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INFRARED SPECTRA OF MARGINALLY METALLIC SYSTEM

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INFRARED SPECTRA OF MARGINALLY METALLIC SYSTEMS

Tad Alan Beckman
(Thesis)
August 1960
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ABSTRACT

Solutions of sodium metal in liquid ammonia have been studied with particular reference to their properties as marginally metallic systems. For this purpose, a general method of reflection spectroscopy has been developed. This method is of particular usefulness for the infrared reflection study of liquids.

Sodium-ammonia solutions were prepared inside of a specially constructed reflection apparatus maintained at -40°C. The plane surface formed by a given solution and a transparent material, or window, sealed to the side of this apparatus was used as the reflection plane. The spectra obtained were interpreted in terms of the standard reflection of a mercury surface under identical conditions.

Predictions of the reflection spectra are made on the basis of classical theories of metallic reflection. Comparison of the observed spectra with these predictions discloses marked deviations from the purely classical form of metallic behavior. These deviations are given an interpretation in terms of the continuous transition of electronic states between those of a perturbed atom and those of sodium metal.
INTRODUCTION

The disposition of electrons in metallic and other solid systems has been the subject of much interest and study since the beginning of this century. The problem as a whole is of no less fundamental importance than its related point of interest, the electronic states of molecules. Both of these broad fields of study, however, are encumbered by mathematical and conceptual difficulties which have made theoretical analysis a heavy task. The degree of refinement approached in the analysis of an isolated atom is quite impossible here; nevertheless, the application of atomic properties and of the properties of periodic potential fields has been extremely valuable in discussing molecular and solid state phenomena. In this context it has become convenient to consider the changing electronic states of a system of atoms as the interatomic distance is varied from infinite separation toward the short range of a crystal lattice constant.

Several of these degrees of coalescence exist in nature and may be subjected to detailed study. The ordinary gaseous state represents one of these. Pressure broadening of spectral lines\(^1\) and deviations from ideal thermodynamic behavior are several of the observed phenomena which give us some information about the distortion of atomic properties arising from a diminishing interatomic distance. We know that alterations in the electronic
states occur to cause these phenomena; indeed, the theory of Van der Waals' forces is built upon this assumption.

The liquid state represents a high degree of coalescence; indeed, the degree of interatomic interaction is so great that very few elements remain atomic to any recognizable extent. Nevertheless, spectral changes in atomic and molecular species which have been incorporated within a liquid substance give some information in regard to the electronic interactions which exist at this distance of separation. The ligand field theory represents an attempt to describe some of these interactions.

Between the liquid and the solid states, however, there is little opportunity to study the changing electronic distributions. It is virtually impossible to change the lattice constant of a crystal and, likewise, quite difficult to compress liquids to any appreciable degree. Perhaps the only outstanding example of work in this field is the high pressure treatment of insulators. Solids which do not conduct electric current at normal pressures can indeed be made conductors by increasing the degree of atomic approach. This is certainly good evidence of the changes in the electron distributions which occur as atoms move towards one another.

The only other promising system of study would seem to be a diluted solid, that is a solid to which some other material has been added. For instance, if some inert, or chemically unreactive, material were placed in a metallic crystal, the interatomic distance of the metal atoms would be forced to increase. If enough inert material were added, the metallic solid would go over into a liquid metal. Ultimately, of course, its metallic properties would be lost and a dilute solution of metal atoms in inert liquid would be obtained. In all of these cases the concentration of
the metal atoms is a measure of their interatomic distance. Systems which lie along this transition between metallic and perturbed atomic states will be called marginally metallic. They provide a good system in which to study the disposition of electrons as atoms tend toward the formation of a regular, periodic lattice.

Solutions of sodium metal in liquid ammonia are excellent examples of marginally metallic systems. Very little chemical decomposition occurs so that both the ammonia and the sodium can be recovered at any time by a simple physical separation. Furthermore, these solutions do behave like liquid metals when sufficiently concentrated with respect to sodium. Kraus succeeded in measuring the concentration dependence of conductance in these solutions. Later on, Kraus and Lucasse were able to observe the temperature coefficients of conductance at various sodium compositions. These data indicate that concentrated solutions of sodium in ammonia tend toward a metallic state similar to that of mercury. In fact, the increase in viscosity and the advent of metal-like reflection of visible light also confirm this notion.

As early as 1907 Kraus discovered the phenomenon of phase separation in these solutions. It was found that a phase of high sodium concentration and with metallic properties could exist in equilibrium with a phase of low sodium concentration. Pitzer has suggested that such phase separation can be interpreted in terms of an equilibrium between a liquid and its vapor. In this terminology the dilute solutions of sodium in ammonia represent systems of highly perturbed gaseous sodium atoms; the concentrated solutions represent actual liquid metals of variable interatomic distance. Taken in
the temperature region where no phase separation occurs, these solutions
give a continuous transition between the electronic states which characterize
an electrolyte or insulator and a metal.

Since spectroscopy is the most powerful tool in observing electronic
states, we must examine the spectroscopic data on the sodium-ammonia system.
The great lack of data on this system, however, is evidence for the need of
further experimental work. Only the dilute solutions have been studied to
any great extent with spectroscopic methods. Even then, only spectra of
the visible and near ultraviolet regions are available. The outer photo-
electric threshold has been determined to be 1.5 ev and the inner photo-
electric threshold has been estimated to be below visible light energies.
No spectroscopic data have been taken on the more concentrated solutions
because of their very high extinction coefficients.

In the interest of completing the spectroscopic study of the liquid
ammonia-sodium solutions and in the hope of obtaining valuable data on the
changes of electronic states in this marginally metallic system, this
research was undertaken.
PART II
Experimental Method

Two broad techniques of spectroscopic study are available; these may be called transmission and reflection spectroscopy. In the former of these the light which a material transmits is analyzed. The intensity of light of any given wavelength which is received through the medium is a function of many factors. Primarily it is a measurement of the extinction coefficient of the substance. But it is also, of course, a function of the length and width of the light path, the density of the absorbing species, and the peculiarities of the optical arrangement employed.

In the method of reflection spectroscopy the light which is reflected from a good optical surface of the medium is subjected to analysis. The intensity of the reflected light at any given wavelength when divided by the intensity of the incident light of that wavelength constitutes the reflection coefficient. Although the mathematical relationship is somewhat more complex, the measured reflection coefficient is also related to the extinction coefficient of the medium. Indeed, with two independent measurements of the reflection coefficient taken at different angles of incidence, the optical constants of the medium may be calculated for each wavelength.

Transmission methods of spectroscopy are very sensitive to small changes in extinction coefficient. With not too elaborate a technique band shapes and intensities can be revealed with good accuracy. Even very small degrees of absorption can be studied conveniently. However, it is impossible to study media which have very large extinction coefficients since little light is transmitted for analysis and accurate detection. Although the net amount of absorption can be reduced by the reduction of path length, there is a practical limit to the cutting of thin crystals, for instance. Unfortunately
sodium-ammonia solutions do have very high extinction coefficients, so that the transmission technique is almost useless.

Reflection methods are relatively insensitive to small changes in the extinction coefficient. Consequently, it is difficult to resolve band structure or to observe relatively weak absorptions. Reproducibility is often poor in reflection work since it is very highly dependent upon the condition of the optical surface. Even the method of preparation may cause substantial changes in the properties of the reflection surface. However, reflection spectroscopy affords virtually the only means by which solids and liquids with large extinction coefficients can be studied optically. The reflection technique has been employed extensively in this research for the spectroscopic study of the ammonia-sodium solutions.

The apparatus used for the spectroscopic analysis of the reflected light was a Perkin Elmer 12c Recording Spectrometer. The electrical signal from a thermocouple in this instrument was amplified with an amplifier of laboratory design and was displayed as a DC voltage on a Brown Recording Potentiometer. The infrared source was a Nernst Glowbar which was heated electrically with approximately 200 watts of power. All mirrors in the optical path were front surface aluminized glass. A chart displaying the prisms used is given below along with other pertinent information.
The construction of a suitable reflection apparatus to be used with this equipment depended upon a number of instrumental, chemical, and physical features. It was necessary, for instance, to provide a good optical surface of the solution to be studied. By good optical surface it is meant that the surface would have to reflect light according to the laws of optics and would have to give reproducible intensity measurements. Obviously, any smooth, regular surface would meet the former requirement, while chemical purity would be an essential for the latter. While various curved surfaces would be possible, a plane surface of solution was undoubtedly the most practical and easily realizable. The restriction of chemical purity required that the solutions be prepared in a vacuum system, indeed that the reflection cell itself should be an evacuable apparatus. Brief thought would reveal that only two types of surface are at all feasible: (1) the interface between the solution and ammonia gas which is formed at the top of the solution when it resides in some cavity, and (2) the interface between the solution and a transparent material which is formed when some optical window is incorporated in the side of the solution cavity.

