

Positron Annihilation in a Dilute Metal: Li-NH₃ Solution*

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The momentum distribution of photons from positrons annihilating in lithium-ammonia solutions of various concentrations has been measured. For all except very dilute solutions, the momentum distribution was found to be independent of concentration and unlike the distribution for ammonia or for a metal. At extremely low concentrations, the distributions resemble more that of pure ammonia. No effect due to a magnetic field was observed for the solutions although a small effect was noted for pure liquid ammonia. In addition the momentum distribution for a concentrated solution was observed to change slightly over the temperature range -164°C to 13°C . These data suggest the formation of a positronium state in this dilute metallic solution.

I. INTRODUCTION

ALKALI metals dissolve readily in liquid ammonia forming solutions with metallic characteristics attributable to the solvated electrons, i.e., the electrons donated to the solutions by the metal atoms. The properties of these solutions have been studied for more than one hundred years¹ yet the exact nature of the "free" electrons in these solutions is not yet resolved. Measurements of transport properties such as Hall coefficient,² electrical conductivity,³ and thermal conductivity⁴ imply that the electrons are almost as free as conduction electrons in a metal. Since positron annihilation has been shown to be a good detector of free electrons in simple metals,⁵ we determined to use this technique to investigate these metallic solutions. If the electrons were free one might expect the data from the usual long-slit angular correlation experiment to have the form of a small parabola (with width and intensity determined by the density of free electrons) superimposed upon the broader distributions which would result from positrons annihilating with the outer electrons of the ammonia molecule. This was not found. Instead, as discussed in Sec. IV, the environment of the positron appears to be quite independent of concentration of electrons in the solution as though some sort of bound state were formed.

Section II contains a short description of the experi-

mental technique. The data are presented and discussed in Secs. III and IV.

II. EXPERIMENTAL TECHNIQUE

Metal ammonia solutions were formed in the stainless-steel measurement cell shown in Fig. 1. Solution preparation procedure was as follows. The cell was carefully cleaned and then evacuated. Special high-purity alkali metal was cut to approximate size with a cork borer. The ends of the cylindrical metal plug were then trimmed to remove any remaining contamination. Cutting was carried out under mineral oil which had been previously outgassed to remove entrapped air. The alkali-metal specimen was then rinsed in xylene followed by 60-90 petroleum ether and subsequently dried under argon and sealed in a small previously weighed plastic cell in an argon atmosphere. After the metal specimen had been weighed in its plastic sack, the measurement cell was filled with argon to a pressure slightly in excess of atmospheric pressure. A small cover plug was then removed from the measurement cell, the plastic sack slit open, and the alkali metal quickly dropped in the cell. The cell

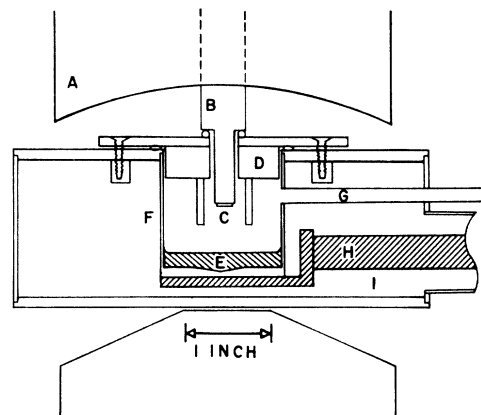


FIG. 1. Measurement system: (A) magnet pole piece; (B) soft iron rod; (C) Cu⁶⁴ foil; (D) plexiglas cover; (E) solution; (F) stainless-steel thin-wall cell; (G) tube to argon, ammonia, and vacuum; (H) copper bar to temperature bath; (I) vacuum insulation.

