \). There are sixteen molecules per unit cell, and the space group is \( C_{2h}^{19} \). According to Halford (5, pp.8-15), this means that the site group for the N₂H₅⁺ ion is \( C_1 \) (no symmetry). Therefore, all fundamental vibrations should appear in both the infrared and Raman spectra. This should also be true for the highest probable symmetry of the N₂H₅⁺ ion alone, consisting merely of a plane (\( C_s \)).

The infrared spectrum of powdered N₂H₅Cl in an oil emulsion has been published for the range from 2 to 15
microns (9, p. 1603) and the Raman spectra of both N₂H₅Cl and N₂D₅Cl in aqueous solution have been studied (3, pp. 225-237), (4, pp. 520-525). In the Raman spectra, nine fundamentals were observed for both compounds, and the NN stretching vibration was identified with a band at 965 cm⁻¹ in the N₂H₅Cl spectrum.

The aim of the present research is to make a detailed study of the infrared spectra of crystalline N₂H₅Cl and N₂H₅Br, and, as far as possible, to identify the fundamental frequencies and interpret them in terms of molecular structure.
GENERAL. In a non-linear molecule composed of $N$ atoms, there are three degrees of freedom associated with each atom. The whole molecule has $3N$ degrees of freedom, of which three are translational, three are rotational, and the remaining $3N-6$ are vibrational. In the solid state, the three translational motions become very low frequency vibrations of the molecule about its equilibrium position in the crystal lattice. Similarly, the rotations are restricted, and so become vibrations of low frequency. Usually these types of vibration, which are frequently designated as "lattice modes", occur at wavelengths beyond the 25 micron limit imposed by the potassium bromide prism, and the remaining $3N-6$ vibrations, designated as "molecular modes", will be primarily considered in the rest of this discussion.

According to the quantum theory, the energies of vibration are quantized, and are given by

$$\varepsilon_v = \hbar \omega \left(v + \frac{1}{2}\right)$$

(1)

where $\varepsilon_v$ is the vibrational energy, $\hbar$ is Planck's constant, $c$ is the velocity of light, $\omega$ is the vibration frequency in waves per centimeter and $v$ is the vibration quantum number which can have any non-negative integral value. This equation is not quite exact, because it assumes the molecule to be a harmonic oscillator, which is
only an approximation. Selection rules limit the change
in \( v \) to \( \pm 1 \), so that if the energy is increased, \( \Delta \epsilon_v = \hbar \omega \). If the vibration in question involves a changing dipole moment, it can interact with radiant energy to absorb a quantum of light \( \hbar \omega = \Delta \epsilon_v \), where \( \omega \), the frequency of the light absorbed in waves per centimeter, or wave numbers, is the same as the vibration frequency. The resulting decrease in intensity of the transmitted light of frequency \( \omega \) appears as an absorption band. It is called a fundamental band when it results from \( \Delta v = 1 \).

Since molecular vibrations are not exactly harmonic, energy changes for \( \Delta v > 1 \)--overtones--may occur, but with a small probability. Similarly, simultaneous absorptions of energy by two different fundamental vibrations may produce a combination band, for which the probability is also small. In general the absorption bands produced by each of these occurrences are weak, and thus are not too easily mistaken for fundamentals.

**CORRELATION OF SPECTRUM WITH STRUCTURE.** In order to correlate the observed fundamentals with particular vibrations of any molecule, a particular structure must be assumed, and equations of motion for the molecule set up, assuming the potential energy to be a quadratic form in the internal coordinates. By introducing normal coordinates, in terms of which the kinetic and potential energies become diagonal forms, the vibrations of a
molecule can be resolved into "normal vibrations", which are independent of translation and rotation. In a normal vibration, all atoms must maintain a simple harmonic motion about their respective equilibrium positions with the same frequency, and the center of gravity must not move. It is found upon study of any molecular structure that \(3N-6\) independent normal vibrations are possible (\(3N-5\) for linear molecules), and their frequencies can be found by solving the \(3N-6\) simultaneous equations of motion.