<table>
<thead>
<tr>
<th>Prism</th>
<th>Region, cm⁻¹</th>
<th>Calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>visible</td>
<td>atomic lines</td>
</tr>
<tr>
<td>LiF</td>
<td>10,000 - 2,000</td>
<td>Hg arc, H₂O, NH₃, CH₄, CO₂, CO</td>
</tr>
<tr>
<td>NaCl</td>
<td>6,000 - 700</td>
<td>H₂O, NH₃</td>
</tr>
<tr>
<td>KBr</td>
<td>800 - 400</td>
<td>H₂O, NH₃, CH₃OH</td>
</tr>
</tbody>
</table>
Another general feature which the reflection apparatus had to meet was the strict requirement of a short optical path. The reflected light must come into reasonable focus at the entrance slit of the spectrometer. This condition, coupled with the size of the mirrors used on the Perkin Elmer instrument and those available for use with the infrared source, required that the apparatus should be reasonably compact. In fact, for perfect focusing of the optical path the apparatus would have to fit closely to the side of the spectrometer. Admittedly, this light path could be lengthened by the use of mirrors with a somewhat longer focal length. However, in order to avoid a severe loss of light with this arrangement the mirrors would have to be large in diameter. The consequent increase in the width of the light beam would require the use of very large apertures in the reflection apparatus. Unfortunately, the window materials which are available and which are safe for use in an evacuated system severely restrict the size of these apertures. Compactness of the reflection cell was to be desired.

The liquid ammonia-sodium system itself offers certain complications to the optical problem. The high efficiency of liquid ammonia as a solvent, equal in many respects to that of water, and the good reducing properties of sodium metal combine to limit severely the number of materials with which the solutions can come in contact. On the other hand, only certain materials have the desired optical properties. Potassium bromide, cesium iodide, sodium chloride, and other common salt windows for infrared use have high solubilities in ammonia. Quartz, lithium fluoride, barium fluoride, and certain plastics are chemically unreactive but have only limited optical usefulness. The former salts were employed where chemical contact was not necessary, but the latter materials had to be used where there was chemical contact.
Still another feature which the reflection cell would have to meet was the necessity of maintaining a low temperature. Temperatures from the boiling point of ammonia (-33.5°C) to about -60°C would have to be attainable and would have to be held moderately constant. If the optical window should come into contact with the cold solution, some means of protecting its outer surface from the atmospheric moisture would also have to be provided.

Several reflection cells were designed and constructed for this research. These will be described in detail at this time. Although attempts were made in the early stages of this work to utilize salt lenses in the optical path, the change in the focal length as a function of wave length and the restrictively small dimensions of these lenses made their application impossible. Consequently, both reflection cells which were used in the experiments to be described utilized front surface aluminum mirrors.

**Reflection Cell No. I** - This reflection apparatus was designed to use the solution - ammonia gas interface which exists at the top of the ammonia solution. Figure No. 1 presents a diagram of this apparatus and Figure No. 2 shows the optical arrangement. Light from the Glowbar source is reflected into a spherical mirror of eleven inch focal length from a single plane mirror. The converging beam of light enters the cell and is reflected down to the solution surface by the first slanted plane mirror. The reflected light from the solution is turned back to a horizontal course by the second slanted plane mirror. And finally, the diverging beam of light enters the spectrometer by way of the standard source optical parts.

The reflection cell itself is constructed from a six inch glass industrial flange joint. The bottom is essentially spherical and is surrounded
Fig. 1. Reflection cell No. 1.

Spherical joints and glass rods

1/2" glass plate

Plane mirrors (2" x 3 1/4") on mirror frame

6" flange joint

Optical window

Side arm to vacuum system

Cooling jacket
Fig. 2. Optical arrangement for reflection cell No. 1.
by a glass jacket through which a suitable cooling liquid can be conducted. The light beam enters the cell and exits through portholes which were drilled through the glass walls of the vessel. Optical windows were sealed onto these portholes with Apiezon W sealing wax; the normal materials such as potassium bromide could be used with this cell since there should be no contact with the solutions. The plane mirrors are mounted on a simple brass frame which is sealed to the top glass plate with a strong epoxy resin. The brass frame consists of a rod which is held in position above the solution by two arms connected to the upper plate. Upon this rod two small brass plates are held in such a way that they can rotate up and down freely and independently. The plane mirrors are held on these plates with small brass clamps. The mirrors can be raised and lowered while the cell is evacuated by way of a simple pulley device. For each mirror a glass rod is conducted into the top of the cell through a small spherical joint which is vacuum tight. This rod can be freely rotated so that it winds or unwinds a silk string leading to the outer end of the mirror mounting. After the optical adjustment is made, the spherical joint can be clamped tightly. The solution can be prepared in an atmosphere of ammonia by distilling ammonia into the cell through the side arm provided and by adding sodium in some manner (see Part III). In practice it was not quite possible to focus the reflected light from this apparatus on the entrance slit of the spectrometer. However, it was found that the extra large plane mirror used with the source utilizes more of the source radiation than the small mirror used on the Perkin Elmer instrument in the equivalent position. Thus, the reflection arrangement is still capable of the good sensitivity obtained with this instrument under the normal optical arrangement.
Temperature maintenance in the reflection cell was made possible by the apparatus outlined in Fig. 3. Reservoir No. 1 contains a mixture of dry ice and acetone at a temperature of approximately -70°C. Reservoir No. 2 contains acetone which is pumped through the cooling jacket of the reflection cell by means of a centrifugal pump. Copper coils which are placed in both reservoirs are filled with acetone which is pumped between these through another centrifugal pump. In this way the acetone of Reservoir No. 2 is cooled. A heater which is immersed in the second reservoir provides heat to the acetone when desired; it is wired into a thermostat circuit which is sensitive to ±.5°C changes in temperature. A crude temperature adjustment can be made by regulating the height of the copper coil in the acetone. The final adjustment can be accomplished by the proper setting of the thermostat. With this arrangement a constant temperature can be maintained for over twenty hours. A double turn of high resistance wire was made around the cell just above the cooling jacket. By applying a small AC voltage to this wire the upper parts of the cell were kept at room temperature; the windows were kept moisture free. The base of the cell was insulated with a cylinder of insulating board so that the heat entrance from the room was held at a minimum.

Although many spectra were taken with the use of this reflection cell, certain severe problems made its continued use impractical. Ammonia gas absorbs light very heavily throughout much of the sodium chloride spectral region, from around 1200 cm⁻¹ to 700 cm⁻¹. The many absorption bands which detract from the reflected light make it virtually impossible to interpret spectra in this region. This problem is especially severe since the amount of ammonia in the light path changes from one solution to the next, the ammonia vapor pressure being a function of the concentration. At the same
Fig. 3. Apparatus for temperature control.
time, the reaction of ammonia and sodium to form hydrogen gas

\[ 2\text{NH}_3 + 2\text{Na} = \text{H}_2 + 2\text{Na}^+ + 2\text{NH}_2^- \]

and the infrared heating of the solution's surface combined to cause rather severe bubbling. This surface disturbance made spectroscopy exceedingly difficult, especially with the concentrated and viscous solutions, and could be avoided only by operating at lower temperatures than desired (that is lower than \(-40^\circ\text{C}\) where phase separation begins). For these reasons another reflection cell was designed and built.

**Reflection Cell No. II** - This reflection apparatus was designed to use the solution - optical window interface formed by including a window in the side of the vessel. Fig. 4 presents a diagram of this apparatus and Fig. 5 shows the optical arrangement which was used with this cell. The same arrangement of mirrors is employed to obtain a converging beam of light. This beam is focused on the reflection cell window so that the reflected, divergent beam just fills the plane mirror of the source optics on the instrument. Optical focusing is perfect so that the maximum light is carried through to the spectrometer.