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¹ An introduction to the properties of these solutions may be found in T. P. Das, *Advances in Chemical Physics*, edited by I. Prigogine, (Interscience Publishers, Inc., New York, 1962), Vol. 4, p. 303, and in the somewhat earlier review of W. L. Jolly, *Progress in Inorganic Chemistry* edited by F. A. Cotton (Interscience Publishers, Inc., New York, 1959), Vol. 1, p. 235. A more recent report is *Solutions Metal-Ammoniac, Colloque Weyl, Lille, 1963*, edited by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964).

² D. S. Kyser and J. C. Thompson, *J. Chem. Phys.* **42**, 3910 (1965).

³ C. A. Kraus, *J. Chem. Ed.* **30**, 86 (1953).

⁴ P. G. Varlashkin and J. C. Thompson, *J. Chem. Phys.* **38**, 1974 (1963).

⁵ P. R. Wallace, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 1.

was then immediately sealed and evacuated. High-purity argon was used.

The foregoing procedure allows the alkali metal to be exposed to air for a total time of less than 1 sec.

After evacuation of the argon, a measured amount of doubly distilled sodium-dried ammonia was distilled into the cell. The cell temperature was controlled by being thermally connected to a thermostating bath by a large copper bar.

Metal-ammonia solutions are unstable in the presence of trace contaminants. Solution decay proceeds via the reaction $M + \text{NH}_3 \rightarrow \text{MNH}_2 + \frac{1}{2}\text{H}_2$. Several metals are known or suspected to be catalysts for the decomposition reaction. Metal-ammonia experiments are customarily conducted in glassware while the experiments reported herein were performed with a stainless-steel cell. Consequently, solution vapor pressure was monitored during each experiment to check for decomposition as indicated by the evolution of hydrogen. The photon angular distribution was measured about once every four hours. Comparison of the angular distributions of successive scans serves as a natural check for significant decomposition. In at least one instance, a solution was preserved for two days without measurable change.

Solutions having concentrations much less than 0.1% could not be formed in this manner for two reasons: (a) the difficulty of preventing oxidation of such a small amount of pure metallic lithium, and (b) because even slight decomposition of very dilute solutions causes appreciable relative concentration change. Thus the very dilute solutions were prepared by following the slow decomposition of a dilute solution prepared in the normal way.

Immediately following distillation of the ammonia onto the lithium, the angular correlation apparatus was set into operation. A complete scan of all angles was made every 2 h and 25 min. The time required to measure the portion of the distribution between half-

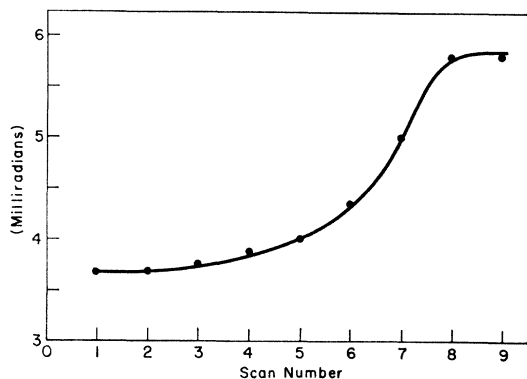


FIG. 2. Decomposition of a lithium-ammonia solution as a function of time as indicated by the full width at half-maximum of the momentum distribution. Each scan equals approximately $2\frac{1}{2}$ h.

maximum points was approximately 30 min. The observed full width at half-maximum for nine successive scans is shown in Fig. 2. If it is assumed that at the beginning of scan 8 the solution is completely decomposed and that the decomposition was linear in time and that there was no initial decomposition, one obtains the concentrations 0.081% (1), 0.069% (2), 0.056% (3), 0.044% (4), 0.031% (5), 0.019% (6), and 0.006% (7) for scans 1 through 7. The assumption of no initial decomposition is certainly wrong⁶ and overestimates the concentration. Further, the assumption of linearity is not apt to be particularly accurate. Therefore, the more dilute concentrations of Fig. 4 are marked LA (linear approximation) to indicate that the figure is not well known. In addition, we measured the half-width at half-maximum for each side of the distribution and found that the decomposition was not so rapid as to distort significantly the shape of the distribution obtained in any one scan.