If a molecule has one or more axes of three-fold or higher symmetry, there will be two or more solutions of the energy equations which coincide, i.e., two or more vibrations have the same frequency. Such vibrations are said to be degenerate. Fewer than \(3N-6\) fundamental bands will then appear. While molecules with lesser symmetry cannot give rise to such degeneracy, local symmetry in a large molecule may cause appropriate frequencies to be so close together that their absorption bands are not resolved experimentally, and the spectrum will appear to be that of a molecule of higher symmetry.

The calculation of the vibration frequencies is a formidable undertaking for a molecule with more than three or four atoms, and the interatomic distances and force constants which are involved may not be known accurately. Further, the equations are based on the assumption of harmonic motion, which is only approximately correct, so
that aside from the other obstacles, there will still be an inherent error between the calculated and observed frequencies.

A less rigorous but much easier approach is the application of a few generalities discovered from other spectral studies. For example, a given bond between two given atoms is usually found to produce an absorption band somewhere within a fairly limited region of the spectrum, and tables listing the usual frequency ranges for all of the ordinary bonds are available (14, p.143). A few common bonds and their usual stretching frequencies are: CH, 2900-3100 cm\(^{-1}\); NH, 3100-3500 cm\(^{-1}\); and OH, 3100-3500 cm\(^{-1}\). Although the above facts obviously take no account of the nature of the rest of the molecule, the fundamental vibration may be thought of as being dominated by vibration of the bond in question.

**The Teller-Redlich product rule.** When an atom in a molecule is replaced by an isotope, the frequencies of the fundamental vibrations change, the amount depending on the extent to which the isotope participates in each given motion. The force constants are practically unchanged by isotopic substitution, since they are determined by the electronic structure, so that a heavier isotope will lower the vibration frequencies. A number of equations have been derived relating the ratios of the fundamental
vibration frequencies before and after substitution to the molecular parameters, the most useful of which is the Teller-Redlich product rule (6, p.231). Applied to the substitution of one isotope in a non-linear molecule, such as deuterium for hydrogen in the hydrazonium ion, this rule states:

\[
\frac{n}{\prod_{i=1}^{n} \left( \frac{\omega^*_{i}}{\omega_1} \right)^2 = \left( \frac{m}{m^*} \right)^n \left( \frac{M^*}{M} \right)^3 \frac{I_x I_y I_z}{I_x I_y I_z}}
\]

where the \( \omega \)'s are fundamental vibration frequencies in wave numbers, \( m \) is the mass of the substituted atom, \( n \) is the number of vibrations in which the substituted atom participates, \( M \) is the molecular weight, the \( I \)'s are the moments of inertia about the three principal axes, and the asterisks refer to the isotopic molecule.

In order to calculate the moments of inertia, a particular geometrical structure must obviously be assumed. If the molecule has symmetry, this general rule may be broken down into simpler equations, separating motions which are symmetric from those which are anti-symmetric with respect to each element of symmetry involved. By fitting the frequencies of the experimentally observed bands into the equations so that good agreement is reached, assignment of the fundamental frequencies may be simplified.
The hydrazonium ion. The N$_2$H$_5$Cl molecule is ionic in aqueous solution, as evidenced by its electrical conductivity (1, p.212). If it were also ionic in the crystalline state, the chlorine atom should have little effect upon the infrared spectrum, the effective structure being then the N$_2$H$_2^+$ ion. If the same applied to N$_2$H$_5$Br, its spectrum should be very similar. The most probable structure for the N$_2$H$_2^+$ ion is the staggered configuration shown in figure 4. Since the plane of symmetry is the only symmetry element, there will be no degeneracy, and all fifteen fundamental vibration frequencies should appear in both the infrared and Raman spectra.
THE INFRARED SPECTROMETER. General. The instrument used for obtaining absorption curves was a Perkin-Elmer model 12-C infrared spectrometer equipped with a number of accessories (6, pp.32-50). The basic unit consists of a Globar source, a Littrow type prism and mirror, a thermocouple detector and appropriate slits and mirrors to complete the optical system. The prism mounting is connected to a hand micrometer to permit rotation of the prism to any desired setting.

In addition to this, an electric motor is connected to the micrometer through a gear box so that the prism can be rotated automatically at any of four speeds--1, 2, 4, or 8 minutes per micrometer revolution. The spectral range corresponding to a micrometer revolution varies with the region covered.