The reflection cell is enclosed within a large heavy glass vessel which can be evacuated. The top of this vessel is a glass plate. A tube sealed into this plate and fitted with a spherical joint just beneath the plate allows entrance to the actual reflection cell. Another system of tubes sealed in the top plate allows the entrance of the cooling liquid to the cell. In the final arrangement, the cell rests upon a plastic template just above the base of the outer vessel. At its top it is clamped tightly to the spherical joint in the plate. Two portholes in the outer jacket permit the entrance and exit of the light beam. These
Fig. 4. Reflection cell No. II.
Fig. 5. Optical arrangement for reflection cell No. II.
portholes are arranged so that the window material is perpendicular to the light beam when the angle of incidence upon the reflection window is approximately forty degrees. Rubber tubing is used to lead the cooling liquid from the tubes sealed in the top plate to the cooling jacket of the cell. Very little leakage of acetone into the evacuated vessel was observed so that the reflection cell window remained well protected from condensation of any kind while there was little temperature problem from convection currents. The room temperature radiation caused some problem at first but was easily prevented by lining most of the outer vessel with aluminum foil on the inside surface.

The reflection cell itself consists primarily of two concentric glass tubes. Near the bottom the inner tube is curved toward the side and is sealed into the side of the outer tube. The outer tube is sealed at both top and bottom while the inner tube has a spherical joint at its top. The outer tube serves as the cooling jacket for the cell. Cooling liquid is conducted into this through a tube just behind the cell window so that the cold liquid thoroughly bathes the window area. The window material is first sealed onto the smooth projecting part of the inner tube. General Electric Company No. 7031 Adhesive and Insulating Varnish (for low temperature use) has been found to be particularly useful for this purpose. Finally the material is clamped lightly in place with a stainless steel template held to the cell with adjustable steel bands. Thermocouples are placed on the steel template and inside of a small well in the cooling jacket.

Since the window material in this reflection cell must come into contact with the sodium-ammonia solution, only those substances which do
not react with either sodium or ammonia could be used. Quartz, lithium fluoride, and barium fluoride are all insoluble in ammonia and were used as optical windows. Potassium chloride has a low solubility in ammonia and might, perhaps, be used to extend the spectra beyond 800 cm\(^{-1}\) in the sodium chloride spectral region. In the potassium bromide spectral region the selection of a window material is infinitely more difficult, however. The common window materials all dissolve in ammonia; in fact, potassium bromide is rendered completely useless by its tendency to crack when it is cooled to low temperatures. Several methods of protecting a cesium iodide window with an inert and non-absorbing material were attempted. However, materials such as paraffin and plastics which are rigidly attached to the window at room temperature crack off when cooled to -40°C. The window which was finally used for the potassium bromide region was made in the following way: a cesium iodide window was coated with Kel-F high vacuum grease on one side and a thin sheet of polyethylene was rolled onto this side until it was flat and had squeezed most of the grease off the window. This window proved to be inert to the sodium-ammonia solutions but did have several broad absorption peaks in the spectral region. However, it was possible to obtain fairly good reflection measurements in a narrow region near 400 cm\(^{-1}\).

Several sources of error are inherent in the reflection methods which we have used. It will be useful to discuss these at the close of this section on the experimental method. The rather severe problem of bubbling was peculiar to the first reflection apparatus. Even when this can be controlled to the extent of allowing spectroscopy at the solution surface,
the deterioration of optical parts, such as the plane mirrors at the top of the cell, results in a considerable error in the intensity measurements. Since spectra are taken in a long series, one after another, the plane mirrors do gradually become speckled with sodium metal, even when the greatest precautions are taken. The over-all degeneration of window material, due also to spattering, is substantial too. Although with proper care this loss of reflected light can be held to about ten percent, the resultant error is too large to be tolerated.

A serious problem involved in the operation of the second reflection cell is the possibility of deterioration in the surface of the optical window. Any reaction of the solutions with the window material will cause pitting and a subsequent loss of reflected light. Also, there is the problem that crystal windows may develop some color center or independent absorption after a number of experiments have been performed. It would be especially damaging if a deposit of sodium metal were to build up just within the surface of the crystal. As yet, the windows employed such as barium fluoride, lithium fluoride, and quartz have shown no tendency toward any of these problems.

A final source of error lies inherently and irreconcilably in the basis of the reflection technique. This is the question of bulk phenomena as contrasted to surface phenomena. While transmission spectroscopy guarantees the observation of bulk phenomena (the properties within the physical chemical system), reflection spectroscopy is completely dependent upon surface properties. It is by no means obvious that the surface of a sodium-ammonia solution is identical in all respects to the bulk of solution within its boundaries. In particular relation to electronic properties, we must realize that the potential field which an electron feels at the
surface of the solution will be quite different from the field to which it is subjected within the solution. The physical properties of a surface may even cause a considerable difference in the composition of the surface layer. Impurities may play a greater part in the reflection of the surface (especially at the top surface) than they would contribute to transmission properties. These error sources are, however, unavoidable and can only be kept well in mind when interpretations are made. Fortunately, one feature of the chemical system is advantageous; the surface and the bulk of solution are in equilibrium with one another. In this liquid system the surface is renewed far more rapidly than it would be in some solid system.
PART III

Experimental Procedure

The liquid ammonia-sodium solutions were prepared inside of the evacuated reflection cell by the following procedure. Ammonia from a Mathieson anhydrous ammonia cylinder was first distilled into an evacuated bulb containing sodium metal. The bulb was cooled with a dewar vessel of dry ice and acetone; about 100 to 200 ml of ammonia was usually dried in this manner. This dry ammonia was distilled into the reflection cell which was cooled to approximately -60°C.

Sodium metal may be obtained in many degrees of purity with varying degrees of difficulty. Sodium azide decomposes to nitrogen gas and very pure sodium metal when it is heated in vacuo. However, this method is definitely restricted to the preparation of relatively small amounts of sodium. The impure metal can be distilled very slowly and over short distances, or it may be melted and run clear of its impurity film. These techniques give rather pure metal but require a fairly complicated vacuum system. It would be difficult to incorporate a system of this sort, capable of handling up to six grams of sodium, in the immediate region of the reflection cell. For this reason a somewhat more practical procedure was adopted. Sodium metal was placed under thiophene-free benzene and was cut into oxide-free blocks. Where the exact concentration of the solution was not desired, the amount of sodium used could be estimated simply by observing the volume of benzene displaced by a given block of sodium. In other experiments the blocks of sodium could be weighed in a small weighing bottle filled with benzene.

Once prepared, the small blocks or cylinders of sodium metal were placed in an addition tube (still under benzene). This device consisted
of several narrow glass tubes sealed onto (and perpendicular to) a common axis. It was sealed into the vacuum system with a ground glass joint in such a way that, when rotated, the narrow side tubes would slant downwards toward the reflection cell. Finally, the entire apparatus was evacuated and the benzene was distilled away from the sodium. The solutions were prepared by dropping sodium pellets into the reflection cell once it contained the desired amount of dry ammonia. A spectrum was begun shortly after each pellet was added so that the only limitation to the number of spectra that could be taken was the number of pellets which could be held in the addition tube and the length of time available. Most experiment series lasted for approximately twenty hours, and generally about ten spectra were taken in this length of time.

It is necessary to determine the concentration of each solution which is studied. Most earlier experimenters have obtained this concentration by analysis. But this technique requires that each solution be decomposed completely and analyzed quantitatively. It would be impossible to obtain more than one spectrum every two days with this procedure; on the other hand, where it is possible to go directly from one solution to another, as many as ten spectra can be taken in the same period of time and under identical optical conditions. This, however, leaves the concentration of a given solution unknown.

Two methods were employed in the concentration determination: weight volume estimates and conductance measurements. The former of these was utilized extensively in the second reflection cell since the inclusion of conductance electrodes in this cell would have made the glass blowing a
formidable task. With this apparatus, the sodium pellets were weighed under benzene to an accuracy of one one-hundredth of one gram. They were placed in known order in the addition tube so that the weight of sodium in each solution could be easily determined. The reflection cell itself was graduated so that the initial volume of ammonia could be read to an accuracy of about ± 3 ml. A simple calculation for a typical solution shows that 125 ml of ammonia and 1.44 g of sodium will result in a dilution (the number of liters of ammonia per gram-atom of sodium) of 2.00 ± 0.06 and a molarity of 0.49 ± 0.02 where the errors indicated are the maximum attainable. Of course, the concentrations of the first solutions were probably more accurate than this estimate indicates, while the concentrations of the later ones were undoubtedly less certain due to successively compounded errors. The dilution was calculated as the chief measure of concentration for all solutions. The molarity, on the other hand, cannot be calculated with such accuracy since the volume expansion due to the sodium must be included and can only be estimated. The mole ratio of ammonia to sodium was calculated instead but assumes a given density of ammonia.

