

AN ESR STUDY OF LINEWIDTHS IN
METAL-AMINE SOLUTIONS AND AN
AB INITIO INVESTIGATION OF THE
LITHIUM-AMMONIA INTERACTION

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VINCENT A. NICELY
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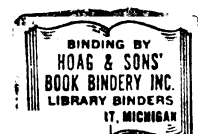
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ABSTRACT

AN ESR STUDY OF LINEWIDTHS IN METAL-AMINE SOLUTIONS AND AN AB INITIO INVESTIGATION OF THE LITHIUM-AMMONIA INTERACTION

By

Vincent A. Nicely

An electron spin resonance (ESR) study of the m_I dependent linewidth of the hyperfine pattern from alkali-metal-amine solutions and an ab initio self-consistent field molecular orbital study of the electronic structure of complexes of lithium atoms and one or two ammonia molecules are reported in this thesis.

The ESR spectrum of the monomer in dilute solutions has Lorentzian-shaped lines. A two-state equilibrium model is sufficient to describe the linewidth dependence upon m_I of an isothermal spectrum. Due to persistent problems with solution decomposition, however, data could not be obtained over a sufficient range of temperature and solvent composition to permit a distinction among several possible models.

A systematic study was made of the solution decomposition at room temperature. Solutions could be prepared which were stable for periods of weeks to months in the presence of excess metal after some initial decomposition. However,

for freshly-prepared dilute solutions without excess metal the decomposition was much faster and depended on the surface to volume ratio of the container. Zero order decay was observed for solutions in a 2 mm diameter tube.

The spectrum of sodium in frozen ethylenediamine below 0°C was reinvestigated. Solutions made with carefully purified solvent gave a spectrum which was very similar to that of highly dispersed sodium metal. Solutions to which ammonia had been added or which were made with solvent which had been allowed to react with metal prior to distillation gave the two line pattern previously reported (1). The narrow line observed from solutions with impure solvent is probably due to liquid solution dispersed throughout the solid.

An ab initio molecular orbital study was made of the stability and electronic structure of lithium-ammonia complexes with a basis of gaussian lobe functions. A complex of lithium with one ammonia molecule is predicted to be stable by 20 kcal/mole relative to a free lithium atom and a free ammonia molecule. The bonding in the complex is primarily through sharing of the lone pair of electrons on ammonia between the ammonia molecule and the lithium atom. The unpaired electron orbital is rearranged upon formation of the complex so that the unpaired electron has very low density in the region of the ammonia with the exception of

a sharp peak in density near the nitrogen nucleus. The complex with two ammonia molecules is nearly isoenergetic with the one ammonia complex plus an ammonia molecule. The addition of the second ammonia causes an increase in the preferred lithium-nitrogen distance and an increase of the occupancy of the nitrogen orbitals by the unpaired electron. The ammonia appears repulsive to the unpaired electron in the diammonia complex, also. The implications of the results for metal ammonia solutions are discussed.

REFERENCE

- (1) Vos, K. D., Ph. D. Thesis, Michigan State University, East Lansing, Michigan, 1963.

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LITHIUM-AMMONIA INTERACTION

By

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To My Parents

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CHAPTER I

INTRODUCTION

Ammonia Solutions

Since the first report that alkali metals dissolve in liquid ammonia (68), the nature of the solute has been an active area of investigation. The solutions have properties which range from electrolytic to metallic as the concentration of dissolved metal is increased. Only solutions which are dilute enough to be non-metallic are considered here. Numerous references to the original literature can be found in several recent articles which review the nature of the physical properties of metal ammonia solutions (34,36,61,63).

The solute species in infinitely dilute solutions are generally considered to be solvated electrons and metal cations. In order to account for the concentration dependent properties of the solutions, several ways of combining these species to form new species have been proposed (see 34 for references). Upon reviewing the data available in the literature, Dye (34) has concluded that the concentration dependence of the conductance, transference number, and activity coefficient data is well represented by simple ion-pairing phenomena. This is in conflict with the usual

interpretations which require a substantial fraction of the total solute to be present as species of stoichiometry M^- or M_2 (where M represents the presence of a metal nucleus in the species). The concentration dependence of the magnetic susceptibility and enthalpy of solution, however, require that some exothermic reaction(s), forming at least one diamagnetic species, be considered. On the basis of these results, Dye has concluded that if the experimental data are accurate, the processes which lead to the concentration dependence of the susceptibility and enthalpy must have only small effects on the electrochemical properties. Furthermore, he has suggested a type of interaction which might cause such results.

The electron spin resonance spectra of europium in ammonia (16) show signals from both the solvated electron and the Eu^{+2} cation, even in the concentration region where extensive ion pairing is expected. Catterall and Symons have concluded that since cation-electron interactions influence the solvated electron linewidth monomeric species must be formed. However, since the spectra of both Eu^{+2} and the solvated electron were observed, they concluded that the monomer must not be centro-symmetric. This led to the conclusion that ion-pairing is the predominant mode of cation-electron interaction.

All of the theoretical studies of the cation-electron interaction (6,45,46,54) assume a centro-symmetric unit

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with stoichiometry M. These calculations indicate a density of unpaired electron at the metal nucleus which agrees approximately with the NMR shift data for ammonia solutions.

In summary, the nature of the solute in metal ammonia solutions is still an unsolved problem, since the models which have been proposed cannot be made to agree with all of the available data. Furthermore, the mechanism of the cation electron interactions which are inferred from experimental data has not been clearly established.

Non-ammonia Solutions

Although metal-ammonia solutions have been studied more extensively, the alkali metals also dissolve in a variety of other solvents including polyethers, amines (15) and hexamethylphosphoramide (see 10 for references). Some mixtures of these solvents with inert diluents also dissolve the metals. As with ammonia solutions, these solutions are electrical conductors, blue in color, and distill into metal and solvent fractions. In the details of their behavior, however, they are significantly different from metal-ammonia solutions. The limited conductance data (30) show some of the differences particularly for sodium solutions. The optical spectra (for references see 10) in some cases are very different from ammonia solutions. Although three bands are commonly observed for some of the metals, one of these bands has been attributed to sodium formed by reaction with

Pyrex (43). Another of the absorption bands (as well as the sodium "impurity" band) has recently been attributed to a species of stoichiometry M^- (51) with unknown structure. The third band is thought to be the solvated electron and electrostatic aggregates of it (25,29). Just as for ammonia solutions (34), the optical spectra do not appear to give specific information about the nature of the species.

Electron spin resonance measurements on some non-ammonia solutions give a hyperfine pattern in addition to or in place of the single line absorption which is observed in ammonia solutions (2,3,4,17,18,19,20,24,33,65,66). The hyperfine pattern is attributed to a contact interaction of the unpaired electron with a metal nucleus, except for lithium solutions in which it is attributed to a contact interaction with four magnetically equivalent nitrogen-14 nuclei. Because of the detailed structural information inherent in the hyperfine structure constant, the electron spin resonance spectra of solutions with measurable concentrations of this species have been intensively investigated. The reported results for a number of different solvent-metal combinations which have the hyperfine splitting from a single metal nucleus can be summarized as follows: The A value increases and the g value decreases with increasing temperature at constant solvent composition. Addition of ammonia at constant temperature to the n-aliphatic amine solutions decreases the A value. The linewidths for the hyperfine lines depend upon solvent, temperature, excess cation concentration,

and perhaps other unknown factors. The linewidths are dependent upon the line, a result referred to as an m_I dependent linewidth.

Spectra from a few solid solutions have been reported to give a single line (66) or a hyperfine pattern (24,33). The nature of the species in the solid has not been studied extensively, however.

Models

Tuttle and co-workers (3,4) postulate that the paramagnetic species with the hyperfine interaction is a monomer similar to that proposed for ammonia by Becker, Lindquist and Alder (5). The solvent-dependent A value is attributed to the medium-dependent volume of the unpaired electron orbital on the monomer. They assume that solvent molecules are bound in the monomer structure with a binding energy which depends on the molecule and the "solvation shell" and that the volume of the unpaired electron is related to the volume of bound solvent. They explain that the solvent dependent properties result from different binding energies for different types of molecules and that the marked temperature dependence occurs because the binding energy is close to kT . For rubidium and cesium solutions they advocate the same model and assume that the m_I dependent linewidth demonstrates the asymmetry of the species; a result which they claim confirms their earlier conjectures about solvent binding.

By an extension of earlier approximate calculations for the ammonia monomer (54), O'Reilly and Tsang (55) interpreted the temperature dependent A value of potassium in ethylamine. The variation in A was attributed to the change in cavity radius of the monomer species.

Dye and co-workers (24) have concluded that neither explanation is quantitatively applicable to their more complete data for potassium in ethylamine-ammonia mixtures. They interpret the variations of A value with temperature and solvent composition as the result of an equilibrium among distinct species, each of which has different magnetic properties. They were able to fit their data by assuming that a solvated metal atom, a monomer with all ethylamine in the first solvation shell and a monomer with one ammonia molecule in the first solvation shell were in equilibrium. Later, they (33) attempted to apply the same model to the m_I dependent linewidth observed for solutions of cesium in ethylamine. Although the m_I dependence could be fit, the electron spin resonance spectra they obtained did not have Lorentzian-shaped lines as required by their model, and their linewidth expression had the wrong temperature dependence.

Two models have been proposed to explain the hyperfine pattern observed in lithium solutions. Tuttle and co-workers (3) have suggested that the species is a monomer as with the other alkali metals. The differences presumably occur because this monomer has a more expanded unpaired electron

orbital and the first solvation shell exchanges with the bulk solvent more slowly. Dye (35) and Catterall et al. (21) have proposed that the species is an ion-pair between a solvated electron and a tetra-coordinated lithium cation. The magnetic equivalence of the nitrogens is obtained by the rotational motion of the lithium cation and its solvation shell according to this proposal.

The Problem

The preceding sections indicate that a number of unsolved problems still remain before a complete physical description of the solute can be given. The study of cation-electron interactions in the amine solutions which have hyperfine splitting should provide information about the nature of the solute as aggregation of cations and solvated electrons occurs. In spite of the many different effects observed, however, no model which is quantitatively applicable has been proposed. Furthermore, the theoretical investigation of the experimental observations has not been very complete.

This thesis reports an investigation of the cation-electron interactions. Both experimental and theoretical methods were used for the study.

The m_I dependent relaxation has been examined in order to find additional information which could be used to ascertain the correct model for the cation-electron interaction.

The method of application of a general relaxation formalism with unspecified chemical models is outlined.

The data obtained, although limited in quantity because of experimental difficulties, indicate that the relaxation formalism is applicable. Solution instability was the primary limitation on the collection of usable experimental data. A systematic investigation of the decomposition revealed that dilute solutions containing only small amounts of decomposition products undergo a decomposition reaction which is catalyzed by the container surface. This is a serious problem because the influence of decomposition products would probably interfere with interpretation of the data. Although the data indicated that the general relaxation formalism is applicable, they could not be used to distinguish among the various models for the cation-electron interaction.

A limited investigation of solid solutions of sodium in ethylenediamine was made to determine whether the monomer could be observed.

The two patterns observed by Vos (66) were reproduced. The sharp line above -90°C is concluded to be due to a liquid dispersed throughout the solid due to impurity. Pure ethylenediamine with sodium shows a resonance characteristic of Na metal, but small quantities of ammonia change the resonance of the solid below -90°C . No explanation is given for this observation.

The electronic structure of some complexes of lithium and ammonia were examined by use of ab initio molecular orbital calculations. The resulting wave functions were analyzed by population analysis and by contour mapping. Although the calculations leave out all long range interactions, the results are of some significance for solution chemistry.

The calculations indicate a stable complex of the stoichiometry LiNH_3 could be formed. Analysis of the charge distribution shows that a net charge transfer from ammonia to lithium occurs and that the unpaired electron avoids the region of space near the ammonia. A substantial contact interaction at nitrogen is predicted, but this represents a peak in the unpaired electron density at nitrogen rather than a large charge transfer into the nitrogen orbitals.

Calculations for $\text{Li}(\text{NH}_3)_2$ were made and analyzed. The results are compared to the results for LiNH_3 and found to be very similar.

CHAPTER II

ESR LINEWIDTHS OF THE MONOMER

In this chapter the characteristics of some electron spin resonance (ESR) patterns from solutions of alkali metals dissolved in amines are examined. The study was undertaken to obtain a better understanding of the unusual effects of the environmental parameters, solvent and temperature, on the spectroscopic parameters, hyperfine splitting constant, g-factor, and linewidth.

On the basis of previous work, other investigators (3,4,17,18,19,20,24,33,55) had suggested explanations for the observed effects of varying the environmental parameters. However, no one has given a description of the phenomena which fits all of the results. The multi-state model (19, 20,24,33) (a special case of a distribution model) is the most promising model proposed to date for quantitative purposes. The author intended at the start to collect quantitative data under conditions which would permit further testing of the proposed models. If the proposed models proved unsatisfactory, an improved model was to be sought.

The conditions required to obtain data appropriate for testing the models proved to be extremely difficult to meet.

In particular, decomposition was found to be rapid for dilute metal-amine solutions placed in containers small enough to use in the ESR spectrometer cavity. Since the study of dilute solutions was required to prevent complications caused by solute-solute interactions, only a few solutions provided information which could be used to test models. One dilute solution of rubidium and one of cesium in a mixed solvent of ethylamine and ammonia were examined in detail over a limited temperature range. The data indicate that the lines are of Lorentzian-shape, contrary to a previous report in the literature (33); thus the relaxation can probably be described by use of the relaxation formalism as adapted for ESR spectra by Freed and Fraenkel (37). This relaxation formulation of the two state model is capable of fitting an isothermal Cs solution spectrum. Insufficient experimental data were available to adequately test this model.

Sodium in solid ethylenediamine was examined in some detail because two different spectral lines had been reported for this system (66). The results indicate that one of the lines probably results from the presence of a multicomponent liquid solution dispersed throughout the solid giving rise to one of the observed patterns.

The Model

Chemical information is derived from spectroscopic observations by means of an interpretative model. An electron

spin resonance (ESR) experiment is usually interpreted by using a mathematical model based upon the formalism of the spin Hamiltonian (39). The spin Hamiltonian operator for a system contains the spin variables explicitly and all non-spin variables as parameters which are chosen either to give the best comparison of the experimental observations to the formal predictions or to satisfy some other, more fundamental experiment. A time independent spin Hamiltonian leads to stationary energy states for the spin system which, with the transition selection rules, yields a theoretical prediction of the spectral line positions. A more detailed knowledge of the processes which govern the transition probabilities is needed to predict the line shapes. The time dependent processes usually responsible for the transitions are treated by time dependent perturbation theory. Formal solutions of both the time dependent and independent Hamiltonians have been presented by other investigators. These formal solutions along with their inherent assumptions will be quoted from their work and used.

Transition Energy

The transition energy is constructed from a spin Hamiltonian which describes the coupling of the external field to the magnetic moments of the system and the inter-moment magnetic coupling in the system. Only two types of magnetic interactions are important in the metal amine solutions as observed in the ESR transition energies.

The first type of resonance shows no resolvable structure (17,18,65,66) thus requiring coupling of the electron magnetic moment to the external field only. The second type of resonance is a multiplet (2,3,4,17,18,19,20,24,33,65,66) which can be interpreted as resulting from hyperfine interaction of the unpaired electron with one or more nuclei, thus requiring coupling of the electron moment to one or more nuclear moments.

The single line is characterized by the spin Hamiltonian

$$(1) \quad \mathcal{H} = -g \beta \bar{H} \cdot \bar{S}$$

where: g is the electronic g factor for the system, β is the Bohr magneton, $\bar{S}$ is the electron spin operator, and $\bar{H}$ is the external magnetic field. This Hamiltonian for a spin of one-half leads to the transition energy given by

$$(2) \quad \Delta E = h\gamma = g \beta H$$

where: ΔE is the transition energy, γ is the frequency of the radiation for the transition, and h is Planck's constant. The Hamiltonian for the multiplet spectrum is written

$$(3) \quad \mathcal{H} = -g\beta\bar{H} \cdot \bar{S} + \sum_{\substack{j= \\ \text{all nuclei}}} g_N \beta_N \bar{H} \cdot \bar{I}_j + \sum_{\substack{j=1 \\ \text{all nuclei}}} A_j \bar{I}_j \cdot \bar{S}$$

where: g_N is the nuclear g factor, β_N is the nuclear magneton, $\bar{I}_j$ is the spin operator for the j -th nucleus, A_j is the hyperfine coupling constant for the j -th nucleus, and all other

symbols are as before. Both A_j and g are treated as scalar constants rather than the more general tensor constants because in the amine solutions only the isotropic (scalar) part can be observed. The energy levels described by the Hamiltonian 3 with one unpaired electron ($S = \frac{1}{2}$) and one nucleus (arbitrary I) are given by (9)

$$(4) E(F, m_F) = - \frac{\Delta W}{2(2I+1)} - \frac{\mu_I}{I} H m_F \pm \frac{\Delta W}{2} \left\{ \sqrt{1 + \frac{2m_F X}{(I+.5)} + X^2} \right\}$$

with: $+$ for $F = I + \frac{1}{2}$, $-$ for $F = I - \frac{1}{2}$,

$$\Delta W = A(2I + 1)/2, \quad X = H_0(g\beta + g_N\beta_N)/A(2I + 1),$$

in which $\bar{F} = \bar{I} + \bar{S}$ is the total angular momentum, $m_F = m_I + m_S$ is the Z projection of the total angular momentum, μ_I is the nuclear moment, and all other symbols are as before. The selection rule for absorption is $\Delta m_F = 1$. Then, the expression for the ESR transition energy is

$$(5) \Delta E(\Delta m_F = 1) = - \frac{\mu_I}{I} H_0 + \frac{\Delta W}{2} \left(\left[1 + \frac{2m_F^P X}{(I+.5)} + X^2 \right]^{\frac{1}{2}} + \left[1 + \frac{2m_F^L X}{(I+.5)} + X^2 \right]^{\frac{1}{2}} \right)$$

where: m_F^P refers to the upper state, m_F^L to the lower state, and the other symbols are as before.

The unknown quantities in equation 5 are A and the electronic g value. Even though measurement of the transition energy and field of any two transitions is sufficient to permit a solution of the expression for A and g , better

values are obtained by measuring more transitions and fitting equation 5 to all of the measurements using a least-squares method. The sign of A is not given by 5 (the equation is written for a $+ |A|$) since changes in sign on various terms accompany a change in sign on $|A|$ to $-|A|$ so that the transition energy expression is the same. Note that equation 5 is non-linear in A and g so an iterative procedure must be used to solve for them.

A function which satisfies equation 3 for each eigenvalue is needed for the relaxation problem to be considered later. These functions are the eigenvectors of the matrix constructed using equation 3 and a suitable complete basis.

Line Shape and Width

The shape and width of spectral lines are often determined by the dynamic interactions of the energy absorbers (or emitters) being observed. Following definitions of shape and width, the formal details of investigating a class of dynamic mechanisms using line shape information will be given.

Characterization of Line Shape (58). A compact description of the distinguishing features of a spectral line represents the desired characterization of it. This description might be a table of constants such as the moments of the line or it might be the specification of a mathematical form (called a shape function) and the values of certain constants in this form. Because of its compactness, the

latter method is preferred if it is possible. The linewidth is the value of a particular constant in a shape function. Two of the most frequently occurring shape functions for symmetrical lines are the Gaussian and the Lorentzian functions. The Gaussian function is

$$(6) \quad g(H-H_0) = C_n \exp \left\{ -.693 \left[(H-H_0) / \frac{1}{2} \Delta H_{\frac{1}{2}} \right]^2 \right\}$$

where: C is a normalization constant, H_0 is the field value at the line center, H is the field value of observation, and $\Delta H_{\frac{1}{2}}$ is the full width at one-half maximum height. The Lorentzian function is

$$(7) \quad l(H-H_0) = C / (1. + ((H-H_0) / \frac{1}{2} \Delta H_{\frac{1}{2}})^2)$$

with the same symbol definitions as before. Most ESR spectra are recorded as the first derivative of the absorption so that the first derivative with respect to H of the given forms should be compared to the recorded spectra.