The Globar light source, which is a carborundum rod heated by passing an electric current through it, emits a spectrum which is very nearly that of a black body. The energy in the infrared is still very low, however, so that the thermocouple output is far too small to be useful directly. For this reason, there is a sector disk in the light path which chops the light into pulses with a frequency of ten cycles per second. The resultant pulsating current from the thermocouple is amplified, rectified and
then fed to an automatic pen recorder, which produces a permanent record of intensity versus wavelength or frequency.

Three interchangeable prisms cover the region 400-4000 wave numbers (25-2.5 microns). The prisms and their regions of best resolution, in wave numbers, are: KBr, 400-1000; NaCl, 700-2000; LiF, 1700-4000. A calibration chart had previously been made for each prism, relating micrometer scale readings to wave numbers. This was accomplished by determining the micrometer scale readings corresponding to absorption bands of known frequency of a number of materials, in particular, H2O, CO2, NH3, HCl, and CH4 vapor. The wave numbers of a sufficient number of such bands were then plotted against the micrometer scale readings, and a smooth curve drawn. This procedure was followed for each prism.

Each time prisms were changed, the one being inserted had to be carefully adjusted to the position at which it had been calibrated. This was done by making some convenient carbon dioxide or water band coincide with a predetermined micrometer setting. The final adjustments were made by recording the spectral region in question. It was noted, however, that the lag in the recorder response with double beam operation (see below) was sufficient to make the calibration vary with the scanning speed. Thus, after careful calibration at a
given speed, a record made at a different speed might be in error up to about 5 cm$^{-1}$, depending on the region. Making runs at or near the speed of calibration minimized the error.

Since the energy emitted by the Globar at a given frequency is a function of that frequency—roughly varying according to the black body curve—each sample run must be supplemented by a blank run made under conditions which are identical except for the absence of the sample. The curve thus obtained represents "100 per cent transmission" at every frequency. The ratio of the transmission of the sample curve to that of the blank curve is then the per cent transmission at each frequency. This is calculated for a sufficient number of points and replotted.

Double beam operation. As can be imagined, the above procedure is very time consuming. It is also subject to the criticism that some of the operating conditions may change in the time between the blank run and the sample run. For instance, a change in atmospheric conditions between runs could easily occur which would affect the record, since both water vapor and carbon dioxide absorption bands appear in the infrared region. For these reasons, the instrument is also equipped with a means for running sample and blank simultaneously and delivering to the recorder the transmission ratio (12, pp. 203-212). This is accomplished by using a
different sector disk which chops the upper and lower halves of the light beam out of phase, the two signals from the detector being separated after amplification by electric switches which are synchronized with the sector disk. The sample is placed in one half of the beam and the blank in the other. The synchronization is difficult to achieve, and quantitative comparisons of the per cent transmission obtained with the double beam and the single beam methods under the same conditions have not been made, so that no absolute significance can be attached to the exact values of per cent transmission obtained by the double beam method. There appears no reason to doubt the relative values, however, and absolute transmission values would be useless, if known, due to the fact that sample thicknesses were not measured.

One inherent disadvantage of the double beam method of operation is that the sample and blank each use only half of the total energy, so that for given conditions, the thermocouple output is only half what it would be under single beam operation. This situation would cause a loss in sensitivity, as the recorder would not respond as readily to the smaller changes in signal corresponding to a given change in transmission. To make up for this, the signal must be amplified to a greater degree, or the slit width must be increased. The first solution introduces too much electrical "noise" into the system--
reducing the accuracy of the record—and the second causes a wider spectral region to be scanned at each instant—decreasing the resolution. The amplification normally used with single beam operation is such that the noise level in the system is the maximum permissible, and any increase in amplification would make the record too erratic to be very useful. Therefore, the slit width must be increased for double beam operation, with some resulting loss in resolution.

**Stray light correction at long wavelengths.**

Because of the very low energy available at the lower frequencies of the potassium bromide prism region, the stray light reaching the thermocouple caused an appreciable error in the observed per cent transmission. The observed transmission ratio at any given frequency can be represented by

\[
\frac{T_s}{T_b} = \frac{I_s + \alpha \beta T_b}{I_b + \beta T_b}
\]

where the T's are observed transmissions, the I's are true transmissions of light of the given frequency, subscripts s and b refer to sample and blank, \( \beta T_b \) is the amount of false light reaching the detector, and \( \alpha \) is the fraction of \( \beta T_b \) transmitted by the sample.