The conduction measurements which were used with the first reflection cell are mentioned last since it is believed that they represent the most satisfactory method of obtaining the concentration. Good data on the dependence of conductance with concentration and temperature can be obtained from Kraus3,4 and other sources. Consequently, a measurement of the conductance of a given solution can be readily translated into a determination of the solution's concentration.

A conductance cell was arranged inside of the reflection cell in the following way. Two platinum electrodes were prepared by sealing a platinum
wire into the end of a glass tube. A piece of wire approximately 4 mm long by .05 mm thick was allowed to remain outside of the tube. These electrodes were fastened to a small glass frame which rested in the bottom of the reflection cell clear of the light path. In this position the electrodes dipped into the solution about two inches apart and one-half inch below the surface. Contact with the electrodes was made by placing a small amount of mercury in each tube and dipping a low resistance copper wire into this. The copper wires were conducted out of the cell through a small side arm fitting. This fitting consisted of a tube sealed onto the system with a ground glass joint. The wires were bent out of this tube and around its edge so that a small glass cup would just fit over the end. When this cup was filled with melted Apiezon W sealing wax and was pushed over the end of the tube, the cold seal was vacuum tight.

Resistance measurements could be made at any time during or after the spectroscopy. These measurements were made with a standard DC Wheatstone Bridge and also with a General Electric Company potentiometer type Double Bridge. The temperature was noted simultaneously with a thermocouple attached to one of the glass electrodes. Measurements were not made with alternating current since no polarization effects have been observed with this system.

In order to obtain the conductance from these measurements of resistance, the conductance cell had to be standardized. An independent standardization, however, is rather difficult. There is a great deal of resistance in the wire leads between electrodes and bridge, and these leads are subjected to a large temperature gradient, about seventy degrees. Obviously, standardization must be achieved at the same conditions as the actual measurement, especially since rather low resistances must be measured.
Several methods of internal standardization are possible and were used. When phase separation occurs, the electrodes dip into the lower of the two phases. This phase is dilute with respect to sodium and has a relatively high resistance, on the order of a strong electrolyte. Furthermore, at a given temperature the concentration of this phase is constant and known. It was possible to measure the resistance of this phase accurately so that this measurement constituted a standardization of the conductance cell at the actual experimental conditions and, indeed, with the same chemical system.

In certain cases, the experiments had to be performed at a higher temperature where phase separation would not occur. In this case internal standardization could still be obtained by measuring the resistance of the saturated solution. Since this concentration is also well known, the purpose was accomplished. However, the resistance of this solution is very low, about that of mercury, so that the measurement was not quite so accurate as in the previous example. At the same time, the saturated solution is more difficult to obtain in the course of an experiment since sodium begins to precipitate immediately and disturbs the electrodes.

The spectra were scanned at a relatively rapid rate of speed. A few of the details are indicated below.

<table>
<thead>
<tr>
<th>Region</th>
<th>Wave numbers scanned</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>8,000</td>
<td>40 min</td>
</tr>
<tr>
<td>NaCl</td>
<td>700</td>
<td>30 min</td>
</tr>
<tr>
<td>KBr</td>
<td>300</td>
<td>45 min</td>
</tr>
</tbody>
</table>
The average slit width used was approximately seventy microns in the high energy regions, ranging to four hundred and fifty microns in the low energy regions. For many of the dilute solutions this opening had to be increased in order to obtain a significant amount of the reflected light. In these cases the difference in the experimental conditions between the standard spectrum (see Part V) and the spectra of the solutions had to be corrected mathematically. Each point in the solution spectrum was multiplied by a factor which was proportional inversely to the square of the slit opening. That is, when the slit opening was doubled, the solution spectrum was multiplied by one-fourth. This procedure was checked by observing the same solution under several slit conditions; the calculated reflection curves agreed with one another to within one percent always.

In the cases where an automatic slit program had to be used (because of a rapidly changing radiation curve) the solutions of low reflectivity had to be observed with a higher amplifier gain than that used for the standard spectrum. Again the necessary correction could be made mathematically. In this case the factor was determined from the experiment by observing the amplification factor. The solution was observed with both amplifier gains, and the two spectra were compared.

If the dispersion of the prisms used is considered, the slit openings given above can be converted to spectral slit widths. The average spectral slit widths were fifteen wave numbers for the high energy regions and ten wave numbers for the low energy regions. Naturally, these values varied slightly, depending upon the exact slit conditions used. Where the solution did not reflect highly, a somewhat larger spectral slit width had to be used.
The data obtained in reflection spectroscopy are sufficiently different from those commonly obtained with transmission methods to merit a limited review of the physical optics involved. It has already been mentioned that reflection measurements do not directly yield the optical constants of a material. The refractive index \((n)\) and the extinction coefficient \((k)\) can be obtained only through the solution of two simultaneous equations. The reflection coefficient of a material at a given wavelength and for normal incidence (angle of incidence equals zero degrees) is

\[
R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad \text{(in vacuo)}.
\]

When the angle of incidence is non-zero, there is an angular dependence in this expression; thus, two measurements at different angles of incidence yield the two necessary equations. Other relationships are also available when it is not convenient to use more than one angle of incidence in the experimental arrangement. An observation of the phase change along with the reflection coefficient will accomplish the same purpose.

The connection between the optical constants of a material and atomic or molecular phenomena is of particular importance here. We shall be especially concerned with the effects which these phenomena will have on the reflectivity at any given wavelength. An analysis of this problem can be found in almost any good book on physical optics. References 10 through 14 were found to be particularly helpful; only the general results will be reviewed here.
The dielectric constant of a material is defined by the relation, \( \vec{D} = \varepsilon \vec{E} \), where \( \vec{D} \) is the electric induction and \( \vec{E} \) is the electric intensity. These are related by \( \vec{D} = \vec{E} + \chi \vec{P} \) where \( \vec{P} \) is called the electric polarization.

When Maxwell's equations are applied to an isotropic non-conducting medium, a wave equation of the form \( K\mu/c^2 \frac{\partial^2 \vec{E}}{\partial t^2} = \nabla^2 \vec{E} \) results. The velocity of the solution wave is the constant \( c \) divided by the square root of \( K\mu \) and where \( \mu \) is the magnetic permeability. Since \( K \) and \( \mu \) are both unity in a vacuum, \( c \) is indeed the velocity of light; \( \sqrt{K\mu} \) is therefore the refractive index of the medium.

If we consider an isotropic but conducting medium, the dielectric constant becomes a function of the frequency of electromagnetic radiation. \( K' = K - 2\pi\sigma T \), where \( \sigma \) is the specific conductivity and \( T \) is the period of the light wave. The relation between atomic and molecular phenomena and the optical constants can be made through this expression.

The Drude theory of dispersion was built upon the existence of charged particles (which were later assigned as electrons) which are bound to molecules within a substance or which are, in the case of metals, relatively free. The equation of motion of these particles was written as

\[
m(d^2x/dt^2) + h(dx/dt) + fx = 0
\]

where \( m \) is the mass of the particle (electron), \( h \) is the damping constant, and \( f \) is the force constant. Solution of Maxwell's equations for this system results in the relation

\[
K' = 1 + 4\pi Ne^2/(f - \omega^2 + i\omega)
\]

where \( \omega \) is the frequency of the light in radian measure. If we make the definition \( K' = (n - ik)^2 \), the latter quantity is called the complex
refractive index; n and k are the optical constants which we want. Equating the real and imaginary terms, we arrive at the following relations which give the optical constants in terms of the characteristic absorptions of the atoms and molecules, $\lambda_o$.

$$n^2 = 1 + k^2 + \frac{M\lambda^2(\lambda^2 - \lambda_o^2)}{[(\lambda^2 - \lambda_o^2)^2 + G^2\lambda^2]}$$

$$M = \frac{Ne^2\lambda_o^2}{\pi mc^2}$$

$$G = \frac{h\lambda_o^2}{2\pi mc}$$

$$\frac{2nk}{m} = \left(\frac{2\pi c}{\lambda_o}\right)^2$$

and $\lambda$ is the wavelength of the incident light.