The Formalism (1,37). The equations presented are the result of a second order, time dependent perturbation treatment of a random stationary process with the restriction that

$$[< |H_1|^2 \tau_c^2 >]^{\frac{1}{2}} \ll 1.$$

where: H_1 is the perturbation magnitude expressed as a frequency, τ_c is a characteristic time for the interaction, and $< >$ symbolizes a statistical average. The working equations are summarized as follows:

$$(8) \quad I_{(w)} = \frac{4}{\pi} \int_0^{\infty} G(t) \cos(wt) dt$$

where: $I_{(w)}$ is the normalized frequency distribution of power absorption and,

$$(9) \quad G(t) = \text{tr} [S_x(t) \cdot S_x(0)]$$

where: tr is the trace operator, $S_x(t)$ is the x component of spin magnetization at time, t , $S_x(0)$ is the x component of spin magnetization at time 0.

$$(10) \quad S_x(t) = \exp\{iH_0 t\} S_x^\dagger(t) \exp\{-iH_0 t\}$$

where: H_0 is the time independent Hamiltonian, $S_x^\dagger(t)$ is the x component of magnetization in the interaction representation.

$$(11) \quad \frac{d}{dt} \langle A | S_x^\dagger(t) | B \rangle = \sum_{C,D} R_{ABCD} \langle C | S_x^\dagger(t) | D \rangle$$

where C and D are states chosen to satisfy

(12) $E_A - E_B = E_C - E_D$, where E is the energy of a state,

$$(13) \quad R_{ABCD} = 2 J_{ACBD}(W_{AC})$$

$$- \sum_{F= \text{All states}} (\delta_{BD} J_{AFCF}(W_{FC}) + \delta_{AC} J_{FBFD}(W_{DF}))$$

where A, B, etc., symbolize the states of the system.

Finally,

$$(14) \quad J_{ABCD}(w) = \frac{1}{2} \int_{-\infty}^{\infty} \langle A | H_1(t) | B \rangle \langle C | H_1(t+\tau) | D \rangle e^{-iw\tau} d\tau$$

where $H_1(t)$ is the time dependent portion of the Hamiltonian for the system.

To use these formulas one must know both the form of the time dependent Hamiltonian and the zero order states. This information is used in the function given by 14. By substitution in the various equations, $I_{(w)}$ is obtained.

Freed and Fraenkel (37) indicated that this formalism predicts a Lorentzian shape for each transition and that non-Lorentzian shapes are due to superposition of lines from (almost) degenerate transitions with either different widths or different centers. It is important, however, to note that this theory predicts Lorentzian lines unless two or more transitions in the spectrum are degenerate. Recently, work by Freed (38) indicates how unsymmetrical lines can occur due to terms from a higher order time-dependent theory. The more detailed theory is not needed for this work.

The special case of hyperfine splitting from a single nucleus is especially important for the metal-amine solutions. For hyperfine splitting much larger than the line-width, equation 11 becomes (due to 12)

$$(15) \quad \frac{d}{dt} \langle A | S_x^\dagger(t) | B \rangle = R_{ABAB} \langle A | S_x^\dagger(t) | B \rangle.$$

For this case, Lorentzian shaped lines centered at $E_A - E_B$ with half-width at half-height of R_{ABAB} are predicted.

Chemical-Physical Models

Use of the formalism requires knowledge of the chemical or physical behavior causing the time dependence of the spectroscopic system. Some possible mechanisms are reviewed in this section. Formulas are presented which aid in testing some of the suggestions for the nuclear magnetic quantum number (m_I) dependent width of the ESR absorption. For solutions of cesium and rubidium in ethylamine Tuttle and co-workers (4) have suggested that the observed linewidth dependence on m_I is due to the low symmetry of the species causing anisotropy of the A and g tensors. The anisotropic species is assumed to tumble in solution which results in the observed m_I dependence by the mechanism of McConnell (48, 52, 71). No quantitative comparison of the model to the experimental results was made by them to confirm their hypothesis. This model will be discussed later even though no quantitative test of it has been made in this work.

To interpret the observed variations of A values as a function of temperature and solvent composition for potassium in a binary solvent of ethylamine and ammonia, Dye and co-workers (24) considered an equilibrium model with two or more species in (rapid) equilibrium causing a complete averaging of the A value. They were able to fit the A value variations. The potassium system exhibits very little m_I dependence of the linewidth; therefore, it does not permit a test of the linewidth predictions of this mechanism.

Cesium in ethylamine, however, does exhibit sufficient m_I dependence of the linewidth to permit comparison with the relaxation predictions of the model. They applied the model to some cesium-ethylamine solutions (33) but did not achieve complete agreement with all of the observations. Other authors (19,20) have suggested this model but made no quantitative comparisons of the model with experiment.

There is the possibility that both the anisotropic rotor and the isotropic modulation of the equilibrium model are present. Other mechanisms also exist which could give the m_I dependence or contribute to it. The necessary attribute of all such mechanisms is time dependence of the A and/or g tensors. One further example of such a process is weak exchange coupling (47).

At this point the method of application of the two state model as a special case will be presented using the previous formalism. It is necessary to assume that the processes which govern the residual contributions to the linewidth have Hamiltonians which commute with the Hamiltonians of the m_I dependent process. If this assumption is not applicable, then coupling terms for the processes must be considered. Since nothing is known of the residual linewidth mechanisms, this assumption will be used.

The time dependent Hamiltonian and the zero order states of the system are needed to calculate the m_I dependent linewidth. The states of the system are the eigenvectors of the

Breit-Rabi Hamiltonian. The time dependent Hamiltonian is assumed to be

$$(16) \quad H(t) = g(t)\beta \bar{H} \cdot \bar{S} + A(t) \bar{I} \cdot \bar{S}$$

where: $g(t)$ is the instantaneous deviation of the g value from its time averaged value, and $A(t)$ is the similar quantity for A . By definition, then, these quantities average over time to zero.

The first step in evaluating the linewidth is to construct the integral, J , of equation 14 using 16 and the zero order states of the system. This expression is

$$(17) \quad J_{ABCD}(\omega) = \beta^2 \langle A | \bar{H} \cdot \bar{S} | \rangle \langle C | \bar{H} \cdot \bar{S} | D \rangle \int_0^\infty \overline{g(t)g(t+\tau)} e^{-i\omega\tau} d\tau \\ + \beta \{ \langle A | \bar{H} \cdot \bar{S} | B \rangle \langle C | \bar{I} \cdot \bar{S} | D \rangle \int_0^\infty \overline{g(t)A(t+\tau)} e^{-i\omega\tau} d\tau \\ + \langle A | \bar{I} \cdot \bar{S} | B \rangle \langle C | \bar{H} \cdot \bar{S} | D \rangle \int_0^\infty \overline{A(t)g(t+\tau)} e^{-i\omega\tau} d\tau \} \\ + \langle A | \bar{I} \cdot \bar{S} | B \rangle \langle C | \bar{I} \cdot \bar{S} | D \rangle \int_0^\infty \overline{A(t)A(t+\tau)} e^{-i\omega\tau} d\tau.$$

with $\langle \rangle$ indicating expectations, and the bar in the time integral indicating an ensemble average.

One must now define more specifically the nature of the time variation of A and g so that the correlation functions of these quantities can be calculated. The four correlation integrals are solved (following Abragam (1), pp. 270-1) in this case by assuming that the correlation is of two random stationary quantities, $f_a(Y_1)$ and $f_b(Y_2)$, which are functions

of time through their dependence on $Y_1(t)$ and $Y_2(t)$ which are random functions of time. Then one calculates the time correlation of the two functions of interest as

$$(18) \quad G_{Ab}(\tau) = \overline{f_A(t) f_b(t+\tau)} = \iint P(Y_1) P(Y_1, Y_2, \tau) f_A(Y_1) f_b^*(Y_2) d_{Y_1} d_{Y_2}$$

where: $P(Y_1)$ is the probability that the value Y_1 occurs, $P(Y_1, Y_2, \tau)$ is the probability that the value Y_2 occurs at τ after the value Y_1 is known to occur, f_A and f_B are two functions of Y for which the correlation is desired*. For the two state problem, the functions of the random variable are δA and Δg , the change of A and g from the average values. (The two state model simply assumes that the paramagnetic species can exist in two distinct forms which have different paramagnetic observables. There is assumed to be an equilibrium between the states which follows the laws of thermodynamics.) For this model Freed and Fraenkel (37) have shown that

$$(19a) \quad \overline{A(t) A(t+\tau)} = P_I P_{II} (A_I - A_{II})^2 \exp\{-\tau/\tau_{C,A}\}$$

By analogous arguments

$$(19b) \quad \overline{g(t) g(t+\tau)} = P_I P_{II} (g_I - g_{II})^2 \exp\{-\tau/\tau_{C,g}\}$$

and

$$(19c) \quad \overline{g(t) A(t+\tau)} = \overline{A(t) g(t+\tau)} = P_I P_{II} (A_I - A_{II}) (g_I - g_{II}) \exp\{-\tau/\tau_{C,gA}\}$$

*

One should also note that using this formalism, the mean value of a derived distribution would be given by $\overline{f_A} = \int P(Y_1) f_A(Y_1) dY_1$. This is in fact the result that Dye et al. Y_1 (24,33) have used to interpret the A value variations in the solutions of potassium in ethylamine-ammonia mixtures.

where P_I and P_{II} are the fractional populations of states I and II, A_I and A_{II} are the A values of states I and II, g_I and g_{II} are the g values of states I and II, and $\tau_{C,S}$ is a correlation time for the process S. By the nature of this model, one expects both A and g to change simultaneously so their correlation times will be the same. The first two functions are positive but the third may be negative if the large value of A goes with the small value of g and vice-versa. The third term can be considered as

$$(19d) \quad \langle \delta g A \rangle = \sqrt{\langle \delta A^2 \rangle \langle \delta g^2 \rangle} \times (\text{correlation coefficient})$$

Using these results, equation 17 becomes

$$(20) \quad J_{ABCD} = \{ \beta^2 \langle A | \bar{H} \cdot \bar{S} | B \rangle \langle C | \bar{H} \cdot \bar{S} | D \rangle \langle \delta g^2 \rangle \\ + \beta [\langle A | \bar{H} \cdot \bar{S} | B \rangle \langle C | \bar{I} \cdot \bar{S} | D \rangle + \langle A | \bar{I} \cdot \bar{S} | B \rangle \langle C | \bar{H} \cdot \bar{S} | D \rangle] \\ \cdot \langle \delta A g \rangle \\ + \langle A | \bar{I} \cdot \bar{S} | B \rangle \langle C | \bar{I} \cdot \bar{S} | D \rangle \langle \delta A^2 \rangle \} \\ \left\{ \frac{1/\tau_c}{(1/\tau_c)^2 + w^2} - \frac{i w}{(1/\tau_c)^2 + w^2} \right\}$$

For each occurrence of a J in equation 15, the form given by equation 20 can be inserted. The spin integrals are easily evaluated with the known zero order functions, but the fluctuation terms (e.g., $\langle \delta A^2 \rangle$) and the correlation times are not known at this time. If no independent determination

of these quantities is available, one can adjust them as parameters to give a least squares fit of the spectrum. Anticipating some later results, the last multiplicative term will be discussed here because it will need to be simplified. The imaginary term contributes a line shift which is small; therefore, it will be neglected. The value of the real term depends on the value of w . For the J 's used in the expansion of R_{ABAB} (equation 15), there are two types of terms. In one type of term, the w magnitude is comparable to $1/\tau_c$, but these terms contribute little because the spin matrix elements multiplying it are small. In the second type of term w is zero; therefore, the term simplifies to τ_c . The terms with non-zero w are the key to an independent evaluation of τ_c . Otherwise, only products of τ_c and the fluctuation quantities occur.

The temperature dependence of the product of one of the fluctuation terms times a correlation time is given by (use A for example)

$$(21) \quad \langle \tau_c \delta A^2 \rangle = \frac{\text{constant} \exp \{ (-2\Delta F + E_B)/RT \}}{[1 - \exp \{ -\Delta F/RT \}]^3}$$

where the symbols have been previously defined. The thermodynamic parameters would be the same as those used to fit the A and g value temperature dependence.

The Experiment

Since the test of the model is based on linewidths and line shapes, the experiment must allow accurate measurement of these. The solutions must be dilute enough in metal to avoid observable concentration dependent solute-solute interactions and effects due to changes or inhomogeneities in the environment of the sample must be negligible. Due to the relative instability of the solutions, the low relative concentrations of paramagnetic material, and the sensitivity of the observables to environmental parameters, good experimental data for the system are difficult to obtain. This section presents the methods used in this investigation.

Measurement of the Spectrum

The ESR. A Varian V-4500 spectrometer with 100KHz field modulation, a Varian 12 inch magnet and a TE-102 rectangular cavity operating at 9.2 to 9.5 GHz were used. Field sweep was controlled by a V-4280A precision scanning unit or by a Helmholtz coil of 4 inches diameter which was driven by a Wavetek model 116 multipurpose VCG wave-form generator.

The field produced by the Helmholtz sweep coil was checked for inhomogeneity and non-linear sweep using a TCNE radical anion solution with linewidths of about 150 milligauss. Over the sweep range used for the amine spectra, no undesirable effects were observed. After the large magnet

was allowed to warm to operating temperature (at least one hour), it was observed to drift about 5 milligauss per minute.

Temperature Control. A special apparatus, similar to the standard equipment but with some differences, was used to control the temperature of the metal-amine solutions. This apparatus has 3 parts: a heat exchanger, a transfer tube, and a sample holder. The heat exchanger is a flat coil of one-quarter inch copper tubing with inlet and outlet through vacuum insulated glass tubes oriented with their axes perpendicular to the plane of the coil; an arrangement which permits a constant heat exchange length regardless of coolant level. The vacuum insulated transfer tube holds the heater-sensor of a V-4540 Varian temperature controller, and the sample holder is a vacuum insulated fused quartz Dewar of 11 mm od: which passes through the cavity. When the flow rate of dry nitrogen was maintained constant through this controller, a thermocouple at the sample indicated that the temperature was constant to within $\pm 0.1^{\circ}\text{C}$.

Field Measurement. The magnetic field was measured with a proton gauss meter described by Buss and Bogart (13,49). The proton magnetic resonance (PMR) was detected by using a 400 Hz field modulation and phase sensitive detector. The PMR signal was displayed on an oscilloscope and used to mark the ESR spectrum as it was recorded in a first derivative mode. The difference of field inside and outside of the

cavity was measured to be about 0.15 gauss. The frequency of the PMR was measured using a Hewlet-Packard Model 524C frequency counter with a model 525A frequency converter to permit the approximately 15 MHz signal to be measured.

Klystron Frequency Measurement. The klystron frequency was measured with a calibrated wavemeter or by comparison to a harmonic from a Micronow calibrator as described by Kuska (49). This frequency measurement should be accurate to 0.1 MHz.

Use of the CAT. Some spectra were recorded in a Varian computer of averaged transients (CAT), C-1024. When the CAT was used the field was swept by the Helmholtz coil (see above). The C-1024 sweep was triggered by a pulse from the wavetek wave form generator so that the sweep of the field and of the CAT were always started synchronously. The ESR spectrum was stored in the first half and the magnetic field markers (proton resonance signals recorded directly) were stored in the second half of the CAT memory. The forward and reverse scan (increasing and decreasing of field with time) of the spectra were recorded so that differences in electronic delay time for the ESR and proton signals could be measured and the field measurement corrected. The spectra were recorded in a time period short enough so that the drift of the large external field was a negligible perturbation on the spectra (see above). After the spectra were recorded in the CAT, a graphic permanent display was produced by

recording the contents of the CAT memory on an X-Y recorder. In this recording the ESR and field markers were displayed with their scales overlayed by using the overlay feature of the C-1024 (see Figure 2). The ESR spectrum was then punched on 80 column cards for further processing by a digital computer (CDC 3600).

Preparation and Use of the Samples

The Rubidium Solutions. These solutions were prepared in a Pyrex vacuum system with all Teflon valves and joints. The sample tube and the associated tube from which the rubidium (Rb) metal was distilled were made of fused quartz.

The glassware was rinsed with a cleaning solution of 2.5% HF, 1% acid soluble detergent, 33% nitric acid, and the remainder distilled water. Rinsing with the cleaning solution was followed by rinsing with distilled water six to ten times. If the glassware would later be in contact with a metal solution, it was further treated with hot aqua regia, again rinsed with distilled water six to ten times, and then, rinsed three times more with triply distilled water.

The vacuum line was evacuated using a Consolidated Vacuum Corporation MCF-60 three stage oil diffusion pump with a Cenco "High Vac 7" used as a backpump. The pumps were separated from the working section of the vacuum line by a liquid nitrogen cooled glass trap. A Dow Corning

silicone oil was used in the pump. An ion gauge was attached near the cold trap on the manifold side of it. A two centimeter diameter tube acted as the manifold to which the various equipment for the solution preparation was attached by means of 5 mm Teflon endjoints made by Fisher-Porter.

The solutions were to be composed of a binary solvent of ethylamine and ammonia. In order to make a known solvent composition, the following procedure was employed. A solvent reservoir containing a pure liquid solvent and a glass bulb with a valve were attached to the vacuum manifold. The glass bulb was immersed in a constant temperature bath. To prepare a measure of solvent, the solvent reservoir was brought to a known, reproducible temperature by using a slush of a pure liquid in equilibrium with its solid. The amine or ammonia vapors were then allowed to equilibrate with the constant temperature bulb. The bulb was closed after the system reached equilibrium, trapping a reproducible amount of solvent in the bulb as vapor. The glass bulbs used for different solvents were calibrated by condensing the vapors in a small glass tube and weighing them. The ethylamine bulb gave 0.01027 moles and the ammonia bulb gave 0.00101 moles so that a sample with one measure from each would be 0.91 mole fraction ethylamine and 0.09 mole fraction ammonia. The standard error from replicate measures of these numbers was less than 0.005 mole fraction.

The ethylamine reservoir was equilibrated by using a water slush and the ammonia reservoir by using a 1,2-dichloroethane slush. The gas bulbs were kept near 25°C with an absolute control of $\pm 0.05^\circ\text{C}$.

Before the metal solution was prepared, the container for it was rinsed with ammonia as follows. The vacuum system was evacuated to at least 5×10^{-6} torr. The vacuum line had attached to it an extra vessel which contained a solution of an alkali metal in ammonia. With the pump closed from the line, some of the ammonia was distilled into the sample tube using a dry ice-propanol bath. Then the ammonia was removed to its original container by distillation. The metal ammonia solution was frozen, pumped on high vacuum, and thawed. This procedure was repeated ten times. After the rinsing with ammonia, the alkali metal to be used to make the solution was distilled to form a thin film on the tube above the region in which the solution was to be contained. Then a portion of ethylamine was measured in the gas bulb and transferred to the sample tube by cooling the sample tube. The metal was introduced into the solution at this time by condensing some of the ethylamine on the metal and letting a few drops of solution run down into the container. Then a portion of ammonia was measured and transferred into the container by condensing it into the container. The solution was frozen and the system was opened to the high vacuum pump. The sample was sealed by fusion of the

container above the solution and removed from the vacuum line. The tubes were sealed so that at room temperature only about 10-20% of the volume of the tube was not filled with solution. This procedure gave solutions which were not saturated with metal. Most of the solutions were not very stable but two were stable enough to provide some ESR spectra.

The original ethylamine (Eastman anhydrous) was probably not ammonia-free because it was dried over sodium-potassium alloy before use. No VPC analysis of this solvent was made. The ammonia (Matheson anhydrous) was dried over alkali metal before use.

The samples were stored in liquid nitrogen until used. The ESR spectra were recorded as described above, by using the C-1024 technique. During the recording of the spectra care was exercised to avoid overmodulation, saturation, and effects of field drift and sweep speed distortion.

The Cesium Solutions. No fresh solutions of Cesium (Cs) which were both dilute enough for use and stable enough to measure could be prepared in containers small enough to fit into the ESR cavity. Because of this instability of dilute solutions in small containers, a flow system was built to provide a steady source of the Cs solution. Only one successful run was made with this flow system, which was intended

to take advantage of the fact that at low temperatures and in large vessels, solutions could be made which were stable for long periods of time (months at least).

The flow system had a large reservoir in which the solution could be prepared and kept. This reservoir was connected to a transfer tube which went through the cavity to another storage reservoir. The first reservoir which contained the solution was kept at -78°C in a dry ice-alcohol bath. An overpressure of about two atmospheres of He was kept on the solution to cause it to flow. The solution transfer tube was enclosed in a Dewar into which temperature controlled gas (obtained as described previously) was blown. The transfer tube held the solution long enough for it to reach thermal equilibrium with the gas. A triple walled Dewar which was of fused quartz and evacuated between the outer two walls passed through the cavity. The solution flowed through the inner tube and gas which had previously reached thermal equilibrium with the solution flowed between the inner two walls. A thermocouple could be placed in the intermediate region to measure the temperature of the gas.