Since most of the false light is of fairly high frequency, due to the black body distribution curve, it was assumed that the light passing a lithium fluoride
plate (above 1500 cm\(^{-1}\)) would include virtually all of the false light, and none of the light in the potassium bromide region. \(T_s\) and \(T_b\) were measured with a lithium fluoride plate covering the light path. Their ratio under these conditions is equal to \(\alpha\), which was thus determined for several samples throughout the KBr region. The values obtained were quite constant at 0.67. By next measuring \(T_b\) with and without a lithium fluoride plate in the light path, \(T_{bf}/T_b = \beta\), where \(T_{bf}\) is the false light transmission, was calculated at various frequencies. It was less than 0.15 above 450 cm\(^{-1}\), but increased very rapidly at longer wavelengths. The true transmission ratio is then

\[
\frac{I_s}{I_b} = \frac{1}{1-\beta} \left(\frac{T_s}{T_b} - \alpha\beta\right)
\]

This equation was used to correct observed transmission ratios at frequencies below about 700 cm\(^{-1}\), above which, the error was negligible.

**PREPARATION OF MATERIALS.** The \(N_2H_4Cl\) was prepared by combining stoichiometric amounts of \(N_2H_4\cdotH_2O\) and C. P. hydrochloric acid. Two methods were used to separate the salt from the water. In one, the solution was partially evaporated in a vacuum desiccator over \(H_2SO_4\) until the solubility concentration was almost reached. An excess of ethyl alcohol was then added, which caused the salt to
precipitate. It was then filtered and was dried over H$_2$SO$_4$ in a vacuum desiccator. Very fine crystals were obtained in this manner. Analysis of the Cl$^-$ content agreed well with that predicted for N$_2$H$_5$Cl: found = 51.5%; calculated = 51.8%.

In the second method, the evaporation of the solution was continued to dryness, and the resulting crystalline solid was fused for about an hour at 105$^\circ$C to expel any excess of either reagent. After cooling, it was ground to a fine powder with a mortar and pestle, and stored over H$_2$SO$_4$ in a vacuum desiccator. The purity was verified by a melting point determination.

The N$_2$H$_5$Br was obtained from Dr. Max B. Williams. Its purity was checked by a determination of the melting point---83$^\circ$C. It was stored under the same conditions as was the chloride.

N$_2$D$_5$Cl and N$_2$D$_5$Br were prepared by dissolving dry salt in D$_2$O and evaporating over P$_2$O$_5$, and repeating until the theoretical deuteration exceeded 99.8%, assuming equilibria between hydrogen and deuterium to be reached each time. This required four to six recrystallizations. Considerable care was taken to minimize exposure of the salt to the atmosphere in order to prevent exchange with water vapor with the consequent loss of deuteration. The deuterated salts were stored in vacuum desiccators over P$_2$O$_5$. 
SAMPLE PREPARATION. In infrared spectroscopy, solid samples are best mounted between alkali halide plates. Both circular and square plates of NaCl, LiF, and KBr, 7 millimeters thick and 6-8 square centimeters in area are available commercially. Each of these materials is particularly suitable for certain spectral regions, being more transparent there than the others. The plates must be kept polished to reduce light loss at the surfaces, and if very thin samples are desired, the surfaces must be very flat. This is best accomplished by grinding on fine sandpaper, and then polishing on a pitch and rouge lap. A good test for flatness is the appearance of Newton’s rings when two plates are pressed together.

N₂H₅Cl samples were originally prepared by making a mull of the precipitated salt with either mineral oil or a fluorocarbon oil. As each of these has its own absorption bands, each was used principally for the spectral regions in which it did not absorb. Best results were obtained by working the mull between the plates for some time before making the run.

Samples prepared in this manner were satisfactory for most of the near infrared spectrum, but were almost opaque at the shorter wavelengths. This was thought to be due to light scattering at wavelengths (3-4 microns) comparable to the particle size of the sample.
The low melting points of the salts suggested the possibility of producing very thin samples of pure salt by fusing a small amount between rock salt plates in an oven. In this way, a very thin capillary film was produced, with which quite satisfactory spectra were obtained.