In regions where little absorption occurs the quantity $(\lambda^2 - \lambda_o^2)$ is large in magnitude; consequently, the refractive index is essentially constant. When an absorption band is approached, the optical constants change rapidly; their behavior is graphed in Fig. 6. In this figure it can be seen that a maximum of reflection occurs just to the high frequency side of the fundamental absorption. The low refractive index on this side may cause a wider region of total reflection if the angle of incidence is sufficiently large; otherwise, the material will be transparent with an absorption maximum as indicated by the maximum value of $k$.

The classical treatment of metals follows immediately from the Drude dispersion formulas if we consider the conduction electrons to be free with an oscillator frequency of zero. Since this absorption lies principally in the infrared region of the spectrum the contributions of bound electrons are generally neglected in the classical approximation. The relations for a metal become
Fig. 6. Optical constants of a dielectric material near an absorption peak. ($\lambda_o = 1.5\mu$, $M = 0.4$, and $G = 0.1$)
\[ n^2 - k^2 = 1 - \frac{4\pi Nf}{m} \left( \omega^2 + \frac{1}{\tau^2} \right)^{-1} \]

\[ nk = \frac{2\pi Nf}{m\omega\tau} \left( \omega^2 + \frac{1}{\tau^2} \right)^{-1} \]

where \( Nf \) is the number of electrons per unit volume and \( \tau \) is the relaxation time which is defined by

\[ \sigma = \frac{Nf^2\tau}{m} \]

The static conductivity can be used to calculate the relaxation time if only low frequencies are under consideration. (The angular frequencies have been used in place of the wavelengths since most of the more modern works use this form of the expression.) The behavior of the optical constants under this set of relations is graphically illustrated in Fig. 7.

All highly conducting metals have very large extinction coefficients in the infrared region; as the figure demonstrates, the reflectivity of these metals is correspondingly high. Another prediction of this classical theory is the existence of a critical frequency \( (\omega_o) \) where the metal becomes transparent and the reflectivity drops rapidly to zero.

\[ \omega_o = \sqrt{\frac{4\pi Nf^2}{m}} \]

One of the earliest verifications of this phenomenon was the study of the alkali metals performed by Wood.\(^{15}\) The calculated values of the number \( f \) (the number of free electrons per atom) are in good agreement with those estimated by other methods. Many metals have common refractive indices (at visible light) which are less than unity as this theory would predict. Indeed the classical theory has been verified in a wide variety of cases.
Fig. 7. Optical constants of a conductor. (mercury, $\sigma_0 = 9.35 \times 10^{15}$ esu, $\tau = 4.56 \times 10^{-16}$ sec, and $N = 8.14 \times 10^{22}$ cm$^{-3}$).
Several corrections to the classical theory must be made, however, if all metals are to be considered. Beattie and Conn\textsuperscript{16} have studied a variety of metals with particular attention to their departure from regular classical behavior. Silver, copper, nickel, and gold (to name a few) exhibit abnormally high absorption in the visible and near infrared regions; this anomalous absorption extends particularly far into the infrared for nickel (up to about 10 $\mu$).

Some reasons for such anomalous absorption have been cited by Mott and Jones.\textsuperscript{13} Metallic electrons are actually not free; they are subject to a periodic potential field. In most cases the result of this field is to reduce the number of actually free electrons; the number $f$ is altered. Photoelectric absorption will result when inner shell electrons can undergo transitions to excited states or when the relatively free electrons of the solid can undergo transitions from one Brillouin Zone to another. And finally, polarization of the inner shell electrons will cause some (essentially constant) increase in the refractive index. Other absorption processes such as vibration and rotation are also possible, of course, but are small in magnitude.

The net effect of these additions to classical theory is an increase in the reflection of the metal at the corresponding wavelengths. When this extra reflection occurs in a region of low metallic reflection, it is generally resolved into a reflection band. In regions of high metallic reflection additional reflection may be difficult to observe unless the optical constants are calculated and compared directly to the classical formulas.
In retrospect, then, we can name several phenomena which should contribute to the reflection of light. Free electrons (electrons which can be promoted to higher, allowed energy levels with very little addition of energy) give rise to absorption, and its corresponding reflection of light, at all wavelengths longer than some critical value. Where the density of free electrons is large, this critical wavelength is found in the near ultraviolet or visible spectral regions. Other electrons which are more tightly bound to atoms or molecules may absorb radiation of smaller wavelengths and cause reflection in these regions. The optical regions where this absorption may occur and the width of the absorption will depend upon the tightness of binding and upon the degrees to which the electrons interact with surrounding species. At the same time, the motions of elemental particles may result in the absorption of energy. The quantized vibrations of the atoms within molecules as well as the over-all thermal motion of molecules and free atoms will give some contribution to the reflection of light. However, because of the very small extinction coefficients for absorption between vibrational energy levels the magnitude of reflection due to this cause is small. Furthermore, the translational motions of relatively free atoms or molecules in the liquid state contribute only a negligible amount to the total reflection; this is primarily due to the very large mass factors which these particles require in the expressions for the optical constants (Page 36). It is only in the case where the translational motions of atoms or molecules become severely restricted by interatomic or intermolecular forces that a sharp absorption of energy and corresponding reflection of light result from this cause. Such lattice mode absorption yields almost total reflection in a wide band of the far infrared frequencies, especially where the damping factor is small.
PART V

Analysis of Results: Observed Spectra

The quantity which is actually observed in these experiments is the intensity of light of a small increment of wavelengths as this is converted into an electrical signal and displayed on the Brown recorder chart. The resulting spectrum contains a great deal of spurious information as far as the reflectivity of the material is concerned. Absorption of light due to the gases in the atmosphere and the window materials combine with the energy distribution of the source radiation to determine the shape of the spectrum. In the final analysis the numbers on the recorder chart have little significance at all. Consequently, this spectrum must be interpreted in terms of the spectrum of some standard material taken under identical conditions.

Liquid mercury makes an ideal standard for several reasons. It can be poured into the actual reflection cell so that every detail of the optical arrangement is the same for both standard and ammonia solution. Furthermore, mercury has been found\(^1\) to obey the classical formulae for the optical constants which were discussed in the preceding section. It is a classical metal and shows no anomalous absorptions in the infrared and visible spectral regions.

All spectra of the liquid ammonia-sodium solutions were divided, point by point, by the mercury reflection spectrum for the appropriate region and set of conditions. The resulting spectra were plotted as a percentage reflection, \(\rho\). Since mercury is a classical metal, the resulting spectra should be straight or slowly curved lines if the solutions are also classical metals. Where reflection peaks arise in this percentage
curve, one or more of the non-classical phenomena must be considered. Since the reflection coefficients of the mercury surface can be calculated, it is also possible to calculate the reflection coefficients of the solutions using the observed percentage curves; however, this calculation would be justified only if better knowledge of the refractive indices of the window materials and of the angle of incidence upon the windows were obtained. For similar reasons it was not possible to calculate the optical constants themselves; for this purpose, an apparatus would have to be so constructed as to allow accurate measurements at more than one angle of incidence.

In Figs. 8, 9, 10, 11, and 12 the reflection curves of various sodium-ammonia solutions are given in terms of \( p \), the percentage of the light reflected by mercury which a given solution reflects. Where it was possible, the existence of a reflection peak was confirmed by observing the peak with two different window materials. The peaks in the lithium fluoride region could all be verified in this manner. However, the large peak in the sodium chloride region was observed only through the barium fluoride window since no other material was available.