A small Cu^{64} foil was mounted on the end of a soft iron rod about $\frac{1}{2}$ in. above the surface of the solutions. The solution chamber was placed between the pole pieces of a magnet which could be used to focus the positrons on the specimen. The soft iron rod on which the foil was mounted served to further enhance the magnetic field.

Angular correlation of photons from positrons annihilating in the solutions was determined with horizontal slit geometry which measures the distribution of one Cartesian component of momentum of the annihilating electron-positron pair.⁷ The surface of the solution was positioned so as to lie at the same elevation as adjacent horizontal lead slits. These slits permitted only those photons originating close to the surface of the solution to reach the photon counters. The angular resolution of the apparatus (taking into account the positron penetration into the low-density metal-ammonia solution) is estimated at about 0.3 mrad, full width at half-maximum.

⁶ I. Warshawsky, in *Solutions Metal-Ammoniac, Colloque Weyl, Lille, 1963*, edited by G. Lepoutre and M. J. Sienko (W. A. Benjamin, Inc., New York, 1964).

⁷ When two long horizontal and parallel slit detectors are used to determine the angular correlation of pairs of annihilation photons emitted from a source placed midway between them but displaced slightly vertically (Z direction) from the plane of the detectors, the coincidence counting rate is given by

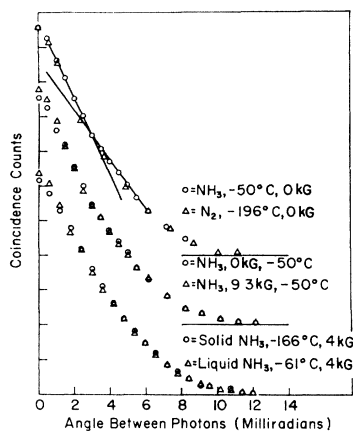
$$N(k_x) = \iint P(\mathbf{k}) dk_x dk_y,$$

where $P(\mathbf{k})$ is the probability that a photon pair has a total momentum $h\mathbf{k}$. The integration over k_x (x is the direction of a line joining the midpoints of the detectors) is required by the fact that the detectors are insensitive to the small Doppler energy shift caused by the momentum of the annihilating pair. The integration over k_y (y is the direction of the long dimension of the slit detectors) is an approximation which is valid if the angle subtended by the length of the slit at the source is large compared with P_y/mc for momenta of interest.

III. DATA AND DISCUSSION: PURE AMMONIA

The angular correlations of photons from positrons annihilating in pure ammonia under various conditions is shown in Fig. 3. Several features of these data should be noted. First of all, the data from positrons annihilating in liquid nitrogen and in liquid ammonia are virtually indistinguishable, implying that most positrons annihilate with outer electrons of the nitrogen atoms which are not greatly different in the two molecules. Secondly, the fairly sharp change of slope (shown in the figure by the two straight lines drawn through some of the experimental points) implies the existence of two separate momentum distributions. This may be expected if some of the positrons form positronium as is the case in other liquid gases.⁸ The intensity of the narrow component, 5–11%, implies about 30% positronium formation in liquid ammonia. This is compatible with Millett's figure⁹ for positronium

FIG. 3. Momentum distribution of photons from positrons annihilating in liquid and solid ammonia and in liquid nitrogen. The liquid-nitrogen data are those of Briscoe and Stewart (Ref. 7).



formation, $\frac{1}{3}I_2 = 37\%$. On the other hand, the small enhancement of the narrow component in a magnetic field, $10_{-5}^{+7}\%$, is just barely in agreement with the enhancement calculated from Millett's pickoff lifetime⁹ and our estimate of magnetic field, viz., $24 \pm 8\%$. Finally we should note that at much lower temperature, in solid ammonia, there appears to be slightly less positronium formation than in the warmer liquid.