It was soon noted that after removal from the oven, the molten film frequently remained in a supercooled state. This could be verified by examining the sample between crossed polaroid lenses, for since the solid form of both salts is uniaxial, distinction between the solid and the isotropic liquid was easy. The supercooled state could not be produced or maintained consistently, however, and no heated cell was available for keeping the sample above the melting point. Consequently, an attempt to cover the complete spectrum with liquid samples was abandoned shortly. In general, the few regions which were scanned with liquid samples confirmed the spectra obtained with samples which were in the crystalline state.

The chloride samples were prepared between NaCl plates and most of the work with them was done by the single beam method. The bromide samples were prepared between KBr plates. They were studied entirely by the double beam method, and the lower resolution is apparent in the spectra. The quantity of salt present was not
known for any of the samples, so that the observed intensities of the absorption bands are significant only for comparison.

The preparation of samples of the deuterated compounds had to be made very carefully and rapidly to avoid contamination by hydrogen through exchange with the atmosphere. A number of samples prepared without sufficient precaution in this respect gave very complicated spectra, presumably due to \( \text{N}_2\text{H}^+ \), \( \text{N}_2\text{D}^+ \) and intermediate compounds. When the hydrogen to deuterium ratio becomes so large that bands due to hydrogen are very noticeable in the spectrum, the number of different isotopes present is considerable. So many different isotopic molecules contribute their individual spectra that the total result becomes too complicated to be useful unless a very detailed and systematic study is made.
RESULTS AND INTERPRETATION

The spectra of $\text{N}_2\text{H}_5\text{Cl}$, $\text{N}_2\text{D}_5\text{Cl}$ and the corresponding bromides appear in figures 1 and 2, and the frequencies of the observed absorption maxima are listed in table 1. Two obvious features are significant—the remarkable similarity of the bromide spectra to the corresponding chloride spectra, and the extreme breadth of the bands from 2500-3300 cm$^{-1}$ in $\text{N}_2\text{H}_5\text{Cl}$ and $\text{N}_2\text{H}_5\text{Br}$ and from 1900-2450 cm$^{-1}$ in the deuterated compounds.

The frequencies of the absorption peaks in the chloride spectra are consistently higher than those of the corresponding bromides—the difference averaging about ten wave numbers—indicating that the halogen atom exerts some influence on the spectrum. However, the corresponding spectra of the chlorides and bromides are so nearly identical, that the ionic structure of both compounds seems to be confirmed.

The extreme breadth of the NH stretching regions is comparable with that observed in water by Cross, Burnham, and Leighton (2, pp. 1134-1147), and attributed by them to the varieties of hydrogen bonding. That hydrogen bonding should exist in these compounds seems not surprising, since in each $\text{N}_2\text{H}_5^+$ ion, one nitrogen atom has an extra hydrogen atom and the other has an unshared pair of electrons. Thus the bonding might be represented
THE INFRA-RED ABSORPTION OF $N_2H_5Cl$ AND $N_2D_5Cl$

Figure 1.
THE INFRA-RED ABSORPTION OF $\text{N}_2\text{H}_5\text{Br}$ AND $\text{N}_2\text{D}_5\text{Br}$

Figure 2.
### TABLE 1

**INFRARED ABSORPTION MAXIMA FOR CRYSTALLINE HYDRAZONE MONOHALIDES**

(cm$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>$\text{N}_2\text{H}_5\text{Cl}$</th>
<th>$\text{N}_2\text{H}_5\text{Br}$</th>
<th>$\text{N}_2\text{D}_5\text{Cl}$</th>
<th>$\text{N}_2\text{D}_5\text{Br}$</th>
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<tr>
<td>973</td>
<td>495</td>
<td>965</td>
<td>790</td>
<td>(&lt;415)</td>
</tr>
<tr>
<td>1101</td>
<td>1095</td>
<td>805</td>
<td>932</td>
<td>1045</td>
</tr>
<tr>
<td>1124</td>
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<td>3245</td>
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(All values in cm$^{-1}$.)
Figure 3. Hydrogen bonding between hydrazonium ions (schematic)

Figure 4. Staggered structure of the hydrazonium ion with normal coordinates
schematically as in figure 3, where the dotted lines indicate hydrogen bonds.