In Fig. 13 the reflection coefficients of mercury surfaces are given for the optical regions in which quartz, lithium fluoride, and barium fluoride are the window materials. These values of the reflectivities were obtained by calculating the optical constants of mercury and employing the formula for reflection at normal incidence; the refractive index of the particular window material was used in place of the number one (for a vacuum) in the latter formula. No reflection coefficients are given for the potassium bromide region since the refractive index of the window used cannot be estimated accurately.
Fig. 8. Reflection of sodium-ammonia solutions relative to mercury, quartz window. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium, and as (mole ratio). (-40°C)
Fig. 9. Reflection of sodium-ammonia solutions relative to mercury, lithium fluoride window. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium, and as (mole ratio). (-40°C)
Fig. 10. Reflection of sodium-ammonia solutions relative to mercury, lithium fluoride window. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium, and as (mole ratio), (-40°C)
Fig. 11. Reflection of sodium-ammonia solutions relative to mercury, barium fluoride window. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium, and as (mole ratio). (-40°C)
Fig. 12. Reflection of sodium-ammonia solutions relative to mercury; cesium iodide, polyethylene, and Kel-F grease window. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium, and as (mole ratio). (-40°C)
Fig. 13. Calculated reflection coefficients of mercury for the window materials indicated.
In Fig. 14 the percentage reflection curves for a number of sodium-ammonia solutions have been predicted from their conductance properties. In Fig. 15 these predicted curves have been repeated with dashed lines, while the solid lines represent the percentage reflection curves which are actually observed for these same concentrations. Points for the experimental curves in Fig. 15 were obtained by the graphical interpolation of the results for all concentrations which were studied. At a given wavelength, the percentage reflection was graphed against concentration of sodium; the reflection at a particular concentration could then be read from the graph.

Many of the reflection spectra which are shown here have small gaps in them. These gaps occur in regions where the absorption by atmospheric gases is so great that no reflection measurements could be made. In Fig. 9, for instance, a gap occurs at about 2.8 μ where there is heavy absorption of light by water vapor; another gap occurs at about 4.3 μ, corresponding to the absorption band of carbon dioxide in that region.

Several phenomena in the percentage reflection spectra are probably spurious. The rapid rise in reflection at the long wavelength end of the sodium chloride spectral region (beginning at 11 μ) seems to be unreasonably large. In fact, a percentage reflection of the magnitude indicated for the most concentrated solutions at 12 μ would suggest reflection coefficients greater than unity. At the same time, the large deviations from linearity in the potassium bromide spectra also seem to be due to factors other than the ammonia-sodium system itself.
Fig. 14. Predicted reflection of sodium-ammonia solutions relative to mercury. Concentration is indicated as dilution, liters of ammonia per gram atom of sodium.
Fig. 15. Predicted and observed reflections of sodium-ammonia solutions relative to mercury. Dashed lines represent the predicted reflections of Fig. 14 while the solid lines represent the observed reflections.
In the latter case, the window material which was used (cesium iodide, Kel-F grease, and polyethylene) has several broad absorption bands in the potassium bromide spectral region. These bands are centered at about 16.8 and 19.6 μ, corresponding to the minima in the percentage reflection curves. It would seem, then, that the window absorption has been superimposed upon the sodium-ammonia reflection. On the other hand, since the same amount of window absorption should occur with mercury as with the solutions, we would not generally expect this absorption to appear in the percentage curves. However, it is possible that, in this case, evacuation of the reflection cell prior to preparing the solutions caused a small amount of the Kel-F grease to be squeezed into the center of the window. This extra amount of the grease, which was present for the solution spectra but not for the mercury spectra, would easily cause the absorption peaks which we have observed in the percentage reflection curves.

The unreasonably high percentage reflections which were observed near 12 μ are probably due to a similar cause. The barium fluoride window which was used for these observations begins to absorb heavily at 11 μ; in fact, at 12 μ about 70% of the incident light is absorbed. Since the percentage curves in this region are obtained by the comparison of small light intensities, any small difference in the absorption of the window or in the quality of the reflection surface will become a large percentage difference. Since the automatic slit program used in this spectral region is not entirely reproducible, small errors in the slit opening will also occur and will appear as large differences in the percentage curves.
PART VI

Interpretation of Spectra

The reflection spectra of sodium in liquid ammonia show a variety of interesting features which must be discussed in some detail. We will first turn to a summary of the reflection peaks which have been observed. In the near infrared, we have found a broad, unsymmetrical band at 6200 cm\(^{-1}\), a weak peak at 3370 cm\(^{-1}\), and a more broad peak at 3190 cm\(^{-1}\). In the longer wave length region of this study, an unsymmetrical peak is to be found at 1030 cm\(^{-1}\). The maximum of this reflection moves toward 1050 cm\(^{-1}\) as the concentration of sodium is increased; there is also a considerable tail of reflection on the low frequency side of this peak. In the original spectra a reflection peak was also observed to be at 3000 cm\(^{-1}\); however, this was found to be spurious, due in fact to an impurity in the oxygen used to flush the instrument monochromator housing.

The reflection band at 6200 cm\(^{-1}\) has no immediate counterpart in the transmission spectra of either liquid or gaseous ammonia. It was not observed to be present in the reflection spectrum of pure ammonia. On the other hand, an absorption band at 6700 cm\(^{-1}\) has been observed by transmission methods in the very dilute sodium-ammonia solutions.\(^7\) It is, indeed, the tail of this absorption which reaches into the visible light region to cause the well known blue color of the dilute solutions. In the past number of years this absorption has received a great deal of attention; however, because of the very high extinction coefficient associated with this band, it has not been observed at sodium concentrations in excess of 0.1 molar. Correspondingly,
the reflection peak which we have observed is very weak in the dilute solutions and has been studied only at concentrations greater than 0.2 molar. Although the frequency difference in these two peaks would seem to be rather large, it is definitely possible that the value for the reflection peak is in error by as much as 300 cm$^{-1}$. The maximum of reflection is expected to be displaced by a certain amount and the dispersion of the lithium fluoride prism is not too great in this frequency region. Although it is still not obvious that the reflection maximum corresponds to the absorption maximum which has been observed, this author feels no justification for assigning some different cause to the reflection peak. We shall therefore treat the two phenomena as though they were identical, aside from the fact that the peak has moved slightly further into the infrared as the sodium concentration increased.

One of the earliest theories of the sodium-ammonia solutions was the electron in a cavity model. In this picture it is assumed that the sodium atom ionizes immediately upon entering the ammonia. The electron which is freed in this manner polarizes the surrounding ammonia molecules, forming a cavity or solvation sphere. The size of this cavity is assumed to be very large and affords a good explanation to the very high volume expansion during the dissolution process. The high conductivity of these solutions is also supported by the cavity model. At the same time the similarity to a crystal $F$ center has inspired a great deal of interest in the magnetic properties of the cavity.

In terms of the cavity theory the 6700 cm$^{-1}$ absorption is interpreted to be the transition of the trapped electron from the low potential of the
solvation shell to the lowest levels of a conduction band. One of the important features of the cavity explanation is that it predicts correctly the observation that the frequency of absorption should be independent of the particular alkali metal which is dissolved.

In competition with the cavity theory is the theory of an expanded orbital around the sodium atom. In this picture the sodium atom is not ionized but is merely perturbed greatly. The 3s electron of sodium feels the potentials due to two major forces, the positive charge of the sodium nucleus and the sphere of polarized ammonia molecules which surrounds the atom. While the central charge of the sodium nucleus holds the electron bound to the sodium atom, the orbital of this electron is considered to be greatly expanded in order to include the low potential of the ammonia hydrogens which are arranged around the atom. The size of this monomeric species is estimated to be of the proper size to account for the volume expansion phenomenon. Furthermore, most of the magnetic and thermodynamic properties can also be explained with some degree of imagination.

In terms of the monomer theory the 6700 cm$^{-1}$ absorption represents an angular momentum transition of the electron in its expanded orbital (3s to 3p in terms of the sodium atom). Since the orbital is very heavily dependent upon the low potential of the ammonia hydrogens, it is believed that the particular alkali metal used to provide the positive central force should make little difference in the position of the absorption maximum. Two pieces of information seem to confirm this notion: x-ray and electrolytic electrons in ammonia do not cause absorption while different solvents (amines) do cause shifts in the peak frequency.
In the reflection measurements, the 6200 cm$^{-1}$ peak has been observed as the concentration of sodium increases. In fact, we have observed its disappearance at a sodium concentration of about two molar. If we accept the explanation of the cavity theory, we would expect a rather severe change in the frequency of this absorption maximum as sodium concentration increases. The rising number of sodium atoms in the immediate vicinity of the cavity should cause a gradual reduction in the potential outside of the cavity. The resultant lowering of the energy levels in the conduction band should then give a noticeable decrease in the energy of this transition. On the other hand, if the monomer model were assumed, it is believed that the rising concentration of sodium atoms should affect this frequency very little. The potential for an angular momentum transition would certainly be less sensitive to sodium concentration than that for a radial transition. The actual behavior of the reflection band is, of course, consistent with the latter of these predictions. It is the belief of this author that, if one of the two prominent theories is to be adopted, the monomer model of a perturbed sodium atom is more consistent with the observed reflection data and is more acceptable. However, we will return to this point in the discussion of the marginally metallic properties of these solutions.