Matheson ethylamine (stated purity, 98.5%) was freeze purified prior to use. After freeze purification, no ammonia or methylamine could be detected by VPC using a column of 15% tetrahydroxyethylethylenediamine and 5% tetraethylenepentamine on chromosorb W 60/80 mesh (64). Before preparation

of the final sample, however, the solvent had been allowed to stand over Rb metal for a few days and then over a Cs metal for a few days at room temperature. No blue solution could be obtained over the Rb metal, but with the Cs metal a blue solution formed very slowly (over a period of days). After the blue Cs solution formed, a sample of the vapor over the solution revealed ammonia (the exact amount was not determined but the VPC peak heights were in a ratio of about 1:25, $\text{NH}_3:\text{EtNH}_2$). An attempt was made to prepare a Cs solution at -78°C from this solvent. The solution could not be made concentrated enough to use. In order to increase the solubility of the metal, about 3 volume percent at -78°C of 99.99% ammonia (J. T. Baker Co.) was added to the ethylamine. After the ammonia was added a solution of sufficient concentration of metal to study could be obtained.

About 1.5 liters of solution were in the bulk vessel. An optical sample was taken from this bulk vessel and then the flow system was assembled and evacuated. The ESR spectra were taken with the solution flowing in the flow system. These spectra were recorded using an X-Y recorder. As for the Rb spectra, the spectrometer was operated to avoid saturation, overmodulation, and sweep distortion. The spectra were recorded by scanning without markers. Then one scan was field marked. Then the $m_I = -1.5$ line was expanded and field marked to give a measure of the absolute width.

Sodium in Ethylenediamine. Spectra of sodium (Na) in ethylenediamine (en) (27,40) were recorded for solutions

below 0°C. The en is a solid at these temperatures. Two preparations of en were used. The first had been freeze purified and then had been allowed to stand over potassium metal for a few months. There had been significant decomposition during storage as judged by the precipitate in the solvent vessel. Before use the solvent was degassed by repeated freeze-pump-thaw cycles. The second preparation of en was also freeze purified. However, in this case the en was not allowed to stand for an extended period of time with metal. The liquid was distilled over potassium metal and the resulting solution allowed to remain overnight. Then the solvent was removed from the potassium by distillation to a clean storage vessel. The en was degassed and then kept in the storage vessel until it was used a few days later. The ammonia used in the mixed solvents was 99.99% anhydrous ammonia from J. T. Baker Co.

Data Analysis

The data analysis to be discussed in this section is the numerical analysis used to find the parameters which give the best fit of the zero order Hamiltonian (equation 3) solutions (equation 5) to the observed transition energies and fields of the spectrum, and to find the parameters which give the best linewidth constants (equation 15) to the observed linewidths of a spectrum. The important questions,

how to obtain the best estimate of the parameters and how to obtain an estimate of the uncertainty in the knowledge of these values will be briefly reviewed. After a brief explanation of the methods used to obtain parameter estimates and uncertainties, the procedure used to analyze the data from the hyperfine splitting pattern will be explained.

Parameter Estimation

The estimation of parameters in equations which are presumed to describe observations can be done in several ways. The method chosen for this work is to apply a least squares criterion, i.e., to take as "best" estimates of a set of parameters those which minimize a functional, ϕ , of the form

$$(22) \quad \phi = \sum w_i (\text{Res}(i))^2$$

where w_i is the weight at the i -th observation, $\text{Res}(i)$ is the residual at the i -th observation.

Two important questions which arise are: 1) How does one specify the weight? 2) How does one formulate the residual ($\text{Res}(i)$)? These questions have been considered by Wentworth (67) for non-linear parameter estimation (also applicable for problems linear in the parameters) using a method due to Deming (28). The summary given here will parallel the work of Wentworth. For data from samples described by independent gaussian distributions of errors with individual variances, a maximum likelihood parameter

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estimation leads to minimizing 22 with w_i defined as proportional to the inverse of the variance for the distribution from which the i -th point was taken. Since it is not possible in general to consider all error to reside in a given one of the observables, however, one minimizes the functional

$$(23) \quad \phi = \sum_{i = \text{observations}} \sum_{j = \text{variables}} w_{ij} R_{ij}^2$$

where w_{ij} is the weight of the i -th observation j -th variable R_{ij} is the difference between the measured and calculated value of the j -th variable using data from the i -th observation,

with the constraint that the function (F) which relates the parameters sought and the observed variables is zero at each point, i.e.,

$$F(\text{parameters, observables}) = 0.$$

This formulation treats each of the variables symmetrically so that it is not necessary to assume one or more of the variables to be known exactly. This form gives a maximum likelihood estimate if each of the R_{ij} is from an independent distribution with variance $\sigma_{ij}^2 = 1/w_{ij}$. Wentworth, using the method of Deming, with the above assumptions shows how to derive the normal equations used to obtain corrections to a given set of parameter estimates. The result is

$$(24) \quad \begin{matrix} \bar{B} \\ B \end{matrix} U = \bar{C}$$

where

$$(25) \quad (\bar{B})_{ij} = \sum_{K=1}^{\text{observations}} \frac{\partial F_K}{\partial u_i} \frac{\partial F_K}{\partial u_j} \cdot \frac{1}{L_K}$$

$$(26) \quad L_K = \sum_{m=1}^{\text{variables}} \left(\frac{\partial F_K}{\partial X_m} \right) \frac{\sigma_{X_m K}^2}{\sigma_o^2}$$

$$(27) \quad (\bar{C})_i = \sum_{K=1}^{\text{observations}} \frac{F_K}{L_K} \frac{\partial F_K}{\partial u_i}$$

F_K is the value of the constitutive equation with the present parameter estimates at the K-th observation

X_m is the m-th observable

u_i is the i-th parameter

L_K is the inverse of the total weight at the K-th observation as given by 26

$\sigma_{X_m K}^2$ is the variance of the X_m -th variable at the K-th observation

σ_o^2 is the variance of unit weight

$(\bar{U})_i$ is the negative of the i-th parameter correction.

An operational procedure to make use of these equations is as follows: Using initial estimates of the parameters, solve for the corrections to the parameters using equation 24. Then form the corrected parameters using the elements of $\bar{U}$ and iterate the above procedure until convergence is obtained.

Before considering the question of convergence, a more powerful method to obtain a non-divergent solution to 24 will be considered. A divergent solution is one which on successive iterations of parameter corrections gives a

sequence of successively larger sums of squares of residuals rather than the desired decreasing sequence. The sum of squares of residuals being considered is (67)

$$(28) \quad S = \sum_{K=1}^{\text{observations}} F_K^2 / L_K$$

The simple cycling procedure often diverges when the initial estimates of the parameters are very different from the best estimates or when the sum of squares of residuals is very non-linear in the parameters. Wentworth suggests a method for overcoming this convergence difficulty but in this work another method has been found much more efficient. A damped least squares method which has been discussed and compared to other methods by Pitha and Jones (57) was used. It is a modification of a procedure which is designed to simultaneously minimize the step length, $\bar{u}$, and the functional S . The iteration step of the method is

$$(29) \quad \bar{u} = (\bar{\bar{B}} - P \bar{\bar{A}})^{-1} \bar{C}$$

where: $\bar{\bar{A}}$ is a matrix which has diagonal elements equal to those of $\bar{\bar{B}}$ and zero off diagonal elements, P is an adjustable constant which is chosen to cause S to be a minimum (optimized at each iteration). A quadratic search procedure on P has been found to be very efficient.

Two basic questions about convergence must now be considered. The first is how to tell when a minimum of S has been found and the second is how to establish that it is the

lowest minimum of S . The first question is the simpler of the two and will be considered first. The most direct test for a minimum is to examine the first derivative of S with respect to each of the parameters to see whether it is zero. (Actually a second derivative test is necessary to establish a minimum but this will not be examined.) Equation 27 is proportional to this derivative if it is assumed that the weighting function, L_K , is independent of the parameters. Actually, L_K is not independent of the parameters, but its dependence is much less than that of the F_K so that equation 27 is a good approximation to the quantity of interest. Consider the relation of the parameter corrections to the elements of the vector given by 27. Equation 24 shows that the parameter corrections are given by a matrix product of $\bar{C}$ and of the inverse of $\bar{B}$. This means that if the elements of $\bar{C}$ are zero then the parameter corrections will also be zero. However, it must be pointed out that the parameter corrections can be small from other causes such as large elements in $\bar{B}$. Nevertheless, one way to test approximately for convergence is to examine the magnitude of the parameter corrections. If they are below some predetermined acceptable value, then the iteration is terminated. The point that this is an approximate minimum test is important and implies that the predetermined level for termination should be significantly smaller than the required accuracy of the parameters. This test is used because it is efficient since

the quantities needed have already been calculated, but some more refined techniques should be used until experience has been gained with any given type of problem.

Another technique which can be used in conjunction with that just discussed is to start with different sets of initial guesses for the parameters to see whether the same parameter values within the needed tolerance are given at convergence. If the different initial parameter estimates give the same result, it is likely that a minimum has been found.

When a minimum has been found, one must ask whether it is the lowest minimum in the functional being minimized. There is no general method known to the author to be sure that a minimum is the lowest or "global" minimum. However, certain considerations can help to solve the problem in many cases of practical importance. An investigator usually knows approximate ranges within which the parameters must lie. If unusual values of the parameters are obtained one might suspect that the minimum of interest has not been found. In other cases, the investigator knows approximately what final value of S is expected. If the value obtained is larger one might suspect the possibility of convergence to a "local" minimum. In such cases a different minimum may be found if significantly different initial guesses for the parameters are employed. For many problems, however, one can never show that convergence to the lowest minimum has been obtained.

When "best" parameters have been obtained, there are some significant points which must be considered about the meaning of the parameters. It is important to know how error in the data effects the values of the parameters. It is also important to know whether the range of the data is sufficient to specify the parameters to within the desired accuracy, and if so, how well the data determined the parameters. Finally, it is important to know how an error in one parameter estimate is likely to effect the estimated values of the other parameters. These important points have been studied and are understood for least squares estimates using mathematical models which are linear in the parameters. For models which are non-linear in the parameters the situation has been studied but the answers are much more restricted. Briefly, the answers may be summarized as follows. For the non-linear estimation problem the inverse of the matrix $\bar{B}$ (equation 24) is proportional to the approximate variance-covariance matrix, just as the inverse of the coefficient matrix of the normal equations is proportional to the variance-covariance matrix for the parameters of the linear estimation problem. In order to find the approximate variance-covariance matrix the proportionality constant which multiplies $\bar{B}^{-1}$ must be found. The proper value of this constant is the magnitude of the variance of unit weight. Usually this constant is unknown, but Deming points out that an approximation to it is given by the sum of squares of the

residuals divided by the number of points minus the number of parameters. (This divisor is often called the degrees of freedom of the problem.) The normalized inverse of $\bar{B}$ is only approximately the variance-covariance matrix since it is based on equations linearized in the parameter corrections and these equations only approximately describe the functional, S , and the normalization constant is also only approximate.

As the name suggests, the variance-covariance matrix for the parameters contains the desired information about the distributions on the parameters. The diagonal elements are the variances for the corresponding parameters, and the off diagonal elements contain the covariance or the correlation coefficients for the parameters. Other statistical quantities related to these may be calculated from the variance-covariance matrix elements but the derived quantities will not be discussed here. The above information answers most of the questions raised except the point alluded to when questioning how errors in the data affect the parameters. The obvious influence of uncertain data is that the variance of the parameters goes up as the data become more uncertain, but there is another more subtle influence possible. In a non-linear problem there is no certainty that the parameter estimates are unbiased, i.e., they may not converge to the true value as the number of data points is increased, holding the variance of the data constant. This problem can be overcome by having better data since

this results in a distribution with smaller variance for the parameters which tends to make any bias less important.

The above techniques have been used in the analysis of the data presented later. The variances on the parameters indicated were derived as indicated above. A program to carry out the manipulations and print the results was coded in FORTRAN for a CDC 3600 computer. The CDC 3600 carries a 48 bit word (the equivalent of 10-11 decimal digits in floating point form) to represent each number.

In summary, the constants in the equations which are presumed to describe the data have been adjusted using the method of generalized, weighted least squares analysis. The outputs of the analysis are estimates for the parameters, estimates for the variances (or standard error) on the parameters, and estimates of the correlations among the parameters.

Reduction of Raw Data to Line Positions and Widths

The data which are obtained from the ESR are not suitable for direct application of the mathematical models of the spectroscopic phenomena. Since the data for the Rb solutions and for the Cs solutions were in somewhat different physical forms, they needed different treatments to yield data which are suitable for studying the model. Therefore, the reduction to widths and positions of the different data will be discussed separately.

Rb Data. The Rb data were obtained using the rapid scan method outlined in the experimental section. Therefore, the data were recorded in the CAT and then from it recorded in two forms: on chart paper (see Figure 1) with the field markers overlaying the ESR lines, and on punched cards. A spectrum, using this technique, is obtained region by region where a region means a portion of the spectrum without significant parts which are not of interest. The Rb spectra were recorded one line at a time with a scan width sufficient to obtain the outer portions of the line. In the cases where Rb^{85} and Rb^{87} lines overlap, both lines were recorded simultaneously. The widths and positions of the lines are such that the lines from a given isotope are well separated in these solutions. Thus, a single line or a pair of lines is represented in each set of punched cards from CAT. From the plotted recording, the fraction of a full scan corresponding to a particular magnetic field could be determined. Usually about five or more markers were used for each line. The recording was arranged so that both the forward and reverse scan were recorded. The field values obtained from the recording were punched on cards and given to the CDC 3600 computer along with the CAT punched, numerically coded spectrum. The computer fitted one or more Lorentzian lines to the segment of the spectrum. (No significant deviations from Lorentzian shape could be found.)

The fact that a forward and reverse scan were used is important since the field marker was amplified by one channel of electronics and the ESR signal by another channel of electronics, and the different electronic pathways have different delay times. What this means is that two signals which were input to the amplifiers at the same time may arrive at the recorder at different times. This was noted to happen when recording the Rb data. However, the fact of the different delays does not affect the results reported since when both upfield and downfield scans are used, the relative delays are equal but in opposite field directions so that an average of the two scans gives cancellation of the delay. This procedure was used in obtaining the positions of the lines for the Rb solutions.

Each line was represented by 100 to 200 points in the data analyzed by the computer. The results given by the computer analysis of the spectra include the width and positions of the lines and estimates of the standard error of these quantities.

Cs Data. The data for the Cs solution were recorded directly on an X-Y recorder. Recording the data was done in several steps as described in the experimental section. The positions of the lines were obtained directly from the chart by using the field marking and linear interpolation. The variance on the position cannot be estimated directly when using this technique, but it is very likely to be equal for

all of the lines. This equality of the variance is an important input for the program to calculate A and g values.

The next quantity of interest is the relative widths of the lines since the relaxation information lies in this observation. Examination of the lines reveals that the lines are very nearly Lorentzian in shape (see Figure 4). The Lorentzian shape means that the area is given by

$$(30) \quad A = \text{constant} \cdot I \cdot \Delta H^2$$

where: A is the area of the integrated line, I is the peak-to-peak intensity of the first derivative presentation, and ΔH is the peak-to-peak width of the first derivative presentation. Since the radical under observation has hyperfine splitting from one nucleus, the lines should all have equal area under the conditions of the experiment. (In cases which have been examined carefully, the lines do, in fact, have equal areas within experimental error.) Using the equal area hypothesis along with equation 30, one can obtain the most sensitive measure of the relative widths of the lines by measuring I and calculating ΔH from it. Then,

$$(31) \quad \Delta H = \text{constant} / I^{\frac{1}{2}}$$

where the constant in 31 is independent of m_I , the nuclear magnetic quantum number.

The relative variance in the widths can be calculated from the formulas for the propagation of error and the

assumption that I can be measured to the same absolute accuracy for each line of the spectrum. This assumption is plausible since the electronically generated noise on the signal is the main limiting factor in the determination. Under this assumption the relative variance on the width is given by

$$\begin{aligned}
 (32) \quad \sigma_{\Delta H}^2 &= \left(\frac{\partial \Delta H}{\partial I} \right)^2 \sigma_I^2 \\
 &= \frac{\text{constant } \sigma_I^2}{I^3}
 \end{aligned}$$

The one remaining quantity needed is the absolute width of the lines. This was obtained by measuring the absolute width of one line in the pattern. The measurement was obtained by displaying one line with field markers on a 15 inch recording so that the features were clearly shown. This permitted measurement of the peak-to-peak width as well as the shape of the line being examined. For Lorentzian lines all other widths can be calculated using equation 30 since this one line allows the constant to be determined.

Reduction to Spectroscopic Quantities

After the data had been treated as listed above, they all had the same form, i.e., the quantities line position, relative variance on line position, line width, relative variance on line width, and transition energy were determined. The A and g values could be calculated directly with equation 5 and the parameter estimation scheme outlined before.

Preliminary analysis indicated that all of the quantities in the relaxation equations (using 15) could not be determinable from the data. In particular, the correlation time and the mean squared width of the distributions are separable only if the nuclear relaxation is a significant factor in the line widths of the observed spectrum. Since this was not expected, a method of analysis was adopted to seek optimum information about this separation. First the analysis used only the terms with $w = 0$ in equation 15. This reduced to solving for the products of the correlation time and the second moment of the distribution, e.g., $\tau_c \langle \delta A^2 \rangle$ plus the residual width. Then the full analysis was performed with all terms to see if the correlation time could be found. In no case was there sufficient information to find this constant.

It is important to realize that with spectra from systems having large hyperfine coupling constant, each line is observed in a different magnitude of external field. This implies that the energy level diagram for the system changes from line to line in both position of levels and in their characteristic dependence on parameters such as A and g , for example. This means that in order to obtain the correct use of the relaxation formula, one must obtain the complete analysis of the energy levels at each transition since at relatively low fields the mixing of the high field states (m_I, m_S) is a function of the field.

Results

The original purpose of this experimental work was to test the proposed mechanisms for the linewidth dependence on m_I ; therefore further testing the model for the environmental dependence of the A and g values. As was pointed out in the previous chapter, a sizable amount of qualitative and semi-quantitative information is available concerning the dependence of A and g on various external parameters of the system. At least the qualitative trends are believed to be well established. However, no quantitative explanation of these trends which fits all of the observations has been demonstrated to be completely satisfactory. The previous sections have indicated the type of experimental results which are necessary to test the linewidth mechanism. Previous work from various laboratories indicated that the linewidths are sensitive to some unknown parameters (18), with concentration of metal probably being one of them. Therefore, it was thought necessary to make measurements at low enough metal concentrations so that all concentration effects were absent; thus showing the intrinsic m_I dependence. Although the preparation of stable solutions has been reported (24), the early attempts to make such solutions

proved unsuccessful and so a more thorough examination of this problem was made. The first part of this section will concentrate on the preliminary examination of the suitability of various systems of solvent and metal, and on the subsequent study of the stability of the solutions under various conditions.

The m_I dependence of some samples was studied quantitatively. The analysis of these measurements will be shown after the preliminary data are presented. Then, the results of a study of solid solutions of sodium in ethylenediamine will be given.

Qualitative Results

The experimental ESR spectrum and the solutions must have certain well-defined characteristics to be used for the study of the m_I dependent linewidth. These characteristics include stability, a relative concentration of the m species to total metal so that m is observable at low metal concentrations, an easily measurable m_I dependence, and a line separation sufficiently larger than the width so that the lines do not overlap significantly.

The Type of Spectrum for Several Systems. A survey was made to assess the properties of several systems as possibly usable for studying the m_I dependence. Studies by ESR for a relatively large number of alkali metal-amine systems have been reported (see for example (26)).

These studies have either reported only if paramagnetism is observed or have reported the spectra and/or the A and g values as a function of temperature. In many cases the reported data are not sufficient to show whether the system would be useful to studies of the m_I dependence of linewidth. In others, the reported data suggest that the systems may be useful. Therefore, ESR spectra for a number of alkali metal solutions in various amines were recorded. In most cases, the solvent had not been carefully purified but had been dried by reaction with excess alkali metal (similar to the procedure used for most work reported in the literature). The results are of qualitative value in representing the expected spectral characteristics since no features are expected to exhibit large changes because of a small amount of impurity.

The ethylamine and propylamine samples used dissolved the alkali metals very slowly, to form very pale blue solutions. The ethylamine samples, when checked by VPC (vapor phase chromatography) analysis, always showed some ammonia (by retention times) after a blue solution had formed, even if none had been detected before solution preparation. The propylamine sample was not checked by VPC. The solutions in ethylamine (with ammonia) showed a hyperfine pattern from one metal nucleus and a single line near the middle of the pattern. Because of the greater number of lines in the

cesium and rubidium spectra, they were studied most extensively. The result was that both the signal to noise ratio and the stability were poor. The n-propylamine sample (of Cs) was blue and gave an ESR signal. The stability and signal to noise ratio of these systems were not good enough to permit them to be used in the linewidth study.

