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ABSORPTION SPECTROSCOPY IN LIQUID AMMONIA

William L. Jolly

October, 1952

Berkeley, California

Table of Contents

Page

1. Brief Review of the Literature 3

1.1 Absorption Spectrum of Liquid Ammonia 3

1.2 Absorption Spectra of Liquid Ammonia Solutions 3

2. Purification of Liquid Ammonia 5

3. Absorption Spectroscopy in the Ultraviolet 5

3.1 The Absorption Spectrum of Iodide 5

4. Absorption Spectroscopy in the Visible and Infra-Red 6

4.1 Experimental Procedure for Exploratory Work 6

4.2 Absorption Spectra of Water, Aqueous Ammonia and Liquid Ammonia 7

4.3 Absorption Spectrum of Cupric Ion 10

4.4 Absorption Spectrum of Permanganate 10

4.5 Absorption Spectra of Polyanions 10

4.6 Absorption Spectrum of Sodium in Liquid Ammonia 12

4.61 Introduction 12

4.62 Experimental 12

4.63 Theoretical 15

5. Acknowledgements 20

6. References 21

ABSORPTION SPECTROSCOPY IN LIQUID AMMONIA

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October, 1952

1. Review of the Literature on Absorption Spectroscopy of Liquid Ammonia and Liquid Ammonia Solutions.

1.1 Absorption Spectrum of Liquid Ammonia.

Prikhot'ko[1,2] measured the absorption spectrum of both liquid and solid ammonia from 2000 Å to 10,140Å. Costeanu and Barchewitz[3] and Costeanu, Freymann and Naherniac[4] measured the absorption spectrum of liquid ammonia and aqueous ammonia solutions from 6000 Å to 10,500 Å. The data of Prikhot'ko and Costeanu et al, are in poor agreement.

Absorption Spectroscopy of liquid ammonia solutions in the ultraviolet is limited to wavelengths greater than about 2400 Å, since a series of intense absorption bands extends from this wavelength down to at least 1765 Å[5]. The practical long wavelength limit is about 10,000 Å, because a series of rather intense bands extends beyond this wavelength. However, as will be shown later, absorption spectra may be measured in liquid ammonia to wavelengths as great as 25,000 Å, if the interfering ammonia bands are accounted for in the "blank" and if the absorption cell is very thin.

1.2 Absorption Spectra of Liquid Ammonia Solutions.

In Table I, an attempt has been made to summarize all the spectroscopic investigations of liquid ammonia solutions up to 1951.

Table 1

Spectroscopic Investigations in Liquid Ammonia.

Investigators	Solutes	Temp.	Spectroscopic Method and Wavelength Range
Ruff[6]	S - H_2S mixtures		
Gibson and Argo[7,8]	Na, Mg, Li, K, Ca	room temp. to -65°C.	monochromator and visual estimation of extinction with polarizers; visible region.
Wood[9]	neodymium ammonium nitrate, and $KMnO_4$	-33°	photographic; visible and near U.V.
Shiba and Inouye[10]	(complex salts of Co, Ni and Cr)		
Garner and Gillbe[11]	m-dinitrobenzene and various dinitrotoluenes		photographic
Ogg[12]	Na, Mg	room temp. to -80°C.	
Vogt[13]	Na, Li		.5 μ to 2 μ
Shatenshtein[14] and Izrailevich	nitro and azo cpds.		visible region
Dykhno and[15,16] Shatenshtein	nitrophenols		visible; near U.V.
Ogg, Leighton[17] and Bergstrom	KNH_2 $NaNH_2$		visible and near U. V.
J. K. Thompson[18] and J. Kleinberg	LiO_2 NaO_2 KO_2	-78°C.	Spectrophotometer 3000-5000 Å

2. Purification of Liquid Ammonia.

Liquid ammonia was drawn from a five pound cylinder of the liquid (Matheson Co., Joliet, Ill.) into a dewar bottle. The liquid was then poured into a glass distillation tube, a small piece of sodium was added, and the tube was connected to a vacuum manifold. After flushing the system with ammonia gas, the liquid was distilled at a pressure of 0.3 - 1.0 atm. into another glass tube by cooling the latter with a Dry-Ice-acetone bath. At the end of the distillation, the distillate was allowed to warm to -33°C. A glass siphon was then inserted in the tube and the vapor pressure of ammonia forced the pure liquid ammonia through the siphon into the absorption cell.