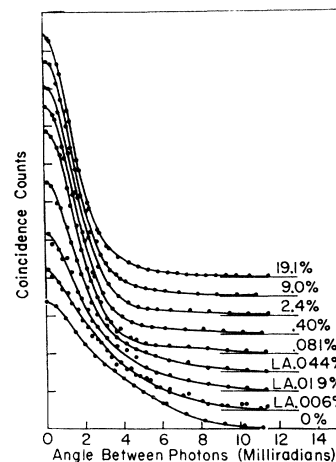
IV. DATA AND DISCUSSION: LI-NH₃ SOLUTIONS

The momentum distributions of photons from positrons annihilating in solutions of lithium in ammonia are shown in Fig. 4. The percentage ratio of the number of lithium ions to the total number of ions plus am-

⁸ C. V. Briscoe and A. T. Stewart, in *Positron Annihilation Conference*, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, to be published).

⁹ W. E. Millett, L. H. Dieterman, and J. C. Thompson, in *Positron Annihilation Conference*, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, to be published).

FIG. 4. Momentum distribution of photons from positrons annihilating in lithium-ammonia solutions of various concentrations.



monia molecules is indicated on each data set. Similar data (not shown) were also obtained for lithium concentrations of 13.0%, 5.6%, 3.5%, 0.63%, 0.069% (LA), 0.056% (LA), and 0.031% (LA). The most striking fact about these data can be seen immediately. Except for very low concentrations all the data sets are indistinguishable. The momentum distributions are concentration-independent. Also, the data for pure ammonia and for the more concentrated solutions are sufficiently different in shape at large angles that they cannot be matched over an appreciable angular range. We conclude that very few positrons annihilate with higher momentum electrons as in the pure liquid ammonia. On the other hand, the narrow component of the pure-liquid-ammonia data can be separated from the broad component in such a way as to make it resemble very much the data for the metallic solutions. It appears as though when lithium is added to ammonia the broad component decreases and is nonexistent at most concentrations.

In other liquefied gases, the narrow component is usually attributed to positronium formation.⁸ Can positronium be formed in this metallic solution? Kahana has shown¹⁰ that in the system consisting only of a positron and a gas of electrons, a positronium-like state can be formed if the electron gas is more dilute than one electron per average volume of $4\pi r_s^3/3$, with $r_s \approx 8$ atomic units (a.u.). (Kahana specifies that a parameter $\tau = 2/\pi a_0 k_f$ should be greater than 2.85.) The Li-NH₃ solutions satisfy this criterion except for the most concentrated, although the validity of this same criterion for these complicated solutions is questionable. If we assume that positronium is formed and is repelled from the molecules of the liquid to form a bubble as Ferrell¹¹ postulated for helium, we can estimate the size of the bubbles. Bubble energy is composed of two terms, the surface-tension energy and the zero-point energy of the positronium atom confined within an

¹⁰ A. Held and S. Kahana, *Can. J. Phys.* **42**, 1908 (1964).

¹¹ R. A. Ferrell, *Phys. Rev.* **108**, 167 (1957).

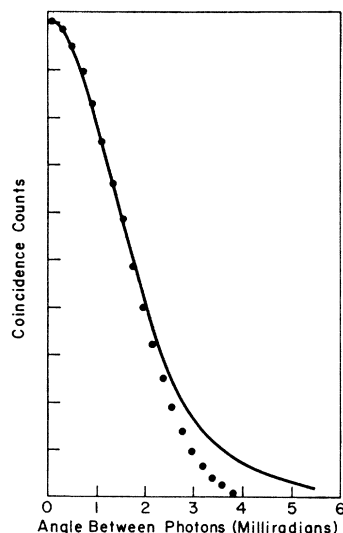


FIG. 5. Momentum distribution of photons from positrons annihilating in a lithium-ammonia solution as predicted by the spherical-potential-well model (circles) and as shown by experiment (9.0%, -57°C).