Some of the diamines solutions do not give an observable ESR hyperfine splitting pattern but do give a single line resonance. In some cases the hyperfine split resonance is observed, however, but in all cases examined two problems occur. All the alkali metals are quite soluble in these lower diamines (ethylenediamine; 1,2-propanediamine; 1,3-propanediamine) and thus very deep blue solutions can be formed, but the monomer (m species) is not favored by these solvents so that its relative concentration is small. The second problem is that, if observed at all, the lines are relatively broader in these solvents. Taken together, these results mean that when the monomer is observed, its ESR spectrum is not useful for linewidth studies since the lines overlap and the single line has become concentration broadened, implying that some concentration dependent fine broadening mechanisms have become operative. For the spectra which were recorded, the A and g were not measured since these measurements were not necessary for the immediate purpose of the investigation.

For the solutions in the diamines, a relatively larger concentration of metal could be achieved and consequently the decomposition was not such a severe limitation. Some spectra of diamine solutions were recorded at temperatures as high as $+80^{\circ}\text{C}$. Even though the solutions were decomposing, eventually turning colorless (pale yellow if enough metal were present) after short periods at high temperatures, they did remain blue long enough for the spectra to be recorded. It should be noted that at higher temperatures the monomer can be seen more easily at constant metal concentration.

Some other systems surveyed included metals in methoxyethylamine and in mixed solvents of dioxane and the diamines. These solvents offered no advantage over the others, and the stability was noticeably less, so only a few solutions were prepared.

After the survey of solvents, a choice of a mixed solvent of ethylamine and ammonia was made. This mixed solvent gives relatively narrow lines, and the monomer can usually be observed. Instability does not seem to be more of a problem than with the other systems.

Systematic Investigation of the Decomposition. In spite of the fact that stable solutions have been reported in the literature, the preliminary search for a suitable system to study was hindered by the persistent tendency of the solutions to decompose, leading to a loss of blue color and paramagnetism. It became apparent that if

the linewidth study were to be continued, the decomposition had to be either controlled or eliminated. Therefore, in order to better understand the factors involved in this reaction, a systematic investigation was made of the conditions which influence solution stability. The first question to be considered is whether some impurity is responsible or whether the reaction occurs with solvent alone. No direct method is available to answer this question, so some experiments were performed which gave indirect evidence. First, the solvent was kept over metal for a long time (months) to remove any residual reactive materials which were present in it. In this case the source of reducible impurities must be either the vacuum system or the metal. The metal was distilled several times prior to use after its last exposure to the atmosphere, so that one would expect any easily reduced materials in the metal to have been reduced by the metal vapor during distillation.

Two sources of impurities can arise from the vacuum system: 1) residual materials on the walls of the vacuum system, and 2) leaks in the system (including outgassing the parts or diffusion of gas by or through parts). The vacuum system was constructed such that all parts not made of Pyrex were made of Teflon (e.g., valves, joints). The pumping system has been described previously, and Appendix I gives the description of the valves and joints invented to give a vacuum tight system. When these parts were used, the

system showed no pressure change when the joints were rotated or when the valves were moved with the pressure at 2×10^{-7} as measured with an ion gauge. Therefore, the leaks were considered removed.

What about impurities on the walls of the apparatus used? Three approaches were used to examine this question. The system was repeatedly flamed until the sodium D line caused the flame to be yellow. The system was repeatedly exposed to the vapors of dried ammonia or ethylamine and evacuated cyclically, and the solution containing part of the apparatus was rinsed (poured in, left to stand for up to 3 days, and poured out) with a solution of alkali metal in ammonia.

With any of these procedures, the results were about the same; the blue color faded in about 10-20 minutes for solutions stored in a 2 mm i.d. tube but slower in larger diameter tubes. This was clearly shown in one experiment in which the solution was contained in a tube which had two sections of different diameter. The solution faded in the small tube much more rapidly than in the larger diameter tube. Subsequent tests showed that very pale blue solutions could be made and kept in 2 cm tubes for a few hours before the color faded. The temperature for these experiments was near room temperature and the total metal was low enough so that the color was pale blue (easily transparent) in a two centimeter tube. The decay of one sample was observed

spectrophotometrically and the results are recorded in Figure 10. Note the fact that the decay is very nearly zero order.

One further experiment was performed which is important. It has been reported that heating an alkali metal in the Pyrex vessel which is to contain the solutions causes greater stability for ammonia solutions (44). To test the applicability of this result to the amine system, a similar test was made using rubidium metal. The metal was refluxed in the sample tube until the tube became lightly amber in color (about 15 minutes). Then all of the metal was distilled into a side arm of the vessel to cause one part of the vessel to have no metal in it. Then solvent was distilled into the metal-free section of the vessel and frozen in liquid nitrogen. The vessel was removed from the vacuum line by fusion of the connection. A solution was made by carefully pouring the solvent onto the metal and then removing the light blue solution which formed into a 2 mm i.d. part of the cell. The solution behaved as in previous preparations, decomposing after a few minutes. Then a new solution was made and the experiment was repeated. After a few of these cycles the solution stability had increased markedly, to give a half life of a few hours. This same solution has now been kept at -20°C for 12 months and is blue, showing no signs of decomposition, i.e., no precipitate is formed and the small amount of metal present is shiny and does

not appear reacted. At the normally observed reaction rate one would expect 0.5 cc of metal to have reacted, but in fact, 1 percent of this amount could have been detected and has not reacted.

The Flow System. The results of the study of the decomposition indicated that a solution could be made stable for longer periods of time if the volume of the sample were large compared to the surface area. These results could be utilized in a flow system in which the solution is kept in a large container until just before the measurement and then allowed to flow into the measurement cavity. Because of the nature of the ESR spectrometer, only a small volume of solution can be placed in the resonant cavity. A flow system was built to make use of these facts, and was used for a number of runs. However, certain difficulties in the design and construction of the flow system were never overcome.

One would like to have the flow system designed in such a manner that only a negligible fraction of the solution decomposes before the measurement is completed. In a large vessel (e.g., a 10 cm diameter cylinder) the decomposition rate of the solutions is negligible (months) for solutions which are no more than 10^{-5} molar in total metal and at -78°C . Therefore, the only concern is decomposition in the tube which transfers the solution to and through the cavity. From the decomposition standpoint then, fast flow is desirable.

However, from a practical standpoint, since linewidth and shape measurements require a long time, a slow flow, which conserves solution, is better. From the known reaction rates (approximate) and the geometry of the flow system, the rate for this flow system which gave less than 5% decomposition at the cavity was 1 ml/min. This rate was also reasonable from the viewpoint of temperature control, since during the transfer stage the temperature of the liquid must be changed from the value in the storage container to that desired in the cavity. The storage container must be kept cold (-78°C proved sufficient) to prevent differential volatilization of the components of the ethylamine-ammonia mixture.

The control of the rate of flow proved to be the most difficult problem. The valve for this job must be: 1) free from influence on the solution; 2) operable over a wide temperature range; and 3) relatively insensitive to small temperature changes. No commercial valve with these properties could be found. Plastic components (e.g., Teflon) do not satisfy criteria 2 and 3. The author designed and built a number of glass valves, none of which worked completely successfully even though the runs were made using these valves. Breakage of these valves or loss of flow control were the primary difficulties encountered in using the flow system.

If a volatile solvent is used, the pressure obtained as the temperature is increased gives problems. The large vessels used in this experiment will not withstand large pressures so that the range of temperature is limited.

A final difficulty to be mentioned is lack of stability in the transfer tube. In every case, the stability in the transfer tube was less than expected based on the previous decomposition studies. Figure 10 shows a quantitative decomposition study using the flow system. The decomposition of both the single and the multiplet pattern is first order in contrast to the zero order decay shown in Figure 10. The difficulty probably arises from poor evacuation of the transfer tubes. Since about 4 feet of 2 mm i.d. tubing is involved, it is not surprising that the system might be contaminated with impurities due to the large surface area involved. This stability is much less than in the bulk, implying impurity contamination during transfer. The first order decay is also consistent with this assumption.

Quantitative Results

Solutions in Ethylamine-Ammonia Mixtures. Of the many samples examined, quantitative linewidth data were collected on two solutions and line position data on a third. These solutions were thought to be dilute in metal, and did not decompose noticeably prior to use so that very little decomposition product could have been present in the solutions.

Figure 3 gives an optical spectrum of the solution used for the Cs run taken in a 1.0 cm Pyrex cell. Figure 4 shows the line of the hyperfine pattern for the Cs solution corresponding to $m_I = 1.5$. Also in Figure 4 one can see the superimposed line shape of a Lorentzian and Gaussian shape function. The line is very nearly Lorentzian in shape as required for application of the relaxation formulas given before. Other solutions which were examined also showed the Lorentzian shape when they were dilute in total metal. Figure 5 shows a representative spectrum of the Cs solution and the calculated spectrum using the line widths given by the best fit of the relaxation formula. Note that the center line is missing from the simulated spectrum, since it comes from another species. Table II shows the A and g values obtained from some Cs spectra.

For the Rb solution no optical spectrum was recorded but the solution was pale blue. Figure 2 shows a line from the ESR spectrum. The lines correspond to $m_I = 0.5$ for ^{87}Rb , and $m_I = 1.5$ for ^{85}Rb . Figure 6 shows the A and g value for ^{85}Rb as a function of temperature for two samples. No difference in the g values of ^{85}Rb and ^{87}Rb could be detected within the rather large experimental uncertainty. The A values were in the ratio expected from the nuclear moments.

Figure 7 summarizes the relaxation analysis as a function of temperature. As is indicated by Figure 5, the two

state model of fluctuation of the isotropic A and g values is capable of describing a given isothermal spectrum within the rather large experimental uncertainties. The question of the applicability of the two state model rests on the ability to correlate the temperature dependence of the constants obtained from the analysis. The figure shows that the Rb solutions have not yielded any definite information. The scatter in the data is large for the A fluctuations, and the analysis found no significant g fluctuations. The Cs data are somewhat better. Both the A fluctuations and g fluctuations show an increase of the quantity on the ordinate with increasing temperature. It is important to note that the fluctuation quantities, $\langle \tau_c \delta g^2 \rangle$ and $\langle \tau_c \cdot \delta A^2 \rangle$, both have the same sign of slope on the figure as is required by equation 21.

The one further quantity to be noted is that the fluctuations of A and g were found to be anti-correlated in every case for Cs. This means that a fluctuation which tends to increase the A value, tends to decrease the g value and vice versa.

Spectra in Solid Ethylenediamine Solutions. Solutions of alkali metals in en have been reported to give two different ESR absorptions depending on the temperature of the sample. In preliminary studies of spectra for this work a similar phenomenon was observed in potassium in 1,2-propanediamine. Whereas the en gave an abrupt

transition between spectra at about -90°C , the propanediamine gave two patterns which appeared to be in equilibrium over a temperature range. This suggested that more than one type of species may be present in the solid. The question is: can this be the m unit? In order to examine these properties further, solution of Na in ethylenediamine were reexamined.

The first experiment was done to verify the reproducibility of the reported phenomena in en. Samples were prepared as indicated earlier using solvent that had been stored over metal for a long time. The result was that two patterns were observed and as indicated by the previous work, the abrupt transition from one type of pattern to the other occurred at -90°C . Since the solvent had been dried over metal and was known to have decomposed significantly during drying, the possibility of impurities in the solvent causing the result was recognized. The most probable impurity is ammonia, but others are certainly possible.

The second experiment, then, required the use of carefully purified solvent which had not been allowed to undergo extensive reaction with metal prior to its use. With this solvent, the effect of added ammonia could be tested. The experiment was performed as described earlier. The results were that the "pure" solvent gave only a broad line up to 0°C and no transition to a sharper line at -90°C , but solutions with ammonia added behaved as in the previous work by

exhibiting two patterns. The results are summarized in Figures 8 and 9. The measured quantity is the peak-to-peak linewidth at each temperature. The significant point to observe is that the sample of the solvent thought to be most pure does not give the abrupt change, but that the samples of solvent which have undergone prior decomposition with metal or have had ammonia added do give the abrupt transition. Furthermore, the samples with ammonia or the ones having solvent with prior decomposition give similar variations of linewidth with temperature, and they are different from the solvent thought to be most pure. Since the two impure samples had widely different metal concentrations (one was dark blue and the other very pale blue) the metal concentration is apparently not an important factor.

TABLE I
RESIDUAL WIDTH IN METAL-AMINE SOLUTIONS

$T(^{\circ}\text{C})$	Metal	$\frac{1}{2} \Delta H_{1/2}$ (Gauss)
-42	Cs	2.25
-53	Cs	2.25, 2.34, 2.30
-62	Cs	1.53
-64	Cs	1.57, 1.63
-41	Rb	0.85, 0.88
-54	Rb	1.04, 1.08
-63	Rb	1.19
-72	Rb	0.98

TABLE II
A AND g IN SOME Cs SOLUTIONS IN A MIXED
ETHYLAMINE-AMMONIA SOLVENT

$T(^{\circ}\text{C})$	A (MHz)	g
-41	122.7 ± 0.3	1.9979 ± 0.0001
-54	115.3 ± 0.2	1.9984 ± 0.0001
-65	104.3 ± 1.6	1.9991 ± 0.0004

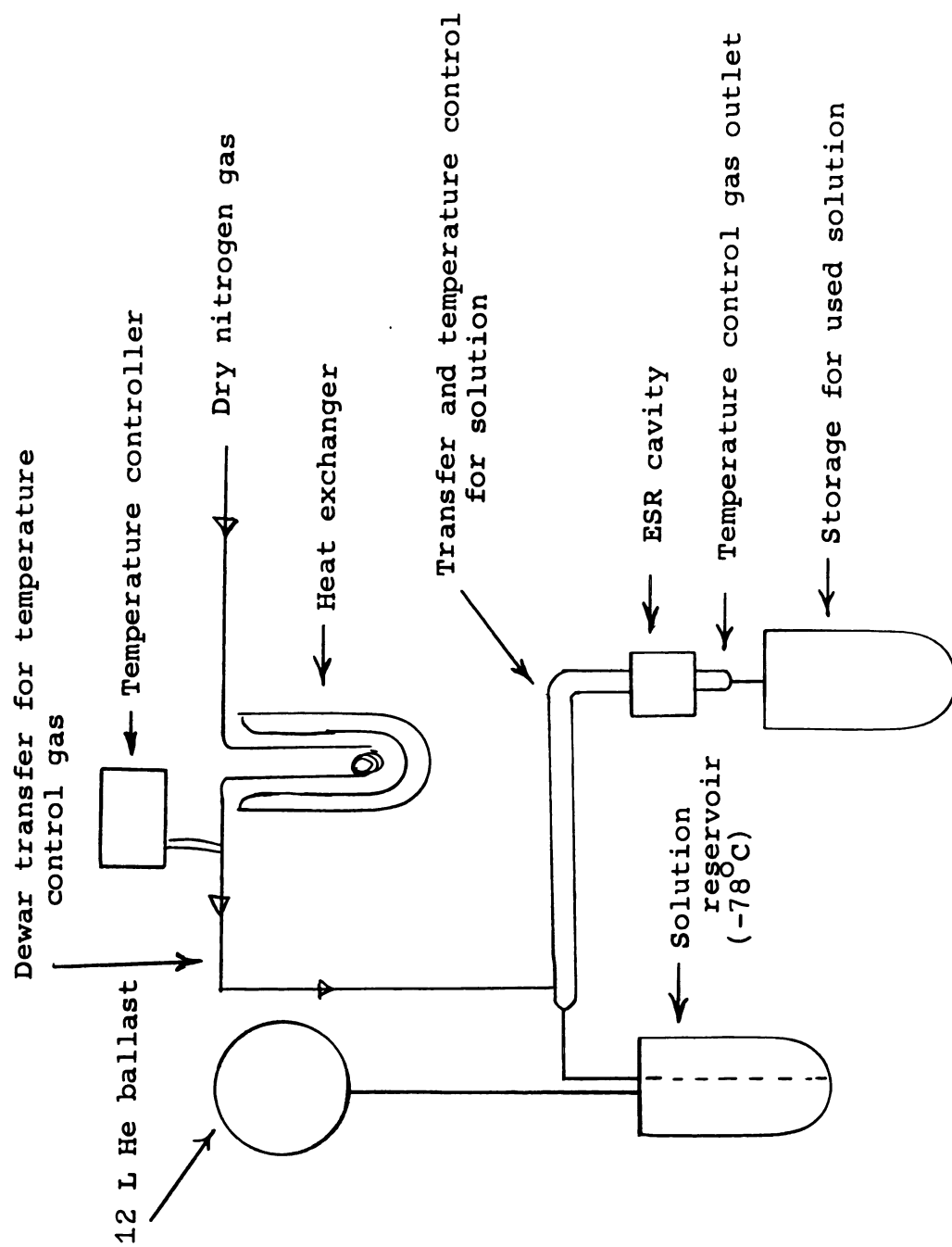


Figure 1. Schematic diagram for the flow system.

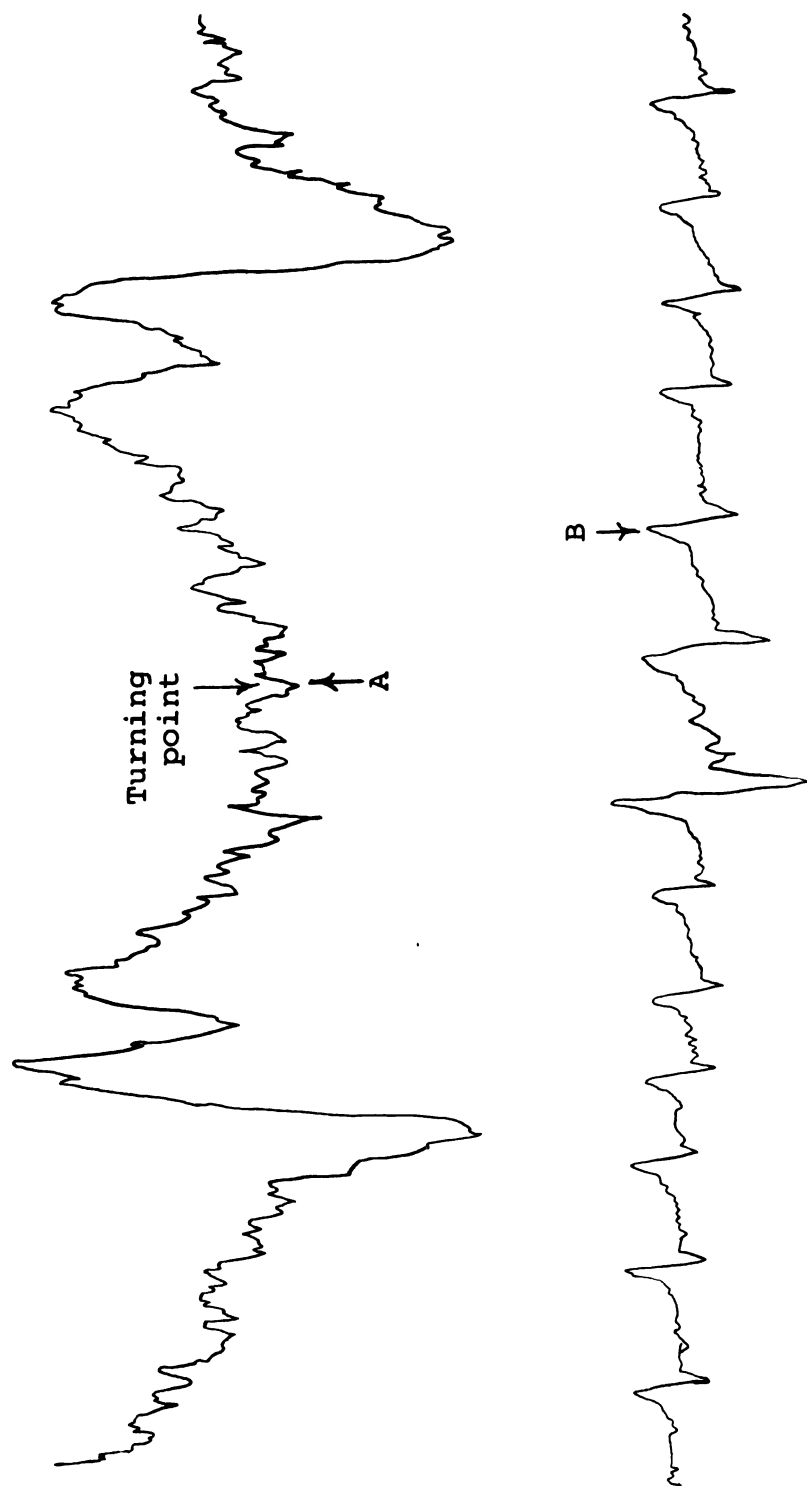


Figure 2. A representative spectral line recorded in the C-1024. The upper curve is a forward and reverse scan of an overlapping pair of rubidium monomer lines. Below is the field marking signal.