3. Absorption Spectroscopy in the Ultraviolet.

3.1 The Absorption Spectrum of Iodide.

A narrow, unsilvered quartz dewar with an inside diameter of ca. 3 cm. was used as an absorption cell. (Black masking tape was used to outline "windows" near the bottom of the dewar). A Cary Recording Spectrophotometer was used for obtaining the spectra. After running the absorption curve for pure liquid ammonia from 2400 Å to 3500 Å, a small crystal of the iodide was added to the ammonia and the spectrum was run again. The difference between the two curves was taken as the absorption curve for iodide in liquid ammonia. After allowing the ammonia to evaporate from the dewar, a known volume of water was added to the iodide residue and the absorption curve of iodide in water was

measured. (The blank with pure water was later run). By accepting the extinction coefficient for iodide in water at 2270 Å ($\epsilon = 1.25 \times 10^4$) determined by Awtrey and Connick[19], it was possible, knowing the volumes of ammonia and water, to calculate the extinction coefficient for iodide in ammonia.*

Three such runs were carried out: using NH_4I, KI and NaI. An iodide absorption peak was observed at 2540 ± 20 Å, with $\epsilon = 1.2 \times 10^4$ liter $mole^{-1}cm^{-1}$. The theoretical significance of this absorption curve has been discussed by Latimer, Connick and Jolly.[20]

4. Absorption Spectroscopy in the Visible and Infra-Red Regions.

4.1 Most of the studies were made using the absorption cell 1, pictured in Fig. 1. This absorption cell was found to be very useful for exploratory work with the Cary Spectrophotometer, the Beckman Model DU Spectrophotometer and the Perkin Elmer Model 12B Infra-Red Spectrometer.

The Cary and Perkin Elmer Spectrometers are so automatic in their operation that nothing need be said regarding the use of these instruments. However, in using the Beckman Spectrophotometer, it is necessary to move the absorption cell in and out of the light path for each measurement at a particular wavelength. The Beckman Spectrophotometer used was equipped with a cell compartment designed for holding 10 cm. cells. The

*Such a procedure was necessary for obtaining the extinction coefficient because there was no means for directly determining the effective light path in the round quartz dewar.

cell carriage and cell top were removed and a black cloth was wrapped around cell 1 to keep room light from affecting the photocell. When actually making measurements with the cell in the light path, it was found necessary to twist the cell back and forth through a vertical axis until the galvanometer indicated a minimum optical density. This procedure was followed to ensure the optical faces of the cell being perpendicular to the light path, inasmuch as the cell was moved entirely by hand and not attached to any "cell holder".

When making measurements beyond 10,000 Å, a Corning No. 2540 infrared filter was inserted between the slit and the cell in order to eliminate scattered light, and minimum possible slit widths were employed. Measurements beyond 12,000 Å on the Beckman Spectrophotometer are of little value; the sensitivity of the photocell is so low that excessive slit widths must be employed. There is also some indication that scattered visible or ultraviolet light reaches the photocell at these wavelength settings (even with the Corning filter in position).

4.2 Absorption Spectra of Water, Aqueous Ammonia and Liquid Ammonia.

The absorption spectra of water, aqueous ammonia and liquid ammonia were determined using cell 1 and the Beckman Spectrophotometer. No corrections were applied due to absorption of the glass cell. These spectra are pictured in Figs. 2, 3 and 4. It was not possible to detect any splitting of the .98 micron peak of water (as has been reported by Dreisch and Trommer[21]).

For data obtained for liquid ammonia with the Perkin Elmer Spectrometer, see the footnote in section 4.62.

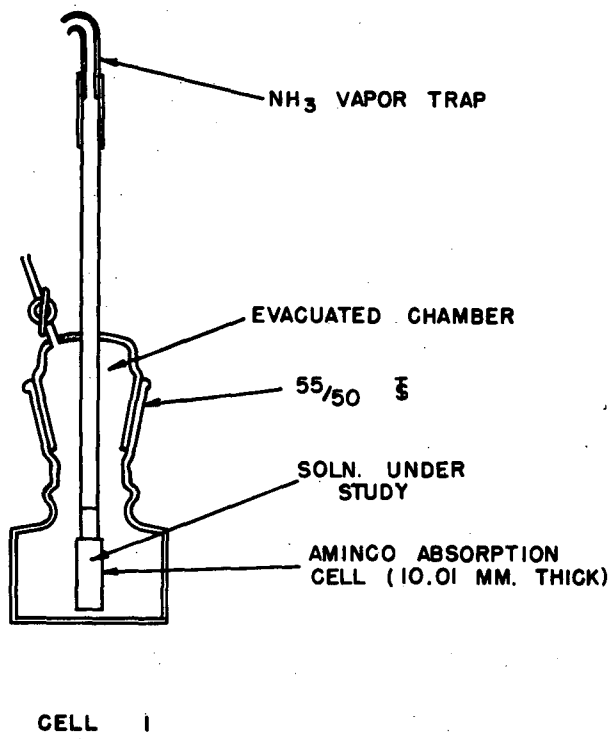


Fig. 1 Absorption cell for liquid ammonia.