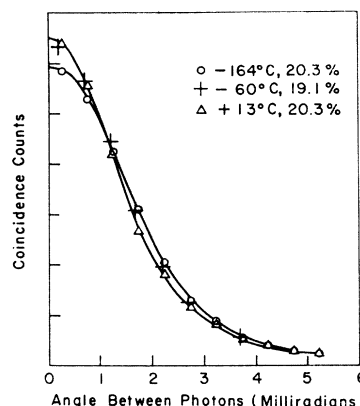


FIG. 6. Temperature dependence of the momentum distribution of photons from positrons annihilating in concentrated lithium-ammonia solutions.

infinite spherical potential well. Bubble radius is determined by minimization of the total energy. The total energy is given by $E = (\pi^2 \hbar^2 / 2mr^2) + 4\pi\sigma r^2$, where σ denotes surface tension and m denotes particle mass. Minimizing yields $r^4 = \pi \hbar^2 / 8m\sigma$.

The surface tension of liquid ammonia as given by Durant¹² and King¹³ shows a linear relationship with temperature. Using these data, and for the lowest temperature a considerable linear extrapolation of the data, the following values of surface tension are obtained: 23.5, 39.4, 64.0 dyn/cm at 13, -57 , and -164°C , respectively. Using these values of surface tension, $r = 5.63 \text{ \AA}$ at 13°C , $r = 4.98 \text{ \AA}$ at -57°C , and $r = 4.40 \text{ \AA}$ at -164°C .

The z component of the zero-point momentum for a particle in an infinite square well of radius 5.0 \AA has been calculated and is shown in Fig. 5 together with the data for 9% Li-NH₃ solution at -57°C . The agreement is quite good. At higher and lower temperatures the surface tension is different as we have seen. The momentum distribution data corresponding to these temperatures is shown in Fig. 6. These distributions differ somewhat less than would be expected from the simple bubble model.

The absence of a magnetic-field effect for these solutions may imply that very fast exchange is taking

place between the electron in positronium and the free electrons. If the exchange were so fast that positronium atoms spent $\frac{1}{4}$ of the time in the singlet state and $\frac{3}{4}$ of the time in the triplet state the annihilation rate would be expected to be

$$\begin{aligned} \lambda &= \frac{1}{4}(\lambda_s + \lambda_p) + \frac{3}{4}(\lambda_t + \lambda_p) \approx \frac{1}{4}\lambda_s + \lambda_p \\ &= 0.2 \cdot 10^{10}/\text{sec} + 0.045 \times 10^{10}/\text{sec} = 0.245 \times 10^{10}/\text{sec} \end{aligned}$$

or $\tau = 4.1 \times 10^{-10}$ sec. (For the pickoff rate λ_p , we have Millett's value⁹ for liquid NH₃ in the absence of any other information.) This analysis, however, implies about 18% "broad component" from pickoff annihilation. It is doubtful if our data allows such a large figure for pickoff annihilation.

If this picture of virtually all positrons decaying by a positronium-like state is correct, one would expect a single lifetime at concentrations above 0.1%. Preliminary data of Millett *et al.*⁹ show that at about this concentration the intensity and lifetime of the long-lived component both decrease rapidly but do not vanish. (His figures show the intensity to decrease from 28 to 14% while the lifetime decreases from 2 nsec to about 1 nsec.) Our simple picture cannot of course account for this weak longer-lived component.

We hope that further work can be done on this interesting metallic liquid which shows evidence of positronium formation.

ACKNOWLEDGMENTS

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¹² A. A. Durant, T. G. Pearson, and P. L. Robinson, *J. Chem. Soc. Part 1*, 730 (1934).

¹³ H. H. King, J. L. Hall, and G. C. Ware, *J. Am. Chem. Soc.* **52**, 5132 (1930).