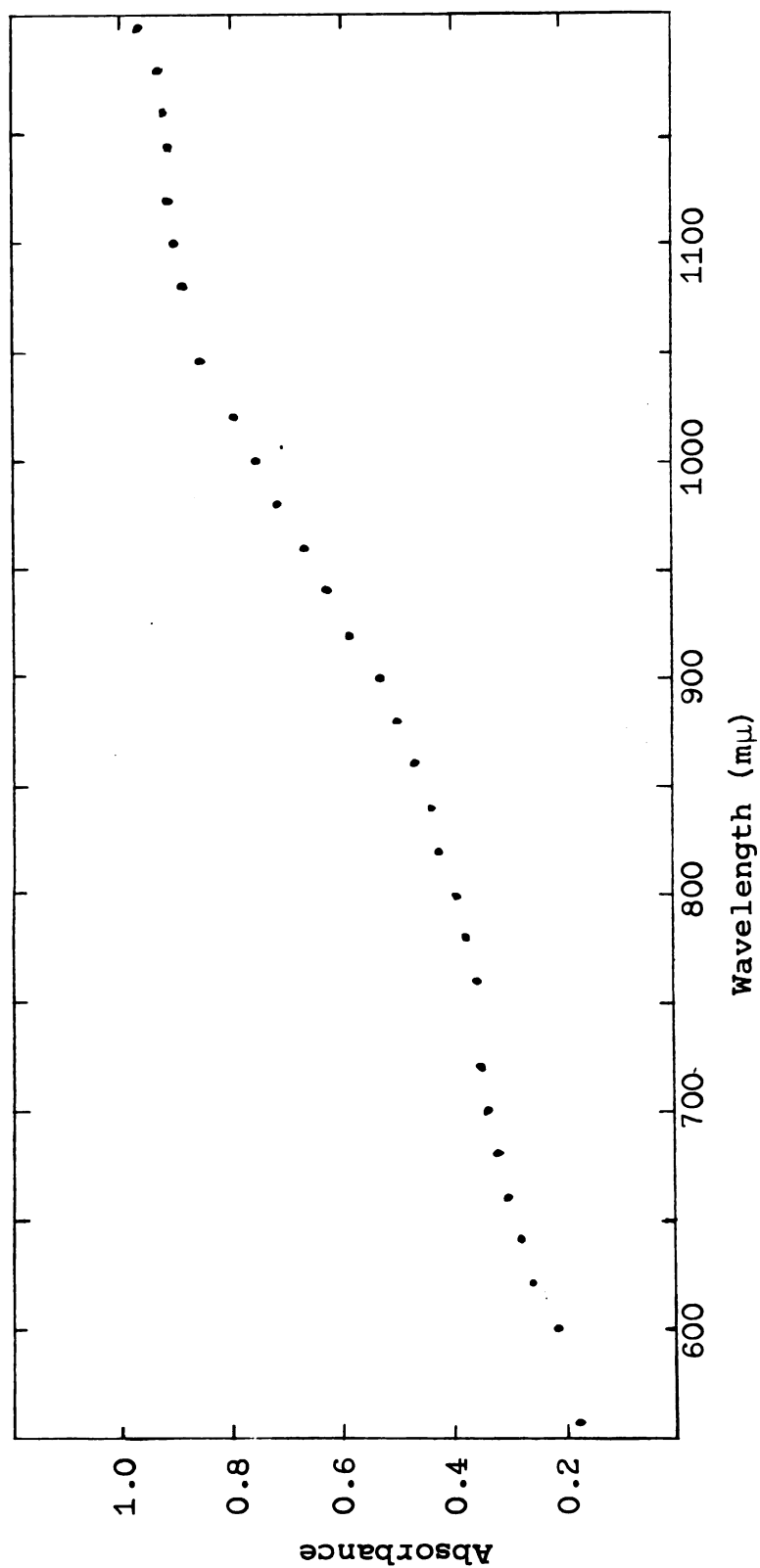


Figure 3. Cesium in ethylamine-ammonia. 1 cm Pyrex cell. The spectrum has been corrected for decay during the scan and for solvent absorbance.

Figure 4. A representative line from the hyperfine pattern of a Cs-ethylamine-ammonia solution.

⊙ represents a Lorentzian shape function.

□ represents a Gaussian shape function.

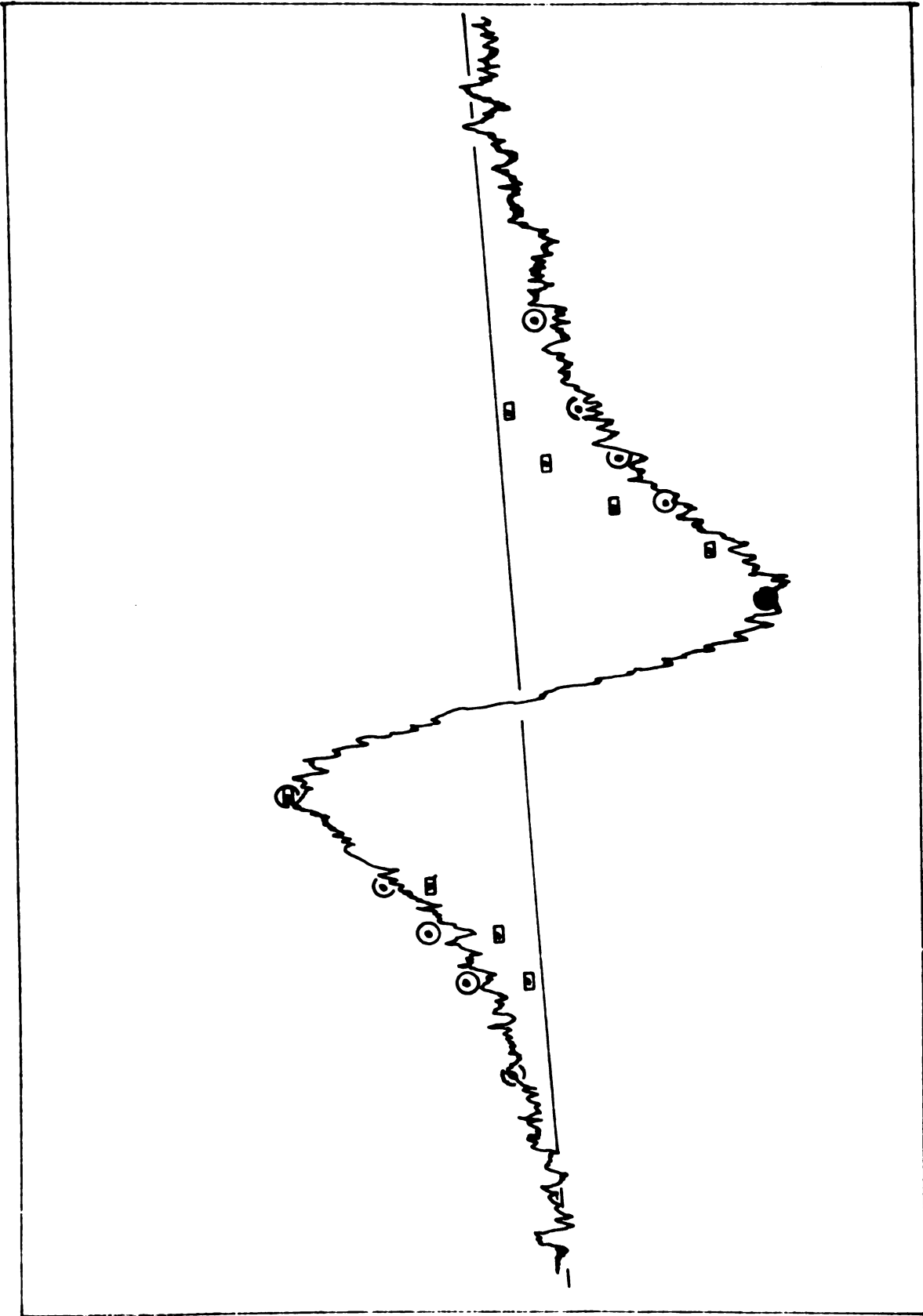


Figure 4

Figure 5. An experimental and theoretical Cs-ethylamine-ammonia hyperfine pattern. The calculated spectrum uses Lorentzian shaped lines with widths given by the two state model.

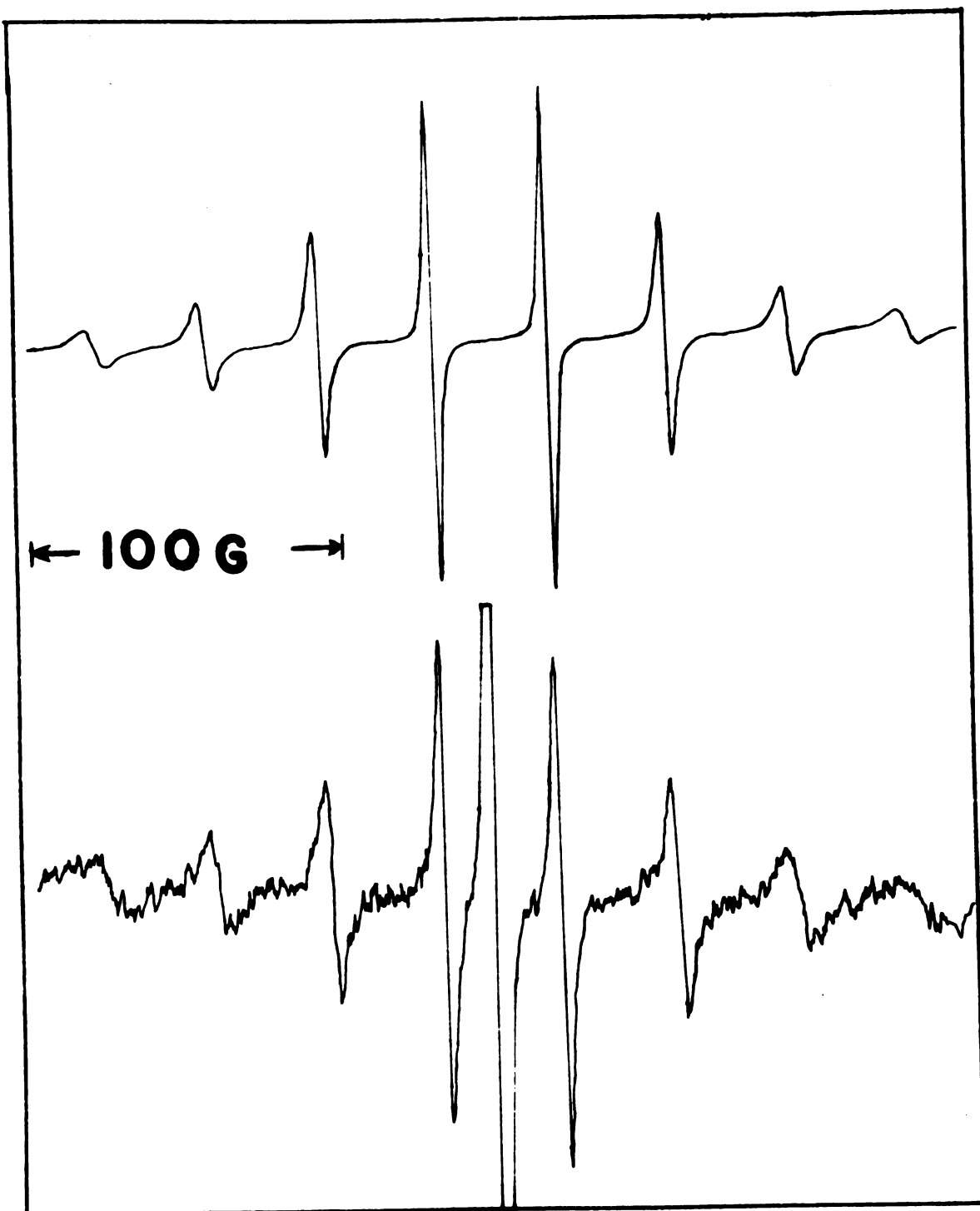


Figure 5

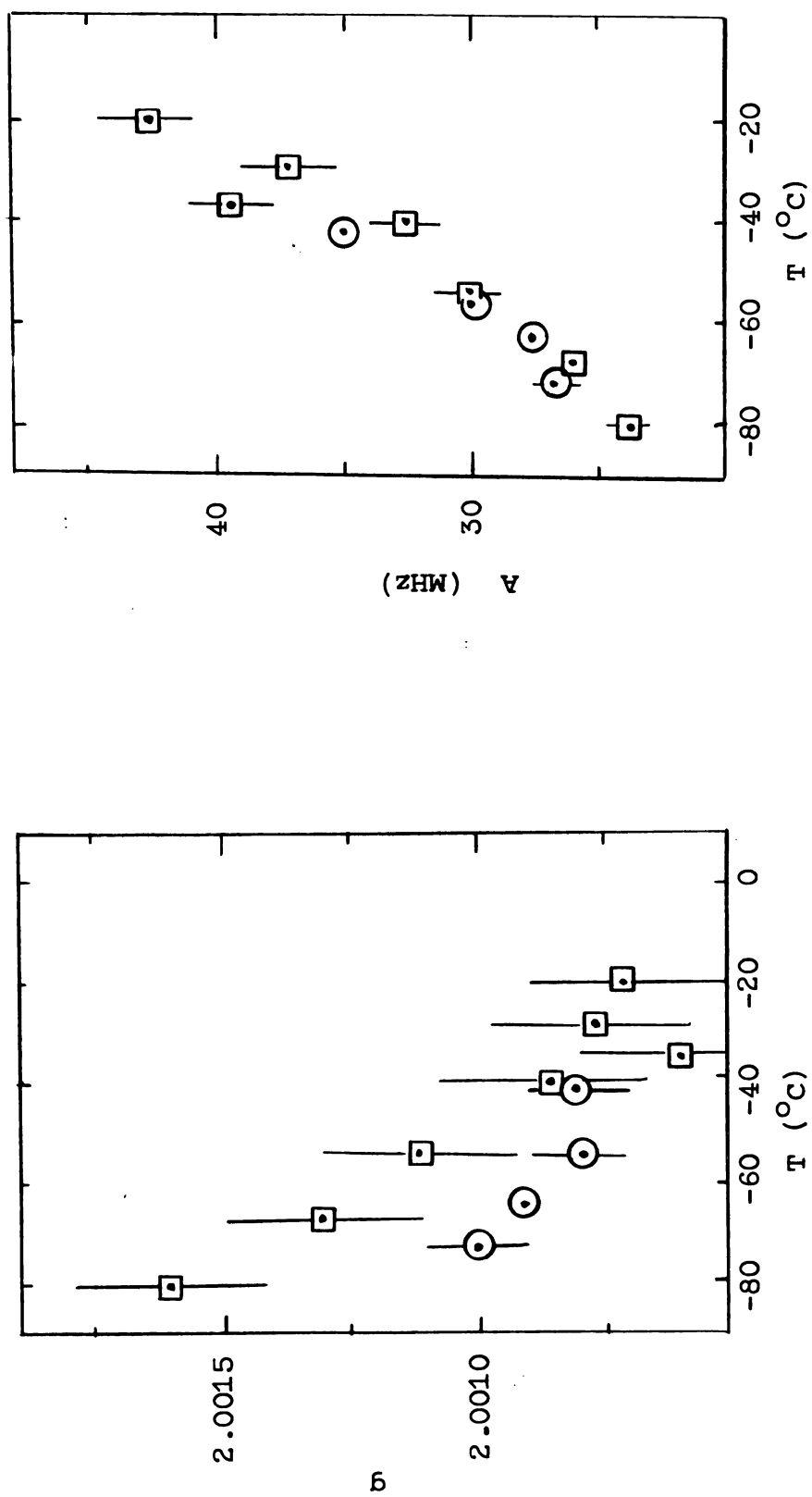


Figure 6. Hyperfine constant and g for two solutions of ^{85}Rb in an ethylamine-ammonia mixture.

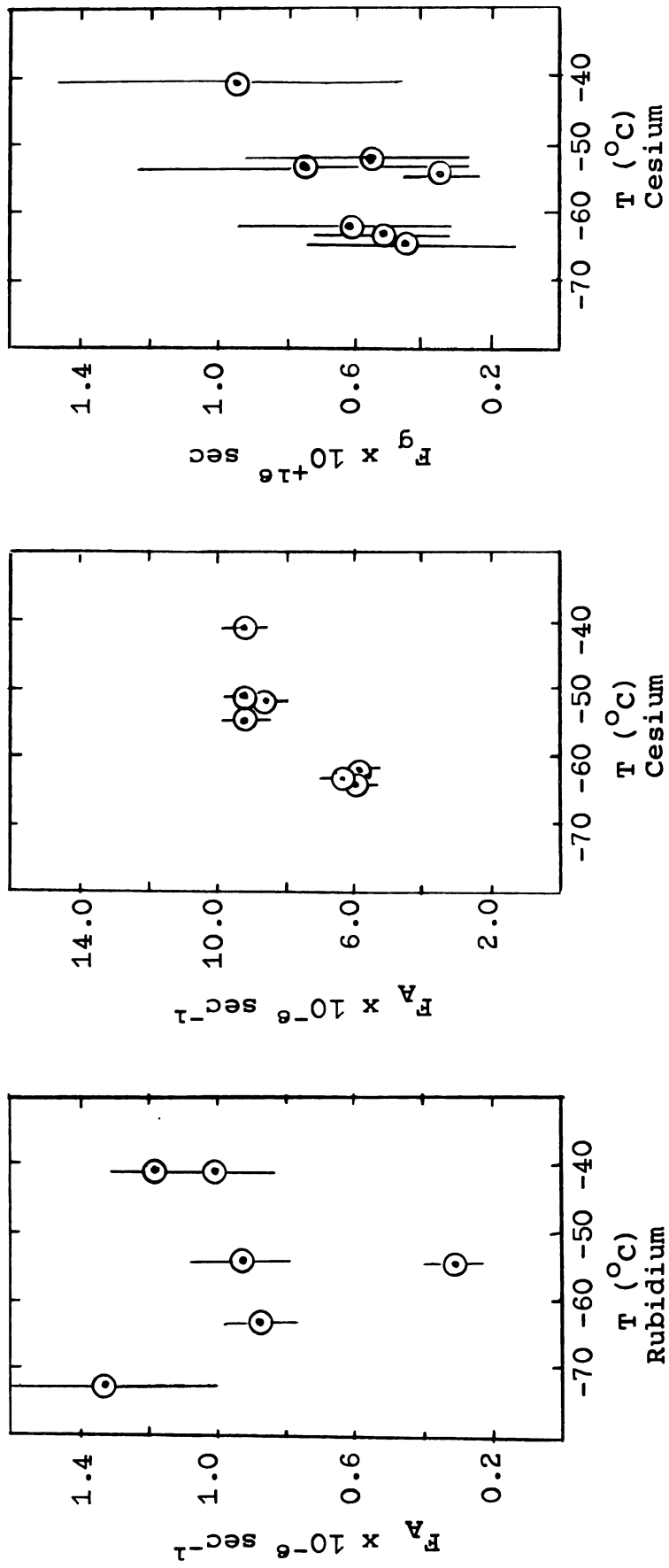


Figure 7. The results of the linewidth analysis. $F_A = \langle \delta A^2 \tau_c \rangle$ and $F_g = \langle \delta g^2 \tau_c \rangle$.