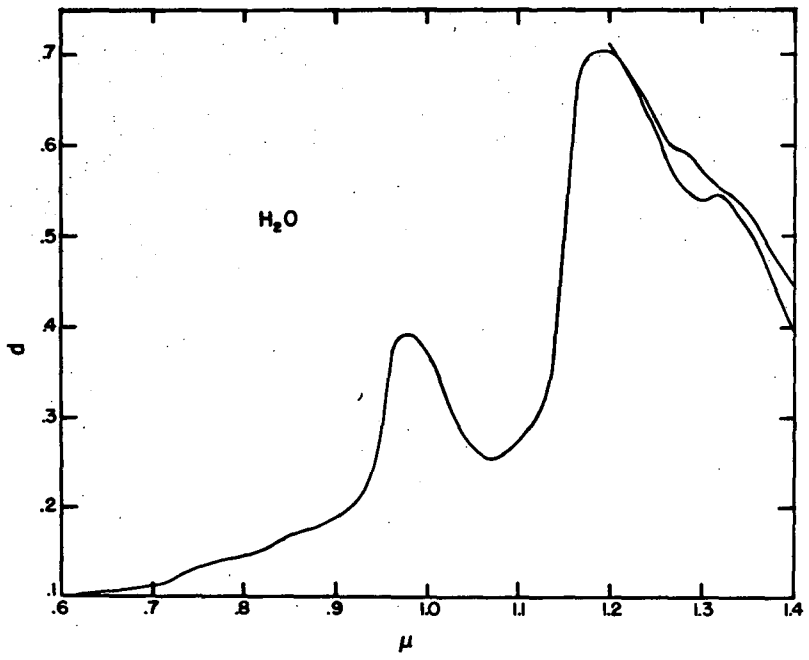


Fig. 2 Absorption spectrum of water.

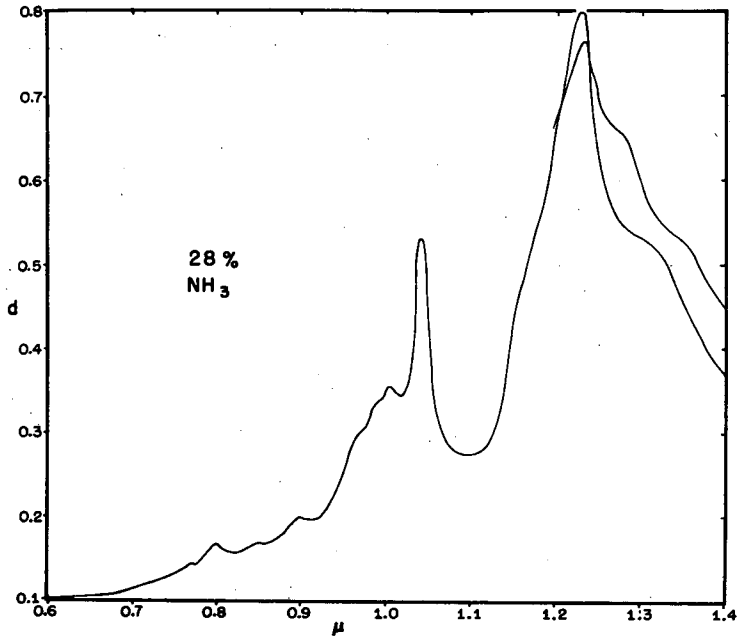


Fig. 3 Absorption spectrum of aqueous ammonia.

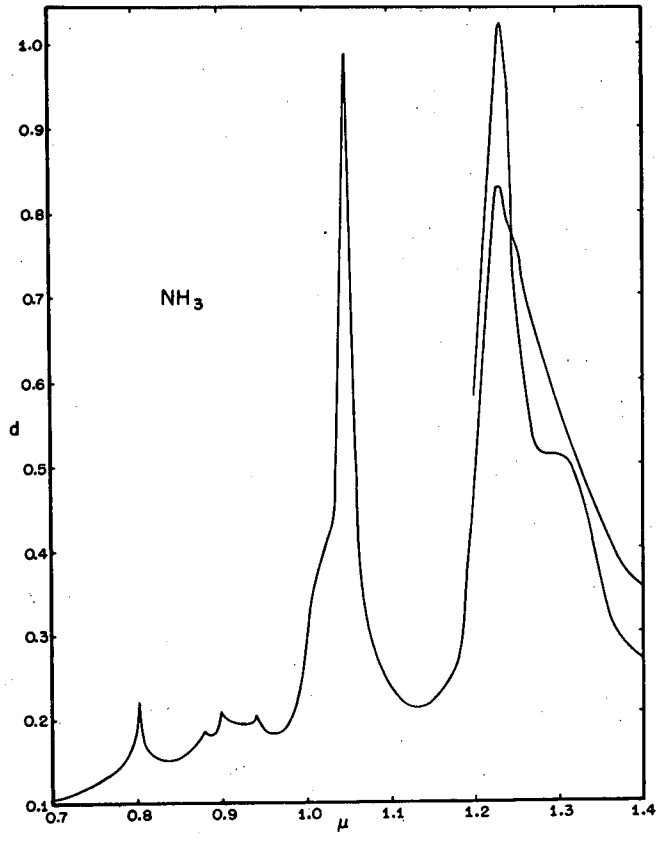


Fig. 4 Absorption spectrum of anhydrous ammonia.