The weak reflection peak at 3370 cm$^{-1}$, as well as the peaks at 3190 cm$^{-1}$ and 1030 cm$^{-1}$, can be assigned to the fundamental vibrations in the ammonia molecule. These peaks are relatively weak in intensity and decrease still further in magnitude as the sodium concentration becomes larger. The 1030 cm$^{-1}$
peak, in fact, vanishes when the solution becomes saturated with respect to sodium. This behavior is certainly more nearly consistent with an explanation in terms of ammonia than with one in terms of sodium. A table of observed frequencies for the ammonia molecule is given for comparison.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency, $\text{cm}^{-1}$</th>
<th>State</th>
<th>Method</th>
<th>Remarks and reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>3335.9</td>
<td>gas</td>
<td>infrared</td>
<td>split by inversion - 23</td>
</tr>
<tr>
<td></td>
<td>3337.5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>3223</td>
<td>crystal</td>
<td>infrared</td>
<td></td>
</tr>
<tr>
<td>$v_2$</td>
<td>931.58</td>
<td>gas</td>
<td>infrared</td>
<td>split by inversion - 23</td>
</tr>
<tr>
<td></td>
<td>968.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1060</td>
<td>crystal</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>$v_3$</td>
<td>3414</td>
<td>gas</td>
<td>infrared</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>3375</td>
<td>crystal</td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>$v_4$</td>
<td>1627.5</td>
<td>gas</td>
<td>infrared</td>
<td></td>
</tr>
<tr>
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<tr>
<td></td>
<td>3160-3330</td>
<td>crystal</td>
<td>Raman</td>
<td></td>
</tr>
</tbody>
</table>

There is certainly every indication that the $v_1$ fundamental should decrease in frequency as a more condensed state is approached. This frequency, being a parallel band, is sensitive to the effects of hydrogen bonding. From the solid state observations above, it would seem that a frequency of 3200 cm$^{-1}$ or less would be a good estimate of the position of this fundamental in the liquid ammonia-sodium solutions, especially where strong polarization due to sodium is expected. Therefore, we feel justi-
fied to assign the reflection peak at 3190 cm\(^{-1}\) to this cause.

The lowering of the \(v_3\) fundamental in condensed systems is not so large since it is not so susceptible to hydrogen bonding effects (being a perpendicular band). The reflection peak at 3370 cm\(^{-1}\) seems to fall into good accord with the frequencies measured for crystalline ammonia; this peak will be attributed to the \(v_3\) vibration.

Finally, the reflection peak at 1030 to 1050 cm\(^{-1}\) seems to be in very good agreement with the solid state observations on ammonia. We will assign its cause to the \(v_2\) vibration fundamental. Unfortunately, no spectra were taken in the region of 1600 cm\(^{-1}\) so that the \(v_4\) vibration could not be located.

Several other absorption peaks might well have been anticipated. In terms of the cavity theory some absorption due to a pair of electrons trapped in the same cavity would be possible. This absorption, however, would be heavily dependent upon the environment of sodium atoms and ammonia molecules; it is not surprising that it was not observed.

We might also consider the possibility of observing electronic transitions for the Na\(_2\) molecule. Presumably when the concentration of sodium becomes sufficiently high, the concentration of diméric and polymeric species increases. In the gas phase the sodium 3s to 3p transition lies at 16960 cm\(^{-1}\)\(^{26}\) while the lowest molecular transitions for the Na\(_2\) molecule lie on either side of this, at 15006.68 cm\(^{-1}\) and at 20301.70 cm\(^{-1}\),\(^{27}\) (for the \(1\Sigma_g^+ \leftrightarrow 1\Sigma_u^+\) and the \(1\Pi_u \leftrightarrow 1\Sigma_g^+\) transitions). If the 6700 cm\(^{-1}\) band is, indeed, the 3s to 3p transition for sodium in the ammonia dielectric
medium, we would expect to find the lower transition of Na₂ in this same spectral region. Although this absorption was not observed as a distinct peak, in the next section we will discuss its possible existence as a very broad band of small intensity.

In Part I we expressed an interest in the properties of the liquid ammonia-sodium solutions as marginally metallic systems; we were particularly concerned with the changes in electronic states which would occur in a system of atoms as the interatomic distances became very short, close to crystal dimensions. It is to this subject, then, that we must now return, presumably with some higher degree of enlightenment.

It is not at all damaging to this discussion if we admit, in a brief paragraph, that the data available are neither sufficiently complete nor accurate to allow more than qualitative conclusions. Indeed, some of the most interesting phenomena in these solutions occur at the very low concentrations of sodium where reflection is poorest; for the study of these solutions the spectroscopic technique which has been described here would have to be refined in several ways. Undoubtedly a different and less efficient reflector would have to be used as a standard for dilute solutions. Amplifier stability and gain would certainly have to be improved. Furthermore, some attempt would have to be made to totally eliminate reflection from the front surface of the window. For this purpose it would probably be necessary to use a 45° prism in place of the plane window used for these experiments. As a final refinement it would undoubtedly be advantageous to calculate the actual optical constants
of these solutions. This research, however, has been concerned pri-
marily with the development of a basic method of reflection spectroscopy;
it is believed that with the suggested improvements this method of study
could yield quantitative information on the electronic processes in the
ammonia-sodium solutions.

In Figure No. 14 some percentage reflection curves are given for the
ammonia-sodium solutions. These reflection curves were predicted on the
basis of the observed conductance values for the concentrations indicated. For this purpose, the optical constants were calculated from the formulas
for metallic optical properties given on page 36 of this text. In these
formulas the effective number of free electrons was assumed to be unity
for each sodium atom; the relaxation times for these electrons were de-
termined directly from the conductivity data. The short relaxation times
result from solutions of low conductivity, or high resistance, and indi-
cate a short mean free path for the electrons. Conversely, the better
conductors give large relaxation times which correspond to long mean free
paths for the conduction electrons. While the density of free electrons in
these solutions increases by one power of ten as saturation is approached,
the relaxation time increases by three powers of ten. It is this quantity
which contributes the greatest amount toward high reflectivity.

Reflection coefficients of these solutions were calculated from the
optical constants using the formula on page 32; in this relation the
number one, which is the refractive index of vacuum, was replaced by the
refractive index of the window material. To be precise the wave length
dependence of this refractive index should also be included in the cal-
calculation. However, not even the refractive index at visible light has been determined accurately for barium fluoride. The Sellmeier dispersion formula would have to be used, but this would require at least several accurate measurements of the refractive index at different wave lengths. In these calculations, then, the refractive index at visible light has been used as the best estimate. Where the actual refractive index is smaller than this estimate, the reflection curves predicted here will be lower than those observed. Fortunately, it would take a rather large deviation in the refractive index to make a considerable error, and some of this error is reduced by taking percentages between mercury and the solutions.

Before we compare the predicted and observed results, we should also realize that the formula which has been used to obtain the reflectivities is the expression for normal incidence. In actual practice the angle of incidence has been between thirty and forth degrees. The angular dependence of this formula results in complex trigonometric functions since the refractive index of an absorbing material is a complex number. The accuracy of the estimated optical constants was not sufficient to warrant the use of this expression, however. Since the relation of reflection to angle of incidence has its steepest increase at angles close to ninety degrees, it is believed that the error in the predicted curves is small for the angular factor.

With this much of an introduction, the reader is invited to compare the observed and predicted reflection curves (Figure No. 15). In general the observed reflection intensities agree rather well to what classical theory predicts, especially in the high energy regions. Metallic reflec-
tion is observed and indicates that relatively free electrons do exist in these solutions. Furthermore, the relaxation times indicated by static conductivity measurements seem to be a fairly good measurement of the degree to which these electrons are free. To this extent the optical information merely confirms the conductance data.