In order to facilitate the assignment of the observed frequencies, the Teller-Redlich product rule was employed. For the calculation of the moments of inertia, the staggered configuration of the hydrazonium ion was assumed, with tetrahedral angles about the nitrogens. Bond lengths used were: NN, 1.40Å and NH, 1.01Å (11, pp. 164, 168). The moments of inertia about the principal axes in gram-cm²·10⁻⁴⁰ are:

<table>
<thead>
<tr>
<th></th>
<th>N₂H⁺</th>
<th>N₂D⁺</th>
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<tbody>
<tr>
<td>Iₓ</td>
<td>7.55</td>
<td>14.99</td>
</tr>
<tr>
<td>Iᵧ</td>
<td>34.94</td>
<td>46.95</td>
</tr>
<tr>
<td>Iₓ</td>
<td>36.13</td>
<td>49.37</td>
</tr>
</tbody>
</table>

and the principal axes are illustrated in figure 4. The Teller-Redlich rule applied to all of the fundamental vibrations is

\[
\prod_{i=1}^{15} \left( \frac{\omega^*_i}{\omega_i} \right)^2 = \left( \frac{1}{2} \right) ^{15} \left( \frac{38.09}{33.06} \right) ^3 \left( \frac{14.99, 46.95, 49.37}{7.55, 34.94, 36.13} \right) = 1.722 \cdot 10^{-4}
\]

This result requires all of the frequency ratios except the NN stretch to average considerably closer to the theoretical limiting ratio (1/√2) than they do. The discrepancy can be blamed in part, at least, on the
hydrogen bonding, which is conducive to anharmonicity.

The product rule was also applied separately to the vibrations which are symmetric and antisymmetric with respect to the plane of symmetry. The result was that the individual frequency ratios—with the exception of the NN stretch—must average the same in both cases, so this proved no help in making assignments.

The fifteen fundamental vibrations to be expected may be accounted for in the following way. There are five NH stretching modes and one NN stretching motion; there are three HNH bending modes at the NH$_3^+$ group, and one HNH bend at the NH$_2$ group; there are two bendings of the NH$_3^+$ group and two of the NH$_2$ group with respect to the NN bond; finally, there will be a low frequency torsional vibration of the end groups about the NN bond if restricted rotation about that bond is assumed.

Assuming the frequencies of the various motions to be about the same as they are in other compounds involving similar bonds, the five NH stretches should be around 3300 cm$^{-1}$, the NN stretch about 1000 cm$^{-1}$, the HNH bendings about 1600 cm$^{-1}$, the bendings of the NH$_3^+$ and NH$_2$ groups between 1000 and 1600 cm$^{-1}$, and the torsion at a very low frequency—probably below 400 cm$^{-1}$. Although there can be no exact degeneracy, the local symmetry of the NH$_3^+$ group might be expected to cause near degeneracy
among some of its modes, if that group is not too greatly influenced by forces from the NH$_2$ group and the lattice. From the ammonia symmetry (6, p. 294), one degeneracy of each motion of the NH$_3^+$ group is to be expected. There will then remain four NH bands around 3300 cm$^{-1}$, the NN band at about 1000 cm$^{-1}$, three HNH bands near 1600 cm$^{-1}$, three bands due to NH$_3^+$ and NH$_2$ group bendings between 1000 and 1600 cm$^{-1}$, and the torsion.

Since the bromide spectra differ so little from those of the chloride, the latter only will be considered in discussing assignments.

The band at 973 cm$^{-1}$ in N$_2$H$_5$Cl is correlated with the 940 cm$^{-1}$ band in N$_2$D$_5$Cl because of the sharpness of both bands. Since it is the only strong band which does not undergo a large isotope shift, it is identified with the NN stretch.