4.3 Absorption Spectrum of Cupric Ion.

The absorption spectra of cupric sulfate in water and in aqueous ammonia and of cupric nitrate in liquid ammonia are shown in Fig. 5. (The concentrations are not the same for these three spectra). $CuSO_4$ and $Cu(NH_3)_4SO_4 \cdot H_2O$ were found to be difficultly soluble, if not insoluble, in liquid ammonia.

Bjerrum[22] has made a careful study of the $Cu^{++} - NH_3$ equilibria in aqueous solution and has assigned individual spectra to each of the five copper-ammonia complex ions. It is interesting to note that the λ_{max} which he reports for the $Cu(NH_3)_5^{++}$ ion is almost the same as that for cupric ion in liquid ammonia.

4.4 Absorption Spectrum of Permanganate.

The absorption spectra of potassium permanganate in both water and liquid ammonia are given in Fig. 6. It is obvious that the band structure is much sharper in ammonia than in water.[9] (The two spectra are arbitrarily plotted as log d vs. λ, and their relative separation is meaningless).

On evaporating the solution of permanganate in liquid ammonia, a water-insoluble, brown residue was obtained.

4.5 Absorption Spectra of Polyanions.

The elements S, Se, Te, Sn and Pb dissolve in metal-in-ammonia solutions with the formation of a variety of-ide salts[6,23]. The solutions absorb light in the visible spectral region and exhibit beautiful dichroism. Typical spectra are given in Fig. 7 for a sodium solution to which various amounts of sulfur were added. On adding sulfur, the color changed from yellow through green to red-brown.

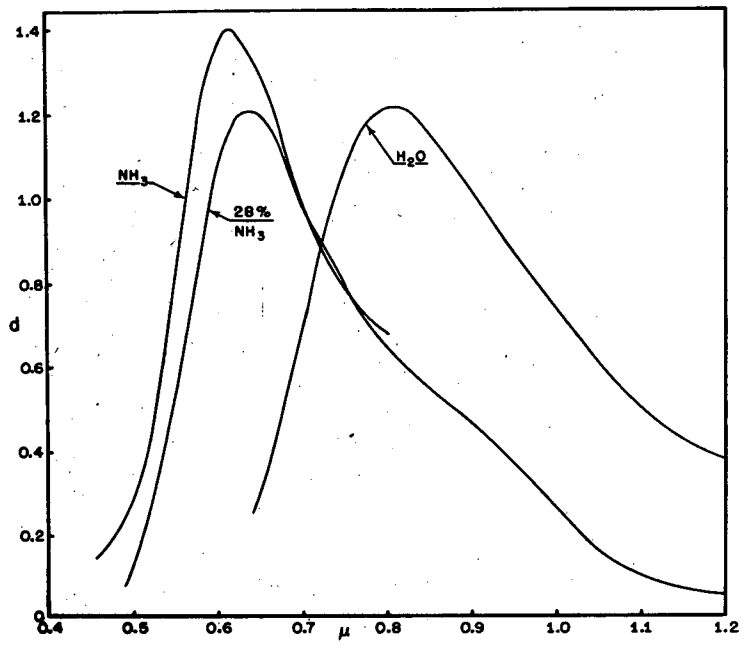


Fig. 5 The absorption spectra of cupric ion in water, aqueous ammonia and anhydrous ammonia.

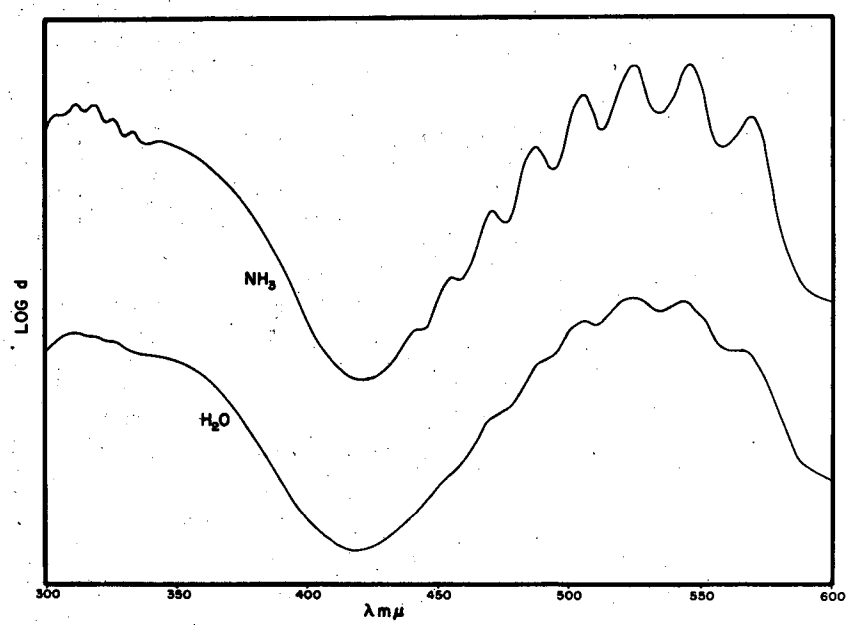


Fig. 6 The absorption spectra of permanganate in water and liquid ammonia.