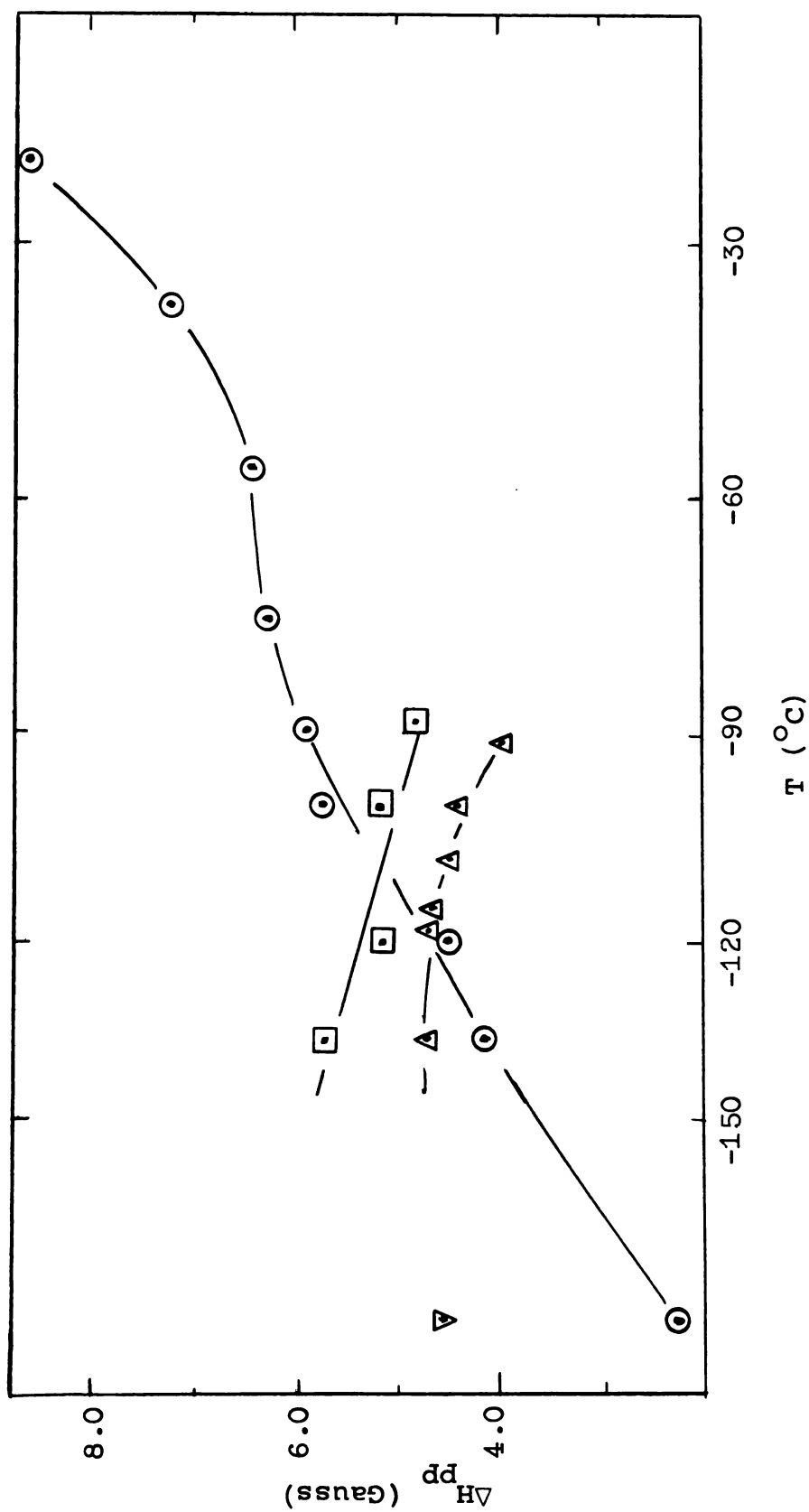


Figure 8. Linewidth of the single line spectra in sodium-ethylenediamine (en) solutions.

○ = "Pure" en
 □ , ▽ = NH₃ + "pure" en
 △ en from decomposed solution.

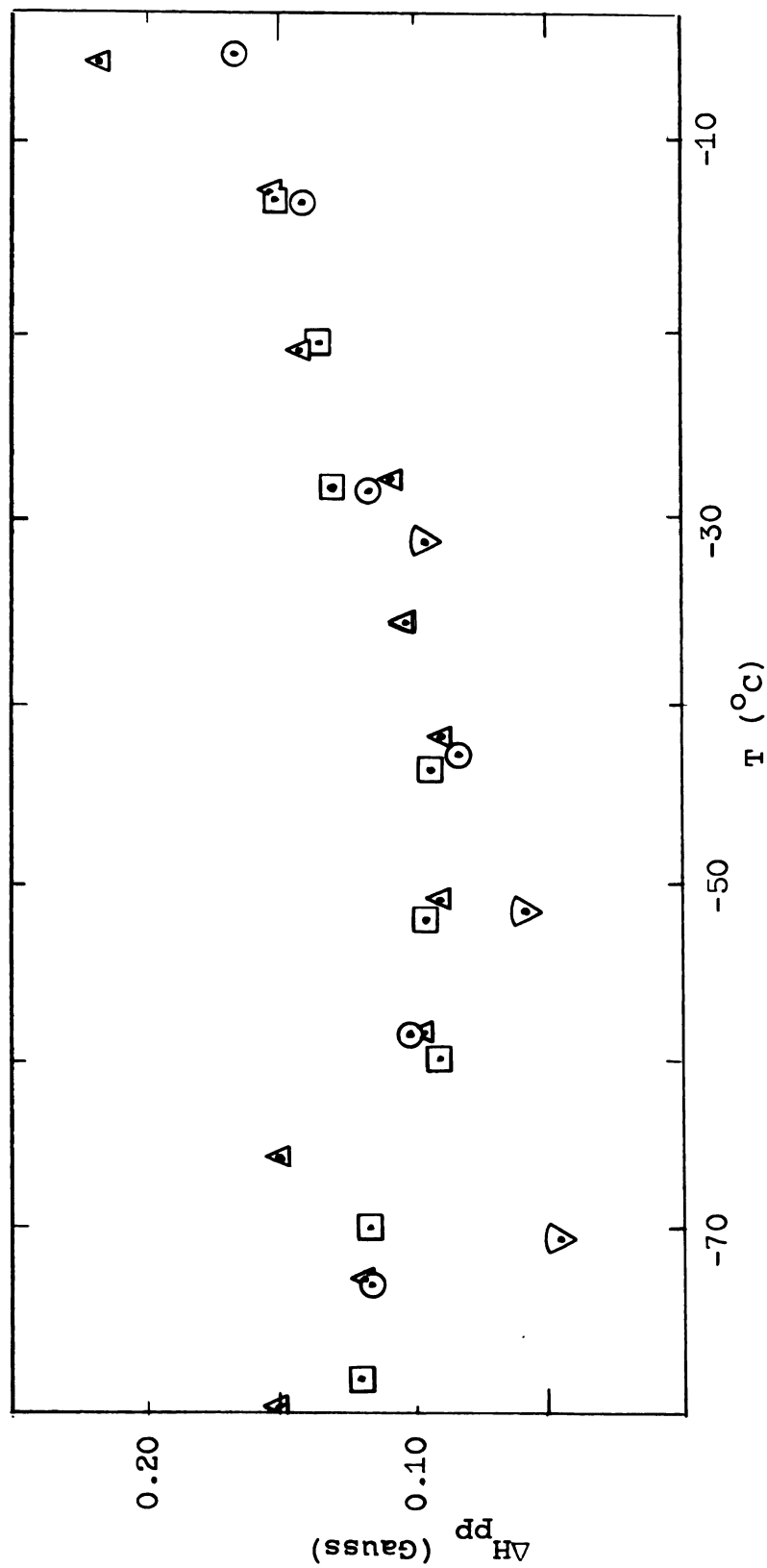


Figure 9. Linewidth of the narrow line in sodium-ethylenediamine (en) "solid" solution above -90°C .

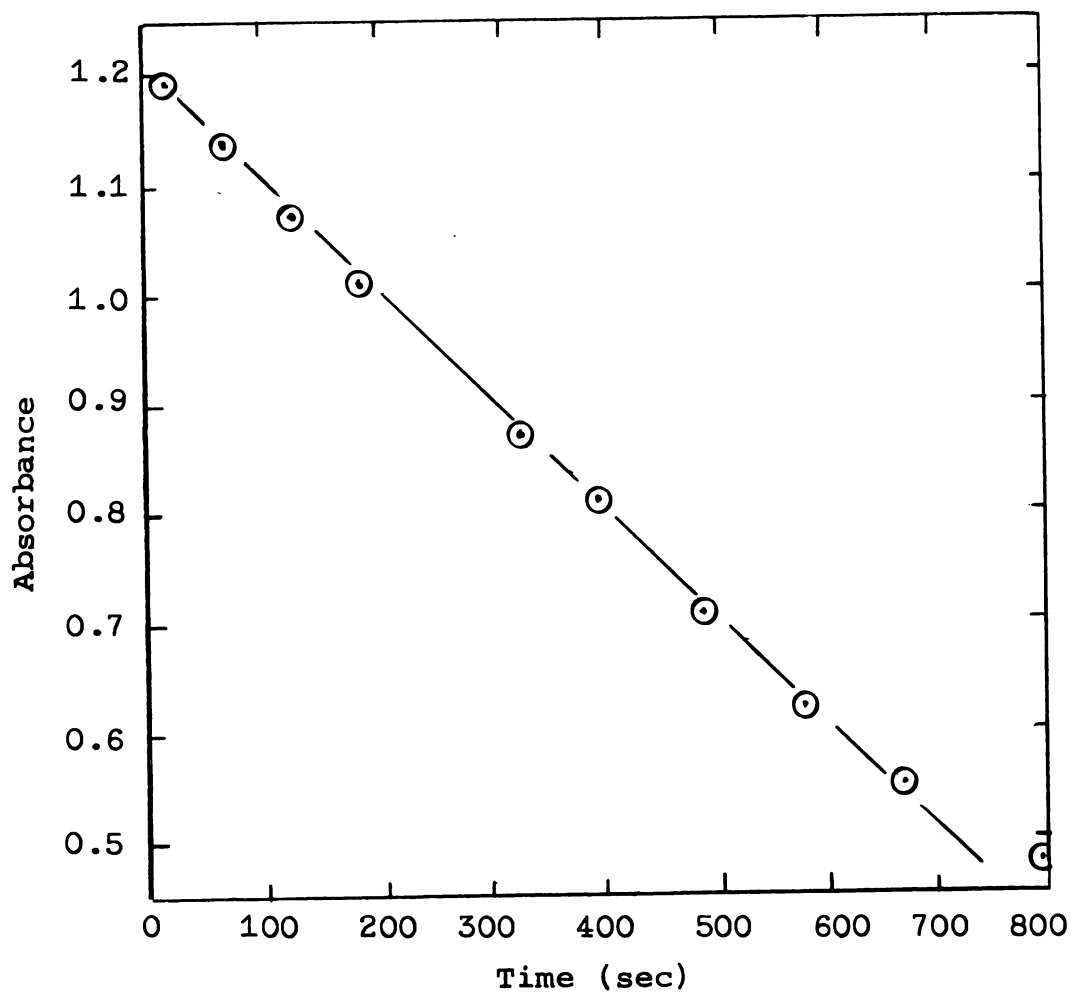
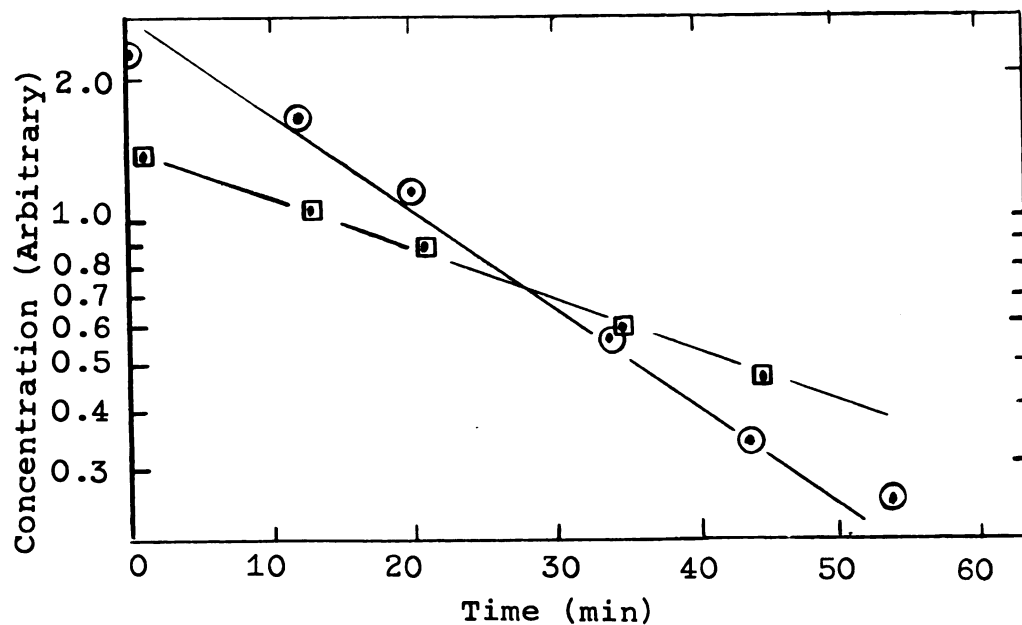
$\odot$ en from decomposed solution, very pale blue at room temperature
 Δ en from decomposed solution, very dark blue at room temperature
 $\square$, ∇ NH_3 added to en which had been carefully purified.

Figure 10. The upper graph shows the first order decay in the flow system with flow stopped.

⊙ represents the area under the hyperfine lines

□ represents the area under the single line.

The lower graph shows the zero order decay of absorbance for a sample carefully prepared under high vacuum conditions in a well-degassed system.



Discussion

The original goal of this investigation was to examine the proposals for the m_I dependent linewidth. Persistent decomposition of the required dilute solutions necessitated a systematic investigation of the decomposition. This section contains a discussion of the meaning of and relations among the results obtained.

The m_I Dependent Linewidth

The interpretation of the only previous systematic investigation of the m_I dependent linewidth (33) did not account for all of the experimental evidence. These investigators found the line to be nearly gaussian in shape with a residual width of about 5 gauss. However, this author found the lines to be very nearly Lorentzian in shape with a residual width of about 2 gauss (Table I) under similar conditions. Catterall et al. (18) report that excess cation broadens the hyperfine lines in potassium-ethylamine solutions. This author's decomposition study makes it plausible to assume that Dye et al. had some excess cation in their solutions due to decomposition. If the cations in cesium

solutions act like those in potassium solutions, it is plausible to expect the lines observed by Dye et al. to be broader than those observed by the author. It is also likely that the cation exchange would cause the line shape to become non-Lorentzian, since with small excess cation concentrations the process would be in the near slow exchange region. The Lorentzian line shape is important because it indicates the process(es) which cause the m_I dependence is rapid on the ESR time scale which is necessary for the application of the relaxation formalism used.

The two-state model is capable of fitting a given spectrum but this does not mean that there are actually two species in equilibrium. It does mean that the relaxation equations which were used are sufficient. Therefore, rapid modulation of the isotropic A and g constants in an anti-correlated manner can describe the data at one temperature. In order to know more specifically the nature of the modulation, the effect of solvent, metal, temperature and pressure on the correlation functions and means of the distributions must be studied. A model should not be rejected if it describes all of the variations observed. It is likely, however, that data for any small range of the variables can be described by more than one model.

The data obtained in this study are for an insufficient range of temperature to distinguish among the possible mechanisms for the m_I dependent linewidth. The data do

indicate, however, that a distribution model with a rapid equilibration among states could describe the data since this study shows the lines to be of the proper shape and a previous study (24) shows that A can be described by a distribution including at least three states. The remaining unsolved problems are the cause and distribution of the states of the system. A much more extensive set of data which is collected under carefully controlled conditions will be necessary for the solution of these problems.

The m_I dependence may be due to anisotropy of the species as has been suggested (4). Since the isotropic A value is strongly influenced by the environment, the anisotropic components of the A tensor are likely to be similarly influenced. In order to test an anisotropic rotor model, the relations of the anisotropy to the environmental conditions must be specified. Therefore, this proposal cannot be tested in the same manner as for solutions of inorganic complexes which have nearly constant magnetic parameters. Whereas the distribution model explains not only the m_I dependent linewidth but also the A and g value shifts, the anisotropic species model explains only the m_I dependent linewidths.

Solution Stability

The systematic investigation of the factors influencing the solution stability indicated that the surface-to-volume

ratio of the container was important because solutions which had a relatively larger surface area at constant volume decomposed more rapidly. These decay studies gave qualitatively reproducible results. The one quantitatively measured decay was zero order. The observations are in agreement with a surface catalyzed reaction mechanism; a result which is similar to that for ammonia solutions (31, 44). Deactivating the surface by reacting metal vapor with it was not completely successful but the reaction did become slower after some initial reaction had taken place.

These results are significant because they indicate that either quartz or Pyrex catalyzes the decomposition reaction. Therefore, it is very difficult to use tube dimensions which permit study of the sample in the 9.2 GHz ESR spectrometer, yet do not cause solution decay.

The decay observed under some circumstances is qualitatively different. One solution in the flow system showed a first order decay of the paramagnetism when the flow was stopped. The rate of this reaction was much more rapid than expected for a well cleaned system at a comparable temperature. The result is probably due to impurities introduced by the flow system reacting with the solute.

In summary, the decomposition in pure solutions appears to be catalyzed by the container surface. No method was found to inhibit the process and avoid decomposition product simultaneously. The ESR experiment requires that one must

use small containers and dilute solutions while avoiding decomposition products if the linewidths are to be reliable. Therefore, the decomposition is a severe limitation to the possible experiments.

Solid Solutions

The reinvestigation of the solid solutions of sodium in ethylenediamine shows that the presence of the sharp line above -90°C is due to impurities in the solid. Ammonia, when introduced deliberately, gives the same results, whereas, carefully purified ethylenediamine does not give the sharp single line, but rather a resonance characteristic of dispersed Na metal (50). The most likely interpretation is that the impurity, which probably is ammonia introduced by decomposition of the solutions in the usual drying procedure, forms a liquid mixture with ethylenediamine which has a eutectic at -90° . Under this hypothesis, the sharp line is characteristic of a liquid solution of sodium in the mixture.

CHAPTER III

AB INITIO STUDY OF LITHIUM AMMONIA INTERACTIONS

Introduction

The Ab Initio M. O. Technique

The ab initio calculation of an all electron wave function for polyatomic non-linear molecules, using a basis of gaussian functions, has become practical since the development of the electronic digital computer. Boys (8) has shown that all of the required integrals can be readily evaluated in terms of tabulated functions if the gaussian function is used as the basic radial function. Two modifications of this procedure are now commonly used. The nuclear centered gaussian function uses a gaussian radial function but maintains the spherical harmonic function to give the angular dependence. Therefore, this technique is the same as that using Slater type orbitals except that the exponential function has been replaced by a gaussian type radial function. A number of recent calculations have successfully used this type of basis for the description of rather large polyatomic molecules (22,23). A second approach uses only primitive spherical gaussian functions, but combines these into fixed linear combinations which represent other types of functions.

In the gaussian lobe modification, as this technique is called, angular dependence is obtained by using linear combinations of functions which have different centers. This technique has also been used to describe the electronic structures of some large molecular systems (11,12,70).

The major problem in past ab initio calculation of electronic structures of polyatomic molecules has been the evaluation of the "multicenter" integrals, that is, integrals which contain functions centered on more than two nuclei. The gaussian technology has removed this problem. Other problems arise, however, for "larger" molecules. The number of integrals needed for the calculation of an electronic structure increases as the fourth power of the number of basis functions. The number of basis functions increases with both the number and complexity of the atoms used. The expense of doing an ab initio calculation is, therefore, a rapidly increasing function of the size of the molecular system and is the primary limitation on the size of the system which can be investigated.

In a recent review article (23) Clementi has discussed the various levels of approximation used in calculations of electronic structure. The method used in the work discussed in this chapter is the single determinant self consistent field molecular orbital scheme in the Born-Oppenheimer approximation which is an adaptation of the atomic Hartree-Fock method to the molecular problem. The best solution in this

approximation is known to be incomplete. Furthermore, if a finite basis set is used, there are errors introduced because the solution obtained is not the best single determinant. The effects of these errors on the properties calculated will be considered when the results are discussed.

Recent publications by many investigators have examined the application of ab initio methods to the solution of problems involving physical and chemical properties of isolated molecules. For example, the energy as a function of nuclear position has been used to calculate force constants (7); the wave functions for near Hartree-Fock solutions have been used to calculate charge densities and to see how bonding affects them for diatomic molecules (14); reaction energies and rotational barriers have been examined (60) and even the energy surface for the reaction of NH_3 and HCl has been studied (22). The method is able to explain (or predict) many properties. The accuracy for specific properties will be discussed in a later section.

The Application

The experimental data relating to monomers in metal-amine solutions potentially contain significant structural information about the solute species present. The lithium monomer is a particularly interesting case because the splitting constant is obtained for some of the solvent as well as an upper limit for splitting by the metal ion. The most puzzling feature of these data is that the unpaired electron

density at the lithium nucleus is small while the unpaired electron density at the solvent nitrogen is significantly larger.