The 2500–3300 cm$^{-1}$ NH stretching region does not permit assignment of individual modes. The bands between 1000 and 1700 cm$^{-1}$ are assigned on the basis of the isotope shift and on the assumption that the frequencies of the HNH bendings are higher than those of the bendings of the end groups about the NN bond. The selected frequencies are listed in table 2 with the Raman data of Edsall (3, pp. 225–237) and Edsall and Scheinberg (4, pp. 520–525) for comparison. The Raman bands at 1274 cm$^{-1}$ and 1533 cm$^{-1}$
<table>
<thead>
<tr>
<th>Vibration</th>
<th>N₂H₅Cl Infrared</th>
<th>N₂H₅Cl Raman</th>
<th>N₂D₅Cl Infrared</th>
<th>N₂D₅Cl Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN</td>
<td>973</td>
<td>965</td>
<td>940</td>
<td>943</td>
</tr>
<tr>
<td>RNN¹</td>
<td>1101 (1124)</td>
<td>1107</td>
<td>790 (805)</td>
<td>838</td>
</tr>
<tr>
<td>RNN</td>
<td>1246</td>
<td>1274</td>
<td>1000</td>
<td>989</td>
</tr>
<tr>
<td>RNN</td>
<td>1417</td>
<td>1424</td>
<td>1100</td>
<td>1098</td>
</tr>
<tr>
<td>HNH</td>
<td>1500</td>
<td>1533</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNH</td>
<td>1564</td>
<td></td>
<td>1155</td>
<td>1158</td>
</tr>
<tr>
<td>HNH</td>
<td>1638 (2585)</td>
<td>1632 (2700)</td>
<td>1190</td>
<td>1198</td>
</tr>
<tr>
<td>NH²</td>
<td>3035 (2965) 3125</td>
<td>3197 (2963) 3245</td>
<td>2390 (2963) 3286</td>
<td>2354 (2240) 2440</td>
</tr>
</tbody>
</table>

¹Bendings of the end groups about the NN bond.
²The selection of individual fundamentals is not possible.
were both reported as weak, and it is difficult to tell whether they are to be identified with observed infrared bands or regarded as distinct modes.

The correlation between the infrared and Raman frequencies is satisfactory in some cases, but for many frequencies, the discrepancy clearly exceeds the experimental errors. An explanation for this is the different physical states of the samples. In aqueous solution, hydrogen bonding could take place to water, in which case the vibration frequencies would be altered. In the solid state, it is shown that the identity of the halogen atom affects the spectrum, however slightly, which should not be true in aqueous solution, and it may be assumed that the neighboring hydrazonium ions in the lattice exert a different effect than in solution, when they are further removed.

Because the number of bands observed in the infrared spectrum corresponds reasonably well with the number expected, the lack of better agreement between the two sets of data is not taken as evidence of higher symmetry for the hydrazonium ion.

It was decided that the band at 495 cm\(^{-1}\) in the bromide spectrum was not due to a molecular vibration because it was absent in the spectrum of a supercooled molten sample which was observed on one occasion.
It is thought to be due to a lattice vibration.

The bands at 1745 cm\(^{-1}\) and 1970 cm\(^{-1}\), along with those above 2450 cm\(^{-1}\) in the deuterated compounds, are believed to be combinations or overtones, although the latter bands may be due to NH stretching resulting from incomplete deuteration.

Certain further experiments suggest themselves from the results obtained here. By the use of a heated cell in which samples could be maintained in the liquid state, bands resulting from lattice vibrations could be recognized. Also, if the bands above 2450 cm\(^{-1}\) in the spectra of the deuterated compounds are NH stretching bands, variation in the degree of deuteration should disclose this and provide a means of obtaining the vibration frequencies of the individual NH stretching motions. Frequencies obtained in this manner have the advantage that the motions are relatively free of the effects of intermolecular vibration coupling (7, pp. 918-919).
SUMMARY

The infrared absorption spectra of crystalline hydrazine monochloride, hydrazine monobromide and the corresponding deuterated compounds have been obtained for the region 3-20 microns. The spectra of the chloride and bromide are almost identical, indicating that the halogen atoms exert little influence on the spectrum of the solid, and that the effective absorbing structure is the hydrazonium ion. There is apparently strong hydrogen bonding in these salts, as evidenced by very broad bands in the NH and ND stretching regions.

The results of applying the Teller-Redlich product rule to the isotope shift indicate that the molecular vibrations are quite anharmonic. The hydrogen bonding is probably largely responsible for this.

Identification and assignment of most of the fundamental bands has been made.
BIBLIOGRAPHY


13. **Williams, M. B.** private communication.