4.6 The Absorption Spectrum of Sodium in Liquid Ammonia.

4.61 Introduction.

Gibson and Argo[7,8] made an extensive study of the absorption spectra of alkali and alkaline earth metal solutions in liquid ammonia, but they were confined to the visible spectral region. Ogg[12,17] briefly reported the results of absorption measurements in the near ultraviolet and visible regions. Vogt[13] extended the absorption curves of sodium and lithium in liquid ammonia to a wavelength of about 2 microns and reported an absorption peak at 1.8 microns. However Vogt gave no experimental details. In the present investigation, the absorption curve of sodium has been measured from 3500 Å to about 25,000 Å. Contrary to the finding of Vogt, the maximum was found at 1.50 ± .15 microns.

4.62 Experimental.

The type of absorption cell finally adopted is pictured in Fig. 8. The thin (ca. 1 mm.) cell pictured was used only in the spectral region from 1 - 2.5 microns, where the extinction coefficient of sodium is very high; a thicker (ca. 1 cm.) cell was used from 3500 Å - 11,000 Å.

Immediately before each run, pure liquid ammonia was transferred to the cell. A tiny piece of freshly cut sodium was then dropped in; the cell was capped, and then a cold stream of nitrogen (cooled by a liquid nitrogen bath) was circulated around the cell. The flow of nitrogen was regulated to keep the temperature between -70° and -40°C.

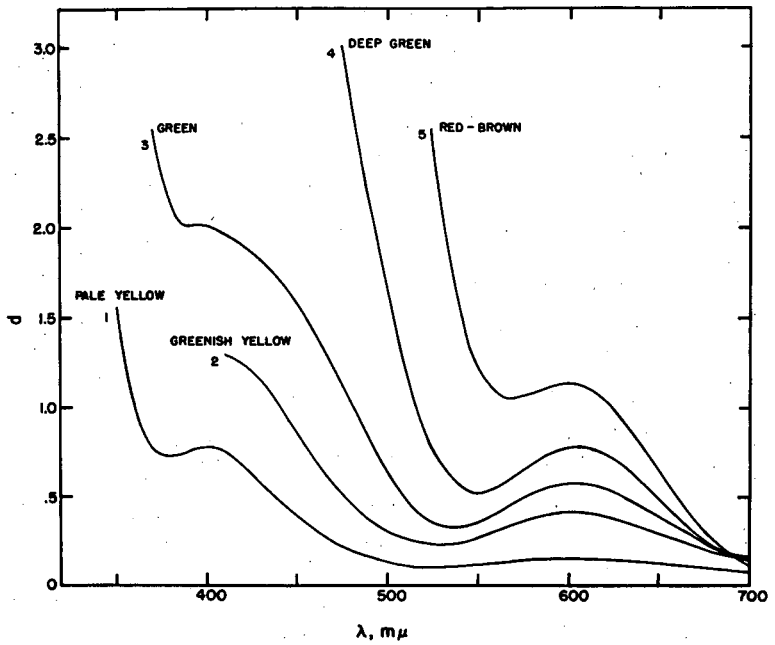


Fig. 7 The absorption spectra of polysulfide in liquid ammonia.

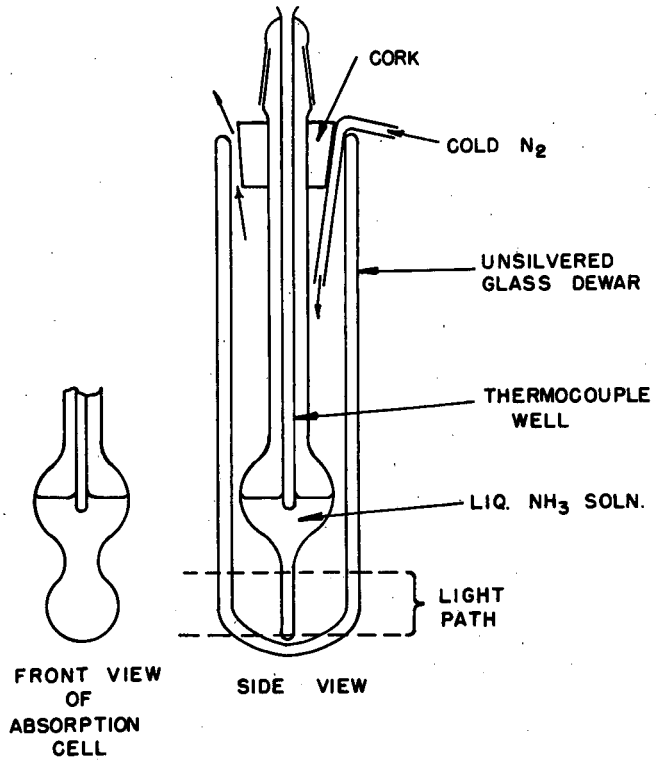


Fig. 8 Refrigerated absorption cell.