The qualitative explanations for the observations are reviewed in Chapter I. The quantitative models for the monomer (6,45,46,54,55) are extensions of the solvated electron models to include a cation. The effects of the medium and metal inner shell electrons have been treated in several ways. For the ammonia monomer of sodium, Jortner treated the solvent and metal inner shell electrons as a continuous dielectric medium. O'Reilly has calculated wave functions for ammonia monomers of all the alkali metals using a continuous dielectric medium with a spherical cavity which contained a point positive charge to represent the cation and point multipoles to represent the first solvent layer. The unpaired electron function was made orthogonal to the metal inner shell orbitals and in some cases, also, the orbitals of the first solvent shell. All molecular orbitals except for the unpaired electron were those for isolated molecule calculations. He later extended the model to the ethylamine monomer of potassium.

These calculations assume that the long range forces are most important in the formation of the species. Any short range interactions of the metal cation, unpaired electron and solvent molecule are specifically left out in these calculations. If the monomer is formed by partial covalent bonding of the solvent and metal or if significant charge is

transferred from the metal atom to specific solvent molecules, the continuous dielectric model would be incapable of predicting it.

Using the gaussian integration technology, the short-range interactions can be examined in detail. With present techniques, examination of conditions representative of the liquid state is not possible because of the amount of labor required. Model systems which can help conceptualize the nature of the interactions in the liquid can be examined, however.

This chapter presents the calculations and analyses of the interaction of a lithium atom with one or two ammonia molecule(s). The gaussian lobe function basis is used to construct the single determinant solution to the Born-Oppenheimer Hamiltonian. Analysis of the results using the energy, charge density, and various populations leads to the conclusion that: 1) a lithium atom--one ammonia molecule complex is stable relative to the separate gas phase molecules, 2) significant hyperfine contact density can occur at the nitrogen nucleus without appreciable charge transfer to the ammonia molecule, 3) ammonia is bound to the lithium atom primarily by a covalent bond utilizing the lithium 2p orbital and the ammonia lone pair of electrons, and 4) the unpaired electron avoids the spatial region containing the ammonia.

Although the calculation does not include possible long range interactions of the unpaired electron with the solvent,

some of the results provide information about short range interactions which might take place in the solutions.

The calculations used ammonia molecules rather than amine molecules because of the time difference involved in the different calculations. It is unlikely, however, that the results for amine molecules will be significantly different, in their qualitative features.

The Methods

The method used to construct the wave function for the molecular species can be described as a self consistent field linear combination of group orbitals (SCF-LCGO). The resulting wave function has been analyzed by using a population analysis scheme due to Mulliken (53) and by contour maps of the charge density and changes in charge density. Although the methods are rather common, they will be outlined in some detail here so that the assumptions made in the calculation can be stated explicitly.

Construction of the Wave Function

The starting point for this calculation is the electronic Hamiltonian in the Born-Oppenheimer approximation. The Hamiltonian is

$$(1) \quad H = \sum_{i=1}^n \left[-\frac{1}{2} \nabla_i^2 + \left(- \sum_{j=1}^m \frac{Z_j}{r_{ij}} \right) \right] + \sum_{k>i}^n \frac{1}{r_{ki}}$$

where:

- $\frac{1}{2} \nabla_i^2$ is the kinetic energy operator of the i-th electron
- $\frac{\tilde{z}_j}{r_{ji}}$ is the potential energy operator for the i-th electron in the field of the j-th nucleus.
- $\frac{1}{r_{ki}}$ is the electron-electron electrostatic interaction (repulsion).

A solution to 1 must obey the Pauli principle for the electrons as a minimum condition. The self consistent field solution is the result of minimizing the expectation value of the operator 1 with a properly anti-symmetric trial solution constructed using a basis of independent particle solutions. The solution to the resultant equations from the minimization are non-linear in the trial function coefficients so that the solution must be achieved in an iterative manner.

The particular method used for the examination of the interaction of lithium and ammonia is based upon a description of the basic independent particle (one electron) functions in terms of linear combinations of gaussian type functions. (This can be viewed as a LCAO basis in which the atomic orbitals (A.O.) have been replaced by group orbitals (G.O.)).

A single determinant trial function is formed from the one electron functions and the total energy of the system (expectation value of operator 1) is minimized with respect to the coefficients of the groups of gaussian functions in the expansion of the one electron basis functions.

The important point is that the Hamiltonian given by 1 is assumed to apply to the system, a basis of gaussian functions is assumed for the system and then the solution to 1 is achieved without further approximation. The programs to generate the integrals and to use them to calculate the SCF solution were generously donated by Professor J. L. Whitten. Two SCF programs were used: one calculated singlet wave functions and the other calculated doublet wave functions. The one used depended on the number of electrons in the system.

The Basis Functions

The molecular orbitals are expanded as a linear combination of basis functions. The basis functions for lithium and nitrogen were taken from the table given by Whitten (70). The hydrogen function contained five terms which had been optimized for use in calculations with C-H bonds (70). The lithium basis was augmented by addition of a two-term gaussian lobe representation of a p function which was scaled to an effective charge of about 0.65 on the lithium (this function was not actually optimized to represent a slater type orbital). The collection of functions outlined above will be referred to as the minimal basis set.

To test the adequacy of the minimal basis, an extended basis was used for some calculations. For the hydrogen function, the five-term representation was split into a

short range group with three terms and a long range group of two terms. The relative coefficients within a group were maintained, and the exponents were not changed. The nitrogen p function was similarly split into a short range function of three terms and a long range function of two terms. In order to allow the possibility of charge transfer, the nitrogen basis was augmented by including a gaussian representation of a Slater three S function with an effective charge of 0.75 (overlap with slater 3 S of 0.9996). The lithium basis was extended to include two 2 p gaussian representations (overlap with Slater 2 p of 0.9984) with effective charges of 0.95 and 1.30 and two 3S representations with effective charges of 1.0 and 0.3. The gaussian representations were constructed by maximizing the overlap of a slater function of the desired type and the gaussian representation of it.

The constants were chosen so that either the neutral or positively charged lithium could be represented. For nitrogen, the 3 S function was chosen to represent a neutral nitrogen atom. This basis is believed to be sufficient to represent the various possible hybridization schemes for the lithium atom and/or to allow the possibility of a transfer of the unpaired electron to the ammonia.

Geometry of the Nuclear Framework

Because these calculations are time consuming on a digital computer, only a limited search of geometry was made. First, the lithium atom was assumed not to strongly perturb the electronic structure of the ammonia molecule. Therefore, it seemed reasonable to assume an equilibrium ammonia geometry for the NH_3 framework. However, the question of the position of the lithium atom relative to the NH_3 molecule arose. One might suspect that placing the lithium on the C_3 axis of the ammonia would be favored, but should it be placed on the same side of the ammonia as the hydrogens or on the opposite side? No obvious means (except calculation) of answering this question was found. Therefore, a number of configurations with the lithium atom on each side of the NH_3 part were tried. All of these calculations used C_{3v} symmetry.

There is also the question of whether such a complex would be stable to autoionization to a free electron and a positively charged species. If a positively charged species could form what would be its properties? To obtain the answers to these questions, a series of calculations were performed for the positively charged complex.

After the calculations for one lithium and one ammonia predicted a bound species, a series of calculations were performed for one lithium atom interacting with two ammonia molecules. All of the two-ammonia calculations were for species with D_{3h} symmetry.

The ammonia molecule was assumed to be of C_{3v} symmetry with $r(\text{N-H}) = 1.918$ a.u. and an angle between the C_3 axis and the NH axis of 68.15 degrees. This is very close to the experimental geometry given in the literature (42). No search of the ammonia geometry was made.

Analysis of the Wave Function

Since it will not be possible in the immediate future to perform ab initio calculations on species likely to be found in solution, understanding the mechanisms of the electronic interaction in model species is important so that they may form a conceptual basis for thinking about the species in solution. In order to better understand the way in which ammonia and lithium interact, the wave functions have been analyzed according to the population analysis scheme of Mulliken (53). Results of only a few of the population breakdown equations will be tabulated. One quantity which is informative is the net overlap between two atoms.

This is given by

$$(2) \quad n(k,l) = \sum_r \begin{matrix} \text{All orbitals} \\ \text{of atom K} \end{matrix} \sum_s \begin{matrix} \text{All orbitals} \\ \text{of atom } \ell \end{matrix} \sum_i \begin{matrix} \text{All m.o.'s} \\ 2n(i) \end{matrix} C_{ir_K} C_{is_\ell} S_{r_K s_\ell}$$

with the definitions:

$n(k,l)$ net overlap between atoms k,l

$n(i)$	number of electrons in m.o. i
C_{ir_K}, C_{iS_1}	coefficient of basis function r_K or S_1 in m.o. i
$S_{r_K S_1}$	overlap between basis functions r_K and S_1

Two other quantities which are of particular interest are the gross population in a given molecular orbital on a particular atom and the total gross population on a given atom.

$$(3) N(i;k) = \sum_r^{\text{All basis functions}} [n(i) C_{ir_K} (C_{ir_K} + \sum_{l \neq K}^{\text{All atoms except K}} C_{iS_l} S_{r_K S_l})]$$

and

$$(4) N(k) = \sum_i^{\text{All m.o.'s}} N(i;k)$$

They are defined by equations 3 and 4 in which the symbols have the same meaning as above.

The method of population analysis is not a rigorous quantum mechanical formalism which relates to observables as the expectation value of physical observables does, but rather, it is a means of forming a conceptual connection between chemical concepts of bonding and the results of quantum mechanical calculations. One must remember that the results of the population analysis are to be used only when they agree conceptually with the results given by expectations of observables (when such a comparison is possible).

The total charge density is a physical observable. One can also measure the density of unpaired electron in the region of certain nuclei because the isotropic hyperfine splitting is directly related to this density. Therefore, these quantities have been calculated for the different nuclear configurations. The Fermi contact density is calculated as the square of the value of the molecular orbital containing the unpaired electron at the position of the nucleus. The total charge density at a point in space is the sum of the squares of the magnitudes of the occupied molecular orbitals times their occupation number.

In order to illustrate the changes in charge density which occur on formation of the interacting aggregate species, two types of contour maps have been prepared. Total charge density maps have been plotted. Since the changes in density are a very small fraction of the total density, charge density difference maps have been prepared as well. These difference maps are prepared by taking the total charge density of the isolated species and subtracting the total charge density of the interacting species, where, of course, both configurations have been superposed. This method clearly identifies areas where charge is gained and lost. At the S C F M O level of approximation, the unpaired electron occupies the orbital which is highest in orbital energy and it is the only orbital with unpaired spin density. With this concept in mind, it is possible to examine the

distribution of the unpaired electron in space and to make maps of the density of unpaired electron under various conditions.

Results

The results summarized in this section are from the SCF calculation and the analysis of the resultant function describing the stationary state of the electrons. The results are of three types and have been separated and tabulated accordingly. First, the direct results of the SCF calculation for the different geometries are presented. Then the results of the population analysis and the contour maps of charge are shown.

The SCF and Population Analysis

Table I contains the tabulated results of the SCF calculation and the value of the Fermi contact density of unpaired electron at various nuclei. The values in Table II are derived from the data listed in Table I.

Table I shows how the energy of the complex varies as its structure is altered. The feature to be noted is that the energy of the neutral species has very little dependence upon the Li-N distance. Further comparison of the values of Table I (see also Table II) indicate that: 1) the neutral complex of lithium and ammonia has a lower energy than the positively charged complex, 2) the lithium ammonia complex

is most stable when the lithium is near the lone pair of electrons on NH_3 , 3) the $\text{Li}(\text{NH}_3)_2$ species is nearly iso-energetic with $\text{LiNH}_3 + \text{NH}_3$, and 4) extending the basis set to include 3S orbitals on both lithium and ammonia, and relaxing the grouping constraints on the nitrogen p orbitals and hydrogen S orbitals has little effect on the calculated stabilization energy of LiNH_3 .

Tables III-V contain the results of evaluating equations 2-4 for the minimum energy configurations of the lithium-ammonia species. The analysis of the calculation using the extended basis is included for comparison. In Table IV only the results for the orbitals which are primarily responsible for the bonding are shown. The lower lying orbitals show a negligible effect of the interaction of the two species.

Charge Density Distributions

Each charge density distribution is presented in two ways to better illustrate the charge distributions. The bottom graph is a plot of the charge density (on a 5 decade logarithmic vertical scale) versus the position in the molecule along the axis. Positioned above this graph is a contour plot of the charge density, with the contours in a reflection plane of the molecule (i.e., a plane which contains one hydrogen, is symmetrically between the other two, and contains the lithium and nitrogen nuclei).

Figures 1, 2, 3, and 4 show the total charge density given by the minimum basis calculation for the ammonia molecule, the lithium atom, the lithium-ammonia complex, and one-half of the lithium diammonia complex, respectively. Figure 5 shows the result of adding the charge densities of lithium and ammonia (properly placed) and subtracting the charge of the complex. Therefore, it represents the shift of total charge upon formation of the complex (note that in this figure and in figure 7, the vertical axis is linear). Figure 6 is a similarly constructed plot for the diammonia complex. Figures 7 through 11 are similar plots for the unpaired electron distribution.

Figure 12 is a comparison of the unpaired electron distribution along the C_3 axis under different conditions. The free atom distribution is compared with the complex of one ammonia when using the minimum and extended basis sets.

TABLE I

SOME RESULTS OF THE SCF CALCULATIONS

Species	Li-N Distance	Energy -e ² /a ₀	$ \Psi(r) ^2$		Fermi N	Contact H	-2K/V VIRIAL Test
			Li	H			
Li	--	7.43119	0.155	--	--	--	1.0000
Li ⁺	--	7.23499					
NH ₃	--	56.14192	--	--	--	--	

LiNH ₃	3.75879	63.60197	0.118	0.0484	8.21x10 ⁻⁵		1.00028
LiNH ₃	3.85879	63.60216	0.120	0.0465	8.04x10 ⁻⁵		1.0020
LiNH ₃	3.95879	63.60197	0.122	0.0448	7.83x10 ⁻⁵		1.00188
LiNH ₃	4.15879	63.60083	0.125	0.0419	7.28x10 ⁻⁵		1.00164
LiNH ₃	4.35879	63.59903	0.128	0.0396	6.79x10 ⁻⁵		1.00144

LiNH ₃ ⁺	3.75879	63.45653	--	--	--		1.00141
LiNH ₃ ⁺	3.85879	63.45614	--	--	--		1.0012
LiNH ₃ ⁺	3.95879	63.45532	--	--	--		1.00098
LiNH ₃ ⁺	4.15879	63.45276	--	--	--		1.00068
LiNH ₃ ⁺	4.35879	63.44939	--	--	--		1.00049

LiH ₃ N ⁺	4.44	63.36736	--	--	--		1.0096
LiH ₃ N ⁺	4.84	63.37115	--	--	--		1.0025

LiH ₃ N	4.44	63.55863	0.138	0.0337	2.11x10 ⁻⁴	1.0027
LiH ₃ N	4.84	63.56337	0.145	0.0272	3.20x10 ⁻⁴	1.0015

Li(NH ₃) ₂	3.95879	119.72167	0.125	0.273	2.07x10 ⁻⁴	1.0033
Li(NH ₃) ₂	4.15879	119.72274	0.134	0.245	1.90x10 ⁻⁴	1.0030
Li(NH ₃) ₂	4.25879	119.72289	0.138	0.231	1.80x10 ⁻⁴	1.0028
Li(NH ₃) ₂	4.35879	119.72288	0.142	0.218	1.7x10 ⁻⁴	1.0027

Li(NH ₃) ₂ ⁺	3.75879	119.66918	--	--	--	1.0016
Li(NH ₃) ₂ ⁺	3.85879	119.66881	--	--	--	1.0014
Li(NH ₃) ₂ ⁺	3.95879	119.66757	--	--	--	1.0012
Li(NH ₃) ₂ ⁺	4.15879	119.66320	--	--	--	1.0009

Extended Bases NH ₃	--	56.14977	--	--	--	1.00073
Extended Bases Li	--	7.43120	--	--	--	1.00019
Extended Bases LiNH ₃	3.85879	63.61320	0.093	0.053	5.3x10 ⁻⁵	1.000006
Extended Bases LiNH ₃	4.15879	63.61138	0.100	0.047	4.9x10 ⁻⁵	0.99967

TABLE II
SOME REACTION ENERGIES*

Reaction	$\Delta E(\text{products}-\text{reactants})$ kcal/mole
$\text{Li} + \text{NH}_3 \rightarrow \text{LiNH}_3$ (minimum basis for each)	-18.2
$\text{Li} + \text{NH}_3 \rightarrow \text{LiNH}_3$ (extended basis for each)	-20.2
$\text{Li}^+ + \text{NH}_3 \rightarrow (\text{LiNH}_3)^+$	-45.0
$(\text{LiNHE})^+ + e^- \rightarrow \text{LiNH}_3$	-91.37
$\text{Li} + 2\text{NH}_3 \rightarrow \text{Li}(\text{NH}_3)_2$	-4.93
$\text{LiNH}_3 + \text{NH}_3 \rightarrow \text{Li}(\text{NH}_3)_2$	+13.3
$\text{Li}^+ + 2\text{NH}_3 \rightarrow (\text{Li}(\text{NH}_3)_2)^+$	-128.8
$(\text{Li}(\text{NH}_3)_2)^+ + e^- \rightarrow \text{Li}(\text{NH}_3)_2$	-33.7

* Calculated using the results of Table I.

TABLE III
TOTAL OVERLAP POPULATIONS BETWEEN ATOM PAIRS

Species	Atom Pair			
	Li,N	Li,H	N,H	H,H
NH ₃ (Minimum Basis)	--	--	0.699	-0.029
LiNH ₃ (Minimum Basis)	+0.074	-0.016	+0.696	-0.024
LiNH ₃ (Extended Basis)	-0.225	-0.012	+0.693	-0.026
Li(NH ₃) ₂ (Minimum Basis)	-0.113	-0.011	0.698 (Atoms in the same NH ₃ moiety)	-0.026 (Atoms in the same moiety)

TABLE IV

GROSS POPULATION IN AN ORBITAL ON AN ATOM

Species	Quantity (M.O.number) [*] (Total number of M.O.'s)	Gross Population in the Orbital on the Atom		
		Li	N	H
Li	2/2	1	--	--
NH ₃	5/5	--	1.950	0.017
LiNH ₃ minimum basis	6/7	0.088	1.848	0.021
$r_{\text{Li-N}} = 3.85\dots$ (unpaired electron)	7/7	0.994	0.006	0.000
LiNH ₃ extended basis	6/7	0.096	1.840	0.021
$r_{\text{Li N}} = 3.85\dots$ (unpaired electron)	7/7	1.084	-0.085	0.000
Li(NH ₃) ₂	10/12	0.098	0.921	0.010
$r_{\text{Li-N}} = 4.25\dots$	11/12	0.097	0.924	0.009
	12/12 (unpaired electron)	0.944	0.026	0.001

* Based on order of increasing orbital energy.

TABLE V

TOTAL GROSS POPULATION ON AN ATOM

Species	Atom		
	Li	N	H
Li	3.000	---	---
NH ₃	---	7.907	0.697
LiNH ₃ (Minimum basis)	3.067	7.933	0.667
LiNH ₃ (Extended basis)	3.160	7.866	0.658
Li(NH ₃) ₂ (Minimum basis)	3.123	7.893	0.682

Figure 1. The total charge density of ammonia. The contours in the upper graph are for values of 10.0, 2.8, 0.77, 0.41, 0.22, 0.11, 0.06, 0.03, 0.02, 0.0088, 0.0046, 0.0025, 0.0013, 0.0007, 0.0004 (a_0^{-3}). The upper graph is for a reflection plane and the lower graph is along the C_3 axis of the molecule.