The observed reflection spectra, however, also show a marked deviation from the shape of the reflection curve anticipated for a classical metal. Many solutions exhibit reflection which is too high in one region of the spectrum and too low in another, generally at the longer wavelengths. To this extent the optical information goes beyond the conductance evidence; the actual shape of the absorption curve can be determined. Furthermore, the shape of the absorption curve may be interpreted in terms of the electronic processes which exist in a given solution.

In order to describe the electronic processes in the ammonia-sodium system it will be necessary to give some interpretation to the electron relaxation times which are observed and then to predict the kind of absorption that can take place. In all of the solutions which have been studied the electron relaxation times are small compared to that which would be expected for sodium metal itself. In terms of the classical conduction theory these small relaxation times must indicate short mean free paths for the conduction electrons. However, there is also a quite reasonable interpretation of this phenomenon in terms of quantum mechanics. Although the outer atomic orbitals of different sodium atoms must overlap with one another considerably so that the valence electrons will attain a high degree of delocalization, these electrons must remain partially bound to atoms or groups of atoms. Thus, especially in the dilute solutions where little metallic
reflection is observed and where conduction predicts a short mean free path, the valence electron of sodium must be bound to an individual atom to a high degree.

In the current theories of metallic conductivity one essential difference between a conduction electron and a bound electron lies in the fact that little or no energy is required to raise a conduction electron to a higher level of energy. The crystal lattice of sodium metal, for instance, is quite similar to an infinitely large molecule where the allowed electronic states lie in bands rather than in the discrete levels of atomic states; the spacing of energy levels within a given band is so close that a band may be considered as a continuous array of allowed levels. In sodium metal half of the valence band energy levels are empty and can be reached by the absorption of little or practically no energy. The absorption curve (the optical constant $k$) for this system is a very broad continuum which has its maximum at a frequency of zero. It is, in fact, this absorption curve which yields the metallic reflection which is predicted by the classical formulas.

If electrons are bound locally to a higher degree, due to a decrease in the overlap of atomic orbitals, the spacing of energy levels in a given band becomes wider, even to the extent of forming discrete energy levels. In this case there must be some finite minimal energy which must be absorbed in order to promote an electron to a higher energy state or to accelerate it for conduction. The absorption curve for this system should have its maximum value considerably removed from zero frequency and should have little absorption near zero. As a result, the optical behavior of this material
should deviate considerably from that predicted by the classical theory of free electrons, giving increased reflection in the near infrared and visible regions but decreased reflection in the far infrared. At the same time, the number of truly free electrons would be reduced to a small number of electrons which had been thermally excited to higher, more closely spaced energy levels. For this reason the intensity of purely metallic reflection should decrease greatly.

As electrons become more strongly bound to individual atoms, the levels of allowed energy will reduce to the discrete energy levels of the atoms and of simple molecules, depending to what extent the atomic orbitals overlap with one another. The minimal energy gap will become very large compared to the small gaps in a metallic system and will approach the lowest lying allowed transitions of the atomic and simple molecular systems. (We have assumed through much of this discussion that rigorous selection rules do not hold in the condensed and highly interacting systems.) Metallic reflection will become zero since not even thermal excitation to high and closely spaced levels will be possible. Absorption in such a system would occur only in bands centered about the allowed atomic and molecular transitions or, in the far infrared, in broad regions corresponding to the lattice modes and other thermal motions of heavy particles. Reflection for these processes should occur in peaks of moderate intensity corresponding to maximum absorption regions.

It is the belief of this author that several of the stages which have been outlined above can be observed in the reflection spectra of the ammonia-sodium system. Changes in the orbital overlap and the degree of
delocalization, which result from the changing internuclear distances between sodium atoms in these solutions, alter the energy level scheme in a way quite analogous to that discussed above. It will be helpful to keep in mind several of the internuclear distances tabulated below.

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Distance Between Sodium Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>12 angstroms</td>
</tr>
<tr>
<td>0.75</td>
<td>11</td>
</tr>
<tr>
<td>0.60</td>
<td>10</td>
</tr>
<tr>
<td>0.40</td>
<td>9.1</td>
</tr>
<tr>
<td>0.30</td>
<td>8.3</td>
</tr>
<tr>
<td>0.135</td>
<td>6.7</td>
</tr>
<tr>
<td>crystal</td>
<td>3.4</td>
</tr>
</tbody>
</table>

In the first section of this discussion we attributed the reflection peak at 6200 cm$^{-1}$ to a transition of the 3s sodium electron (the weakly bound valence electron) to a 3p state of the highly perturbed sodium atom. The presence of this phenomenon in only the dilute solutions where the internuclear separation (for sodium atoms) is greater than ten angstroms is certainly consistent with the conclusions of the preceding discussion. It indicates that while the sodium atoms are situated far apart there is little overlap or interaction of orbitals; consequently, the electrons remain localized on individual, but perturbed atoms. Only atomic transitions are found, along with a certain amount of absorption due to thermal motion of the heavy particles in the liquid state.
Aside from the angular momentum transition (3s-3p) radial transitions of the valence electron are likely. If predictions of the inner photoelectric threshold are correct, the radial transitions, leading to ionization, should originate in the infrared region. However, we would not expect these transitions to occur in a sharp sequence of absorption peaks since the constant motion of particles in the liquid state would undoubtedly spread this absorption into a wide band. The effect of the liquid state would be especially more noticeable in the radial transition, as compared to the angular momentum transition, since the potential for the former is more highly dependent upon the surrounding atoms. What we do, in fact, observe is a very broad band of increased reflection, or absorption, in the region from 1 to 5 microns. For dilutions of 0.75 and 0.60 the reflection curves average about twelve per cent more reflection in this region than classical theory would predict. The same solutions yield only low reflection in the long wave length regions, corresponding to absorption for thermal motions.

In solutions of higher concentration the 6200 cm⁻¹ peak disappears while reflection as a whole increases in intensity. We may interpret this behavior as direct evidence that the sodium valence electron has attained a high degree of delocalization so that the atomic energy levels have given way to an increasing development of molecular states. Moreover this process seems quite reasonable when we consider the internuclear distances between sodium atoms in these more concentrated solutions. When the dilution is 0.40, the sodium atoms are separated by only nine angstroms; if the estimated three and one-half angstrom radius of a 3s orbital is correct for the sodium atom in ammonia, we would certainly
expect overlap of these orbitals and the corresponding delocalization of the electrons into molecular type states. It is also in this region that phase separation occurs; evidently, when overlapping of the 3s orbitals begins, there is a strong tendency to form a phase of still higher concentration where the interaction of orbitals can be even more complete. It seems reasonable, then, to explain the high reflection of this solution in the near infrared (1 to 12 microns) in terms of absorption between the energy levels of small aggregates of sodium atoms. Furthermore, the low reflection of this solution in the 25 micron region is due to the fact that a minimal absorption of energy exists in correspondence to the lowest transition of the largest aggregation of sodium atoms.

When the dilution becomes 0.30, the internuclear distance has decreased to about eight angstroms. We assume that the 3s orbitals interact very heavily at this distance so that the electron wave functions center about increasingly large numbers of sodium atoms. As we have seen, the energy levels for these more complicated molecular states lie closely spaced. In fact, we observe in the reflection spectra that absorption of all infrared wave lengths increases at this concentration. Again, the reflection is lower than anticipated in the 25 micron region, and this corresponds to the existence of a minimal absorption of energy. However, reflection in this region does increase with concentration, indicating that the minimal absorption moves gradually toward longer wave lengths as larger aggregates are formed.

Finally, in the saturated solution we observe that the reflection in the far infrared is in good agreement with the predicted value; while some additional absorption of energy still causes a higher reflection than expected in the near infrared. Evidently the delocalization of electrons
in this system is so great that very large aggregates of sodium atoms are included within a given orbital. The energy levels for these large aggregations are so closely spaced that the absorption curve approaches that for free electrons. The slight deviation of this system from a system of truly free electrons causes the reflection to be higher than expected in the near infrared and, undoubtedly, lower in the very far infrared region. The saturated solution is, indeed, so close in its electronic properties to a true metal (where the electron is delocalized over an infinitely large aggregation of sodium atoms) that any attempt to raise the concentration further results in precipitation of the metal itself.

Although more experimental information is necessary in order to verify the conclusions which have been drawn here, it is believed that these fundamental changes in the electronic structure of the ammonia-sodium system do exist and are in evidence in the optical method of study which has been discussed.
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PART VIII

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