The sodium solutions investigated were about 10^{-4} molar.

The spectral region 3,500 - 11,000 Å was investigated with a Cary Recording Spectrophotometer and a Beckman Model DU Quartz Spectrophotometer. The solutions were found to fade rather rapidly (ca. 30% per hour). Hence it was necessary to record the readings at various wavelengths as a function of time and to interpolate the readings to a common time. The optical densities measured were corrected for the absorption of the solvent.* Inasmuch as the sodium concentrations were not known exactly, it was impossible to calculate molar extinction coefficients.

Plots of the logarithm of optical density vs. wavelength (3,500 - 11,000 Å) for various concentrations of sodium yielded parallel straight lines, whose slope may be represented by

$$\log_{10} \frac{d_x}{d_y} = .000210(x - y),$$

where d_x and d_y are the optical densities at wavelengths (in Ångstrom units) x and y, respectively. This finding is in agreement with the data of Gibson and Argo[7,8].

The spectral region 1 - 2.5 microns was investigated with a Perkin-Elmer Recording Infra-red Spectrometer (Model 12B). A quartz prism and globar light source were employed. Wavelength calibration

*Measurements with pure liquid ammonia, using the Beckman Spectrophotometer and the Perkin-Elmer Spectrometer, yielded the following absorption bands (in microns): 0.802 (w), 1.01 (shoulder), 1.04 (s), 1.20 (shoulder), 1.232 (s), 1.270 (w), 1.305 (s), 1.53 (vs), 1.64 (s), 2.00 (vs), 2.24 (vs).

was accomplished with a mercury arc and with the absorption bands[24] of liquid chloroform and liquid benzene. The results of one run are given in Fig. 9. Five successive tracings were made (at approximately 20 minute intervals). The separation in the tracings is due to the gradual fading of the sodium solution. The apparent drop in transmissivity toward long and short wavelengths is not entirely due to ammonia absorption. The short wavelength drop is due to low output of the globar and insensitivity of the detecting thermocouple, whereas the long wavelength drop is due to increasing absorption of the glass cell and quartz prism. By measuring the relative separations of the various traced curves from the 0% transmission line, the absorption curve of sodium can be calculated. The data of four runs give an absorption peak for sodium at 1.50 ± .15 microns, a result .3 micron less than that of Vogt[13]. (In view of the findings of Ogg[12], that the absorption spectrum is markedly dependent on temperature, this discrepancy may be due to a difference in the temperatures employed). One calculates from the data of Gibson and Argo[7] an approximate value for the molar extinction coefficient of sodium at 5,000 Å, $\epsilon = 325$ liter $cm.^{-1} mole^{-1}$. By extrapolation to 1.5 microns, an estimate can be made for the extinction coefficient at the maximum, $\epsilon = 4 \times 10^4$ liter $cm.^{-1} mole^{-1}$.

4.63 Theoretical

It has been fairly well established that in moderately dilute solutions of metals in liquid ammonia (10^{-2} molar and lower), the electrons exist as individual solvated ions - as electron pairs,