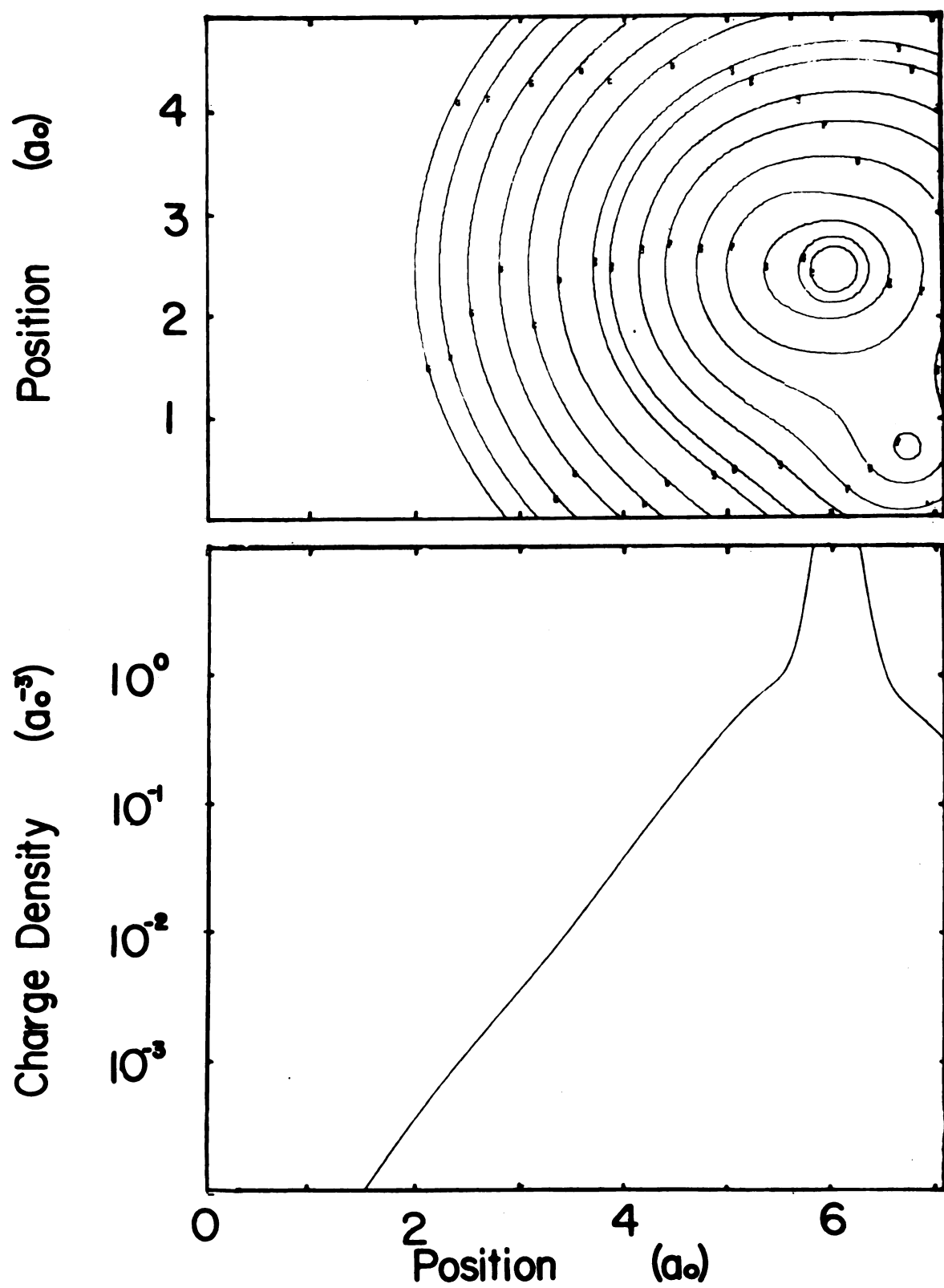


Figure 1

Figure 2. The total charge density of the lithium atom. The contours in the upper graph are for values of 10.0, 2.8, 0.77, 0.41, 0.22, 0.11, 0.06, 0.03, 0.02, 0.0088, 0.0046, 0.0025, 0.0013, 0.0007, 0.0004 (a_0^{-3}). The upper graph is for a plane containing the lithium nucleus and the lower graph is for a line containing the lithium nucleus.

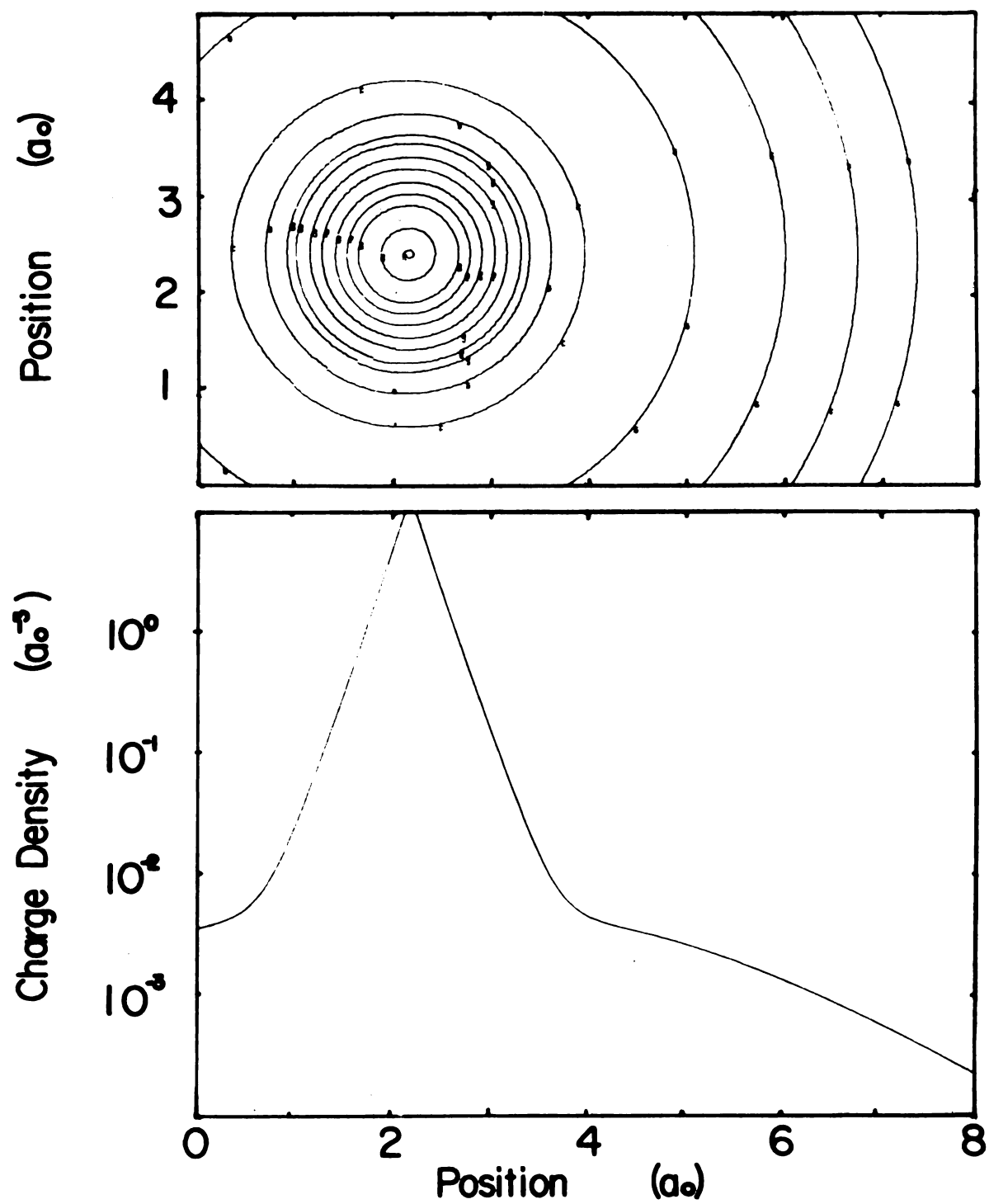


Figure 2

Figure 3. The total charge density of the lithium ammonia complex. The contours in the upper graph are for values of 10.0, 2.8, 0.77, 0.41, 0.22, 0.11, 0.06, 0.03, 0.02, 0.0088, 0.0046, 0.0025, 0.0013, 0.0007, 0.0004 (a_0^{-3}). The upper graph is for a reflection plane and the lower graph is along a C_3 axis of the molecule.

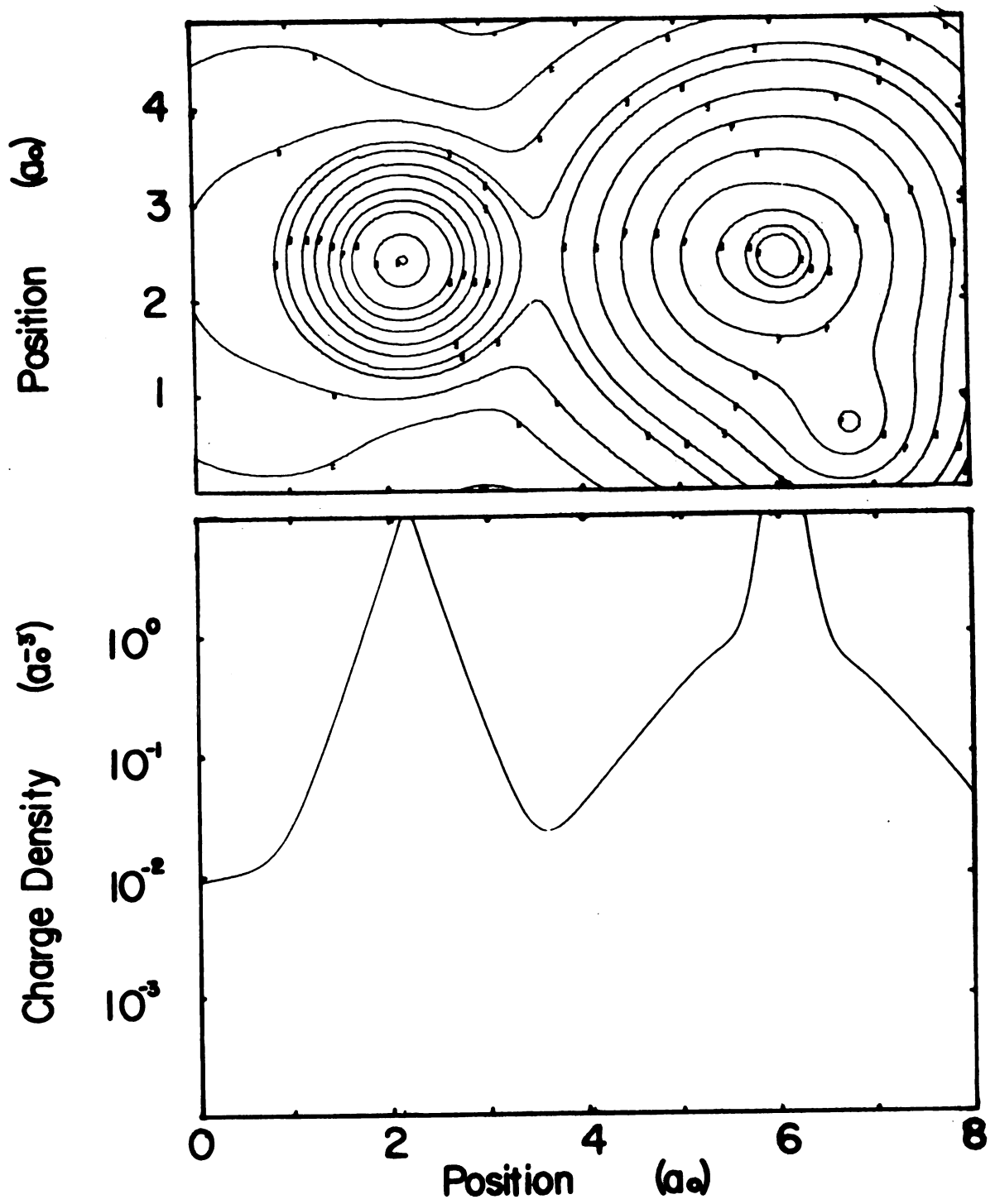


Figure 3

Figure 4. The total charge density of the lithium diammonia complex. The contours in the upper graph are for values of 10.0, 2.8, 0.77, 0.41, 0.22, 0.11, 0.06, 0.03, 0.02, 0.0088, 0.0046, 0.0025, 0.0013, 0.0007, 0.0004 (a_0^{-3}). The upper graph is for a reflection plane and the lower graph along a C_3 axis of the molecule. Only one-half of the molecule is shown.

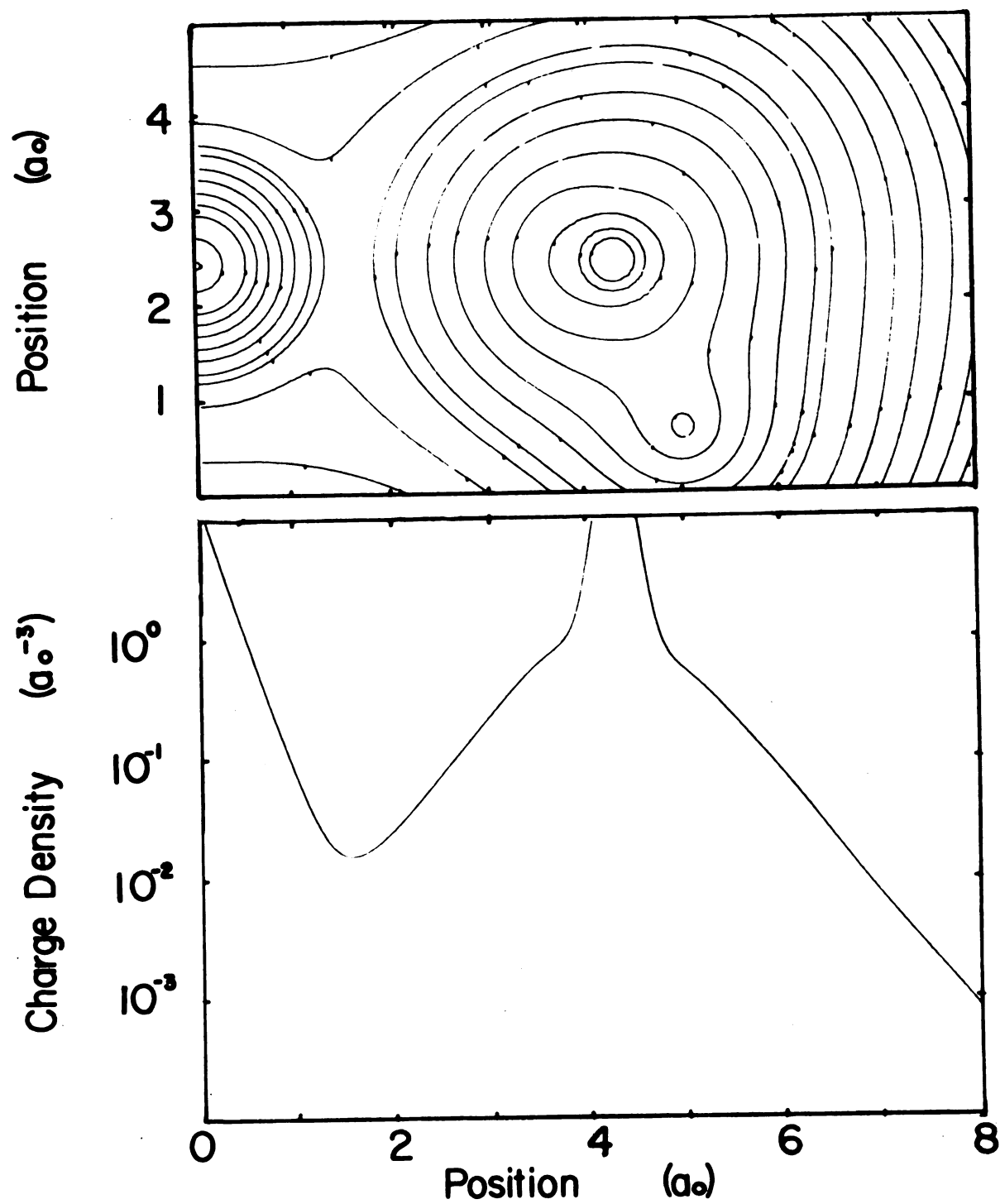


Figure 4

Figure 5. The charge density difference is for the lithium ammonia complex total charge density. The values of the contours in the upper graph are 0.01, 0.008, 0.006, 0.004, 0.002, 0.001, -0.01, -0.008, -0.006, -0.004, -0.002, and -0.001 (a_0^{-3}). The upper graph is for a reflection plane of the molecule and the lower graph is along a C_3 axis of the molecule. The two maxima which are not shown in the lower graph have values of 0.052 and 0.056. A positive difference shows charge density decrease in the complex relative to the sum of the lithium atom and ammonia molecule.

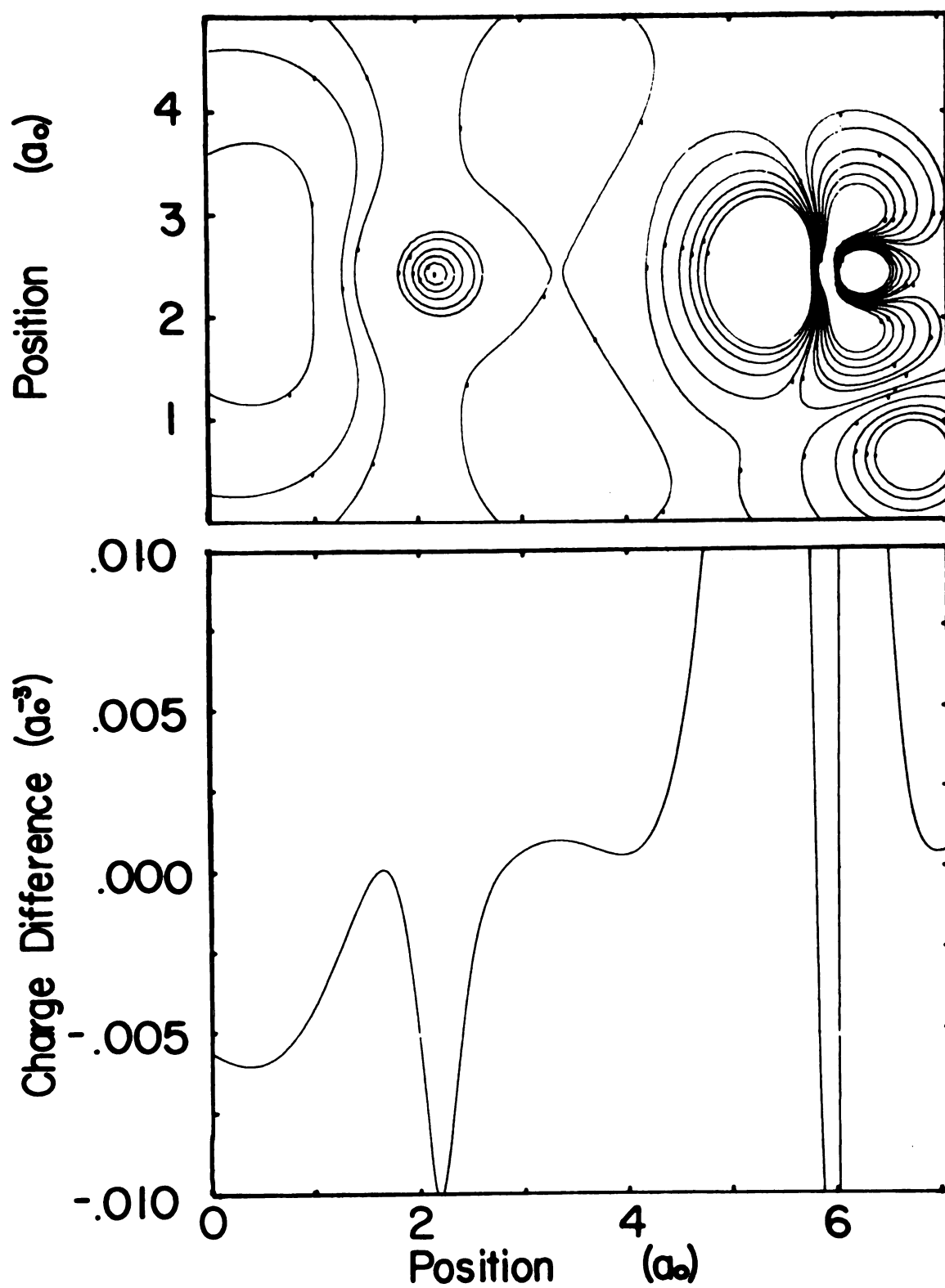


Figure 5

Figure 6. The charge density difference is for the total charge density of the lithium diammonia complex. The values of the contours in the upper graph are 0.01, 0.008, 0.006, 0.004, 0.002, 0.001, -0.01, -0.008, -0.006, -0.004, -0.002, and -0.001 (a_0^{-3}). The upper graph is for a reflection plane of the molecule and the lower graph is along a C_3 axis of the molecule. The minimum and maxima for which the values are not shown in the lower graph are: -0.19, +0.033, +0.030. A positive difference shows charge density decrease in the complex relative to the sum of charge densities of the lithium atom and two ammonia molecules.