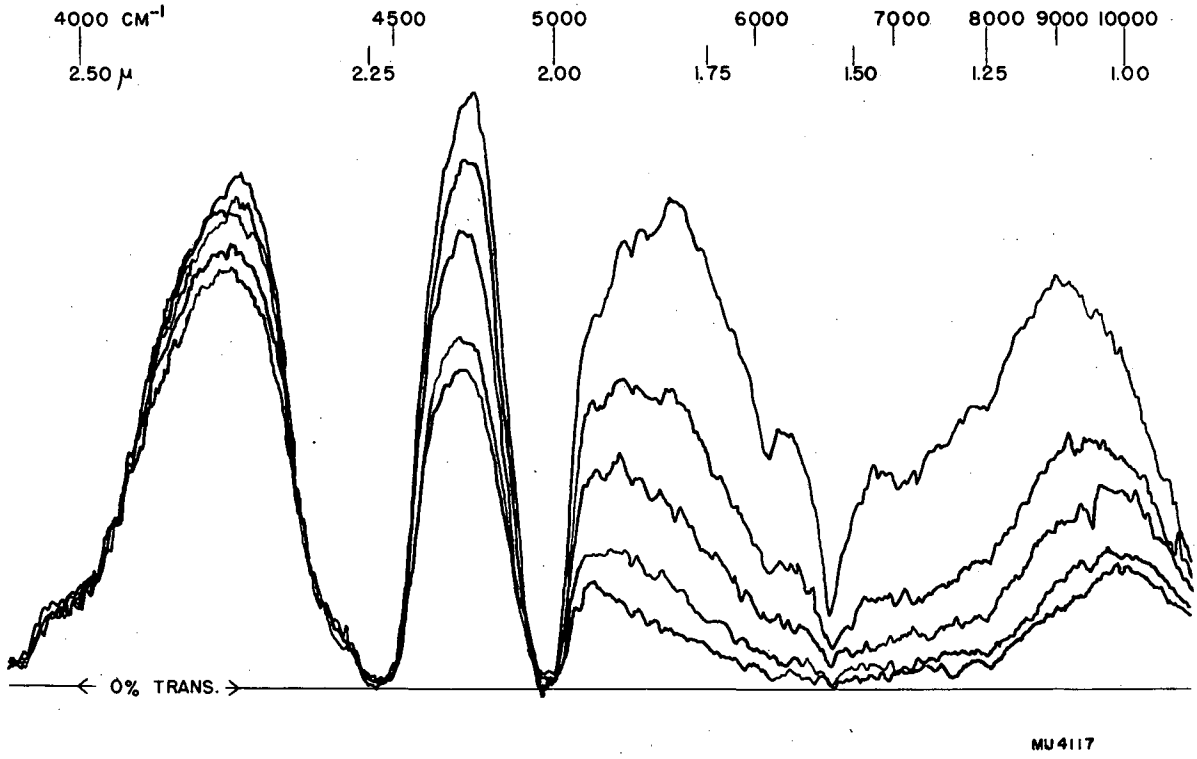


Fig. 9 Absorption spectra of sodium-ammonia solutions in the near infra-red.

$e_2^{--}(am)$, and as unpaired electrons, $e^-(am)$. These species are in rapid equilibrium:

$$e_2^{--}(am) = 2\ e^-(am).$$

The heat of unpairing has been calorimetrically determined as ca. 4 kcal./mole.[25]

The "Outer" Photoelectric Effect.[26]

Direct measurements of the photoelectric threshold for relatively concentrated metal solutions in ammonia ($10^0 - 10^{-2}$ molar) by Häsing[27] and Teal[28] place the work function at 1.40 - 1.60 volts (0.85 micron). Ogg,[29] however, working with very dilute solutions ($10^{-5} - 10^{-4}$ molar), measured a work function of about 0.8 volt (1.5 microns). Ogg explains the variation of work function with concentration as due to the equilibrium between paired and unpaired electrons. He postulates the photo-threshold at 1.5 microns as due to the process

$$e^-(am) + h\nu = e^-(g),$$

and the photo-threshold at ca. 0.85 micron as due to the process

$$e_2^{--}(am) + h\nu = e^-(am) + e^-(g).$$

It should be pointed out that these mechanisms do not explain all the facts. First, it is not immediately apparent why long wavelength thresholds were observed for the more concentrated solutions at wavelengths corresponding to ca. 1.50 volts, since these solutions contained a higher concentration of unpaired electrons than the more dilute solutions studied by Ogg. It is suspected that pseudo-thresholds

were observed, where the photoelectric current dropped considerably at about 0.85 micron, but would not have completely dropped off until still longer wavelengths were reached. Second, the mechanisms proposed by Ogg predict an energy of 0.7 volt (16 kcal./mole) for the unpairing of an electron pair, in complete disagreement with calorimetric studies.

It is conceivable that a photon could excite both electrons in an electron pair to the gaseous state. If we are willing to admit such a process in addition to the two proposed by Ogg, then energies can be assigned to the three processes which are consistent with the calorimetric heat of unpairing.

The "Inner" Photoelectric Effect.

Ogg[30] reported that dilute sodium solutions displayed a marked increase in electrical conductivity upon irradiation with visible light. This phenomenon can be explained by proposing that, in the absorption of light, the ammonated electron is excited to a conduction band. Inasmuch as the long wavelength threshold for this photoconduction was not determined, the energy of the process is unknown.

Thermodynamic Data.

The heat of formation of the electron in ammonia is 43.5 kcal./mole.[31] This heat corresponds to the process

$$1/2\ H_2(g) = H^+(am) + e^-(am).$$

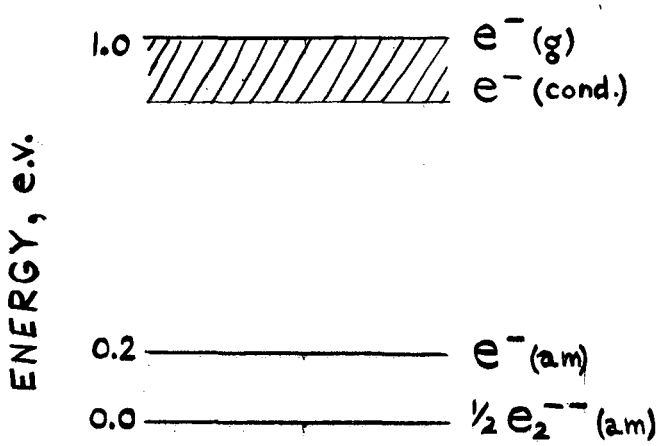
In order to evaluate the energy of the process

$$e^-(am) = e^-(g),$$

it is necessary to split up the ammonation energies of pairs of ions into those for individual ions. Unfortunately, there is no thermodynamic method for evaluating individual ammonation energies and the separation must be done somewhat arbitrarily. (As Ogg[29] has pointed out, measurement of the photoelectric threshold for the ammoniacal electron promises to solve this predicament).

The Absorption Spectrum of the Electron in Ammonia.

The absorption peak at 1.5 microns corresponds to an energy of about 0.83 volt. It is proposed that this energy corresponds to the excitation of the unpaired electron to a conduction band (as in the inner photoelectric effect). An electron in the conduction band is probably equivalent to the "free" or unsolvated, electron described in the early literature[32], which electron is not trapped by any ammonia molecules and is free to move about in the liquid.* One would expect such an electron to differ very little in energy from a gaseous electron. The following energy scheme is proposed to graphically represent the observed facts:



*The "free" electrons proposed by Kraus were supposed to exist in concentrated solutions in order to account for the high conductance of such solutions.

It is apparent that further experimentation is necessary to verify or disprove the above ideas. An obvious experiment is to measure the long wavelength threshold for the inner photoelectric effect.

5. Acknowledgements.

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6. References.

(1) A. Prikhot'ko, J. Expt'l. Theoret. Phys. (U.S.S.R.) 10, 398-406 (1940); C. A. 35, 383 (1941).

(2) A. Prikhot'ko, Acta Physicochim U.S.S.R. 12, 559-64, 565-72 (1940) (In English).

(3) G. Costeanu and P. Barchewitz, Comptes rendus 203, 1499-1501 (1936).

(4) G. Costeanu, R. Freymann and A. Naherniac, Comptes rendus 200, 819 (1935).

(5) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions", Prentice-Hall, New York, 1939, pp. 181 ff.

(6) O. Ruff, Z. physik. Chem. 76, 21-57 (1911).

(7) G. E. Gibson and W. L. Argo, Phys. Rev. 7, 33-48 (1916).

(8) G. E. Gibson and W. L. Argo, J. Am. Chem. Soc. 40, 1327-61 (1918).

(9) R. W. Wood, Phys. Rev. 38, 1648-50 (1931).

(10) H. Shiba and T. Inouye, J. Chem. Soc. Japan, 56, 213-20 (1935).

(11) W. E. Garner and H. F. Gillbe, J. Chem. Soc. 1928, 2889-2904.

(12) R. A. Ogg, J. Chem. Phys., 14, 114-5 (1946).

(13) E. Vogt, Z. Elektrochem., 45, 597 (1939).

(14) A. I. Shatenshtein and E. A. Izrailevich, Acta Physicochim. U.S.S.R., 12, 73-98 (1940).

(15) N. Dykhno and A. Shatenshtein, Acta Physicochim. U.S.S.R., 17, 230-6 (1942).

(16) N. Dykhno and A. Shatenshtein, ibid., 20, 645-52 (1945).

(17) R. A. Ogg, P. A. Leighton and F. W. Bergstrom, J. Am. Chem. Soc., 55, 1754-66(1933).

(18) J. K. Thompson and J. Kleinberg, J. Am. Chem. Soc., 73, 1243 (1951).

(19) A. D. Awtrey and R. E. Connick, J. Am. Chem. Soc. 73, 1842 (1951).

(20) W. M. Latimer, R. E. Connick and W. L. Jolly, Science, 115, 483-4 (1952).

(21) T. Dreisch and W. Trommer, Z. physik. Chem. B 37, 37(1937).

(22) J. Bjerrum, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd., 11, No. 10 (1932) and ibid., 21, No. 4 (1944).

(23) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry", Prentice-Hall, New York, 1944, pp. 151-2.

(24) R. Mecke and F. Oswald, Z. physik, 130, 445-8 (1951).

(25) L. V. Coulter, National Meeting, American Chem. Soc., Sept., 1952.

(26) Early references to the photoelectric effect with liquid ammonia solutions of sodium:

a. C. A. Kraus, J. Am. Chem. Soc., 43, 749 (1921).

b. Chittum and Hunt, J. Phys. Chem., 40, 581 (1936).

c. Crapple, Unpublished dissertation, Univ. of Chigago, 1933.

d. G. M. Schmeing, Ph.D. Dissertation, University of Chicago, 1939.

(27) J. Häsing, Ann. Physik, 37, 509-33 (1940).

(28) G. K. Teal, Phys. Rev., 71, 138 (1947).

(29) R. A. Ogg, J. Chem. Phys. 14, 295 (1946).

(30) R. A. Ogg, J. Am. Chem. Soc. 68, 155 (1946).

(31) W. L. Jolly, Chem. Rev. 50, 351 (1952).

(32) C. A. Kraus, J. Am. Chem. Soc. 30, 1197 (1908); ibid., 36, 864 (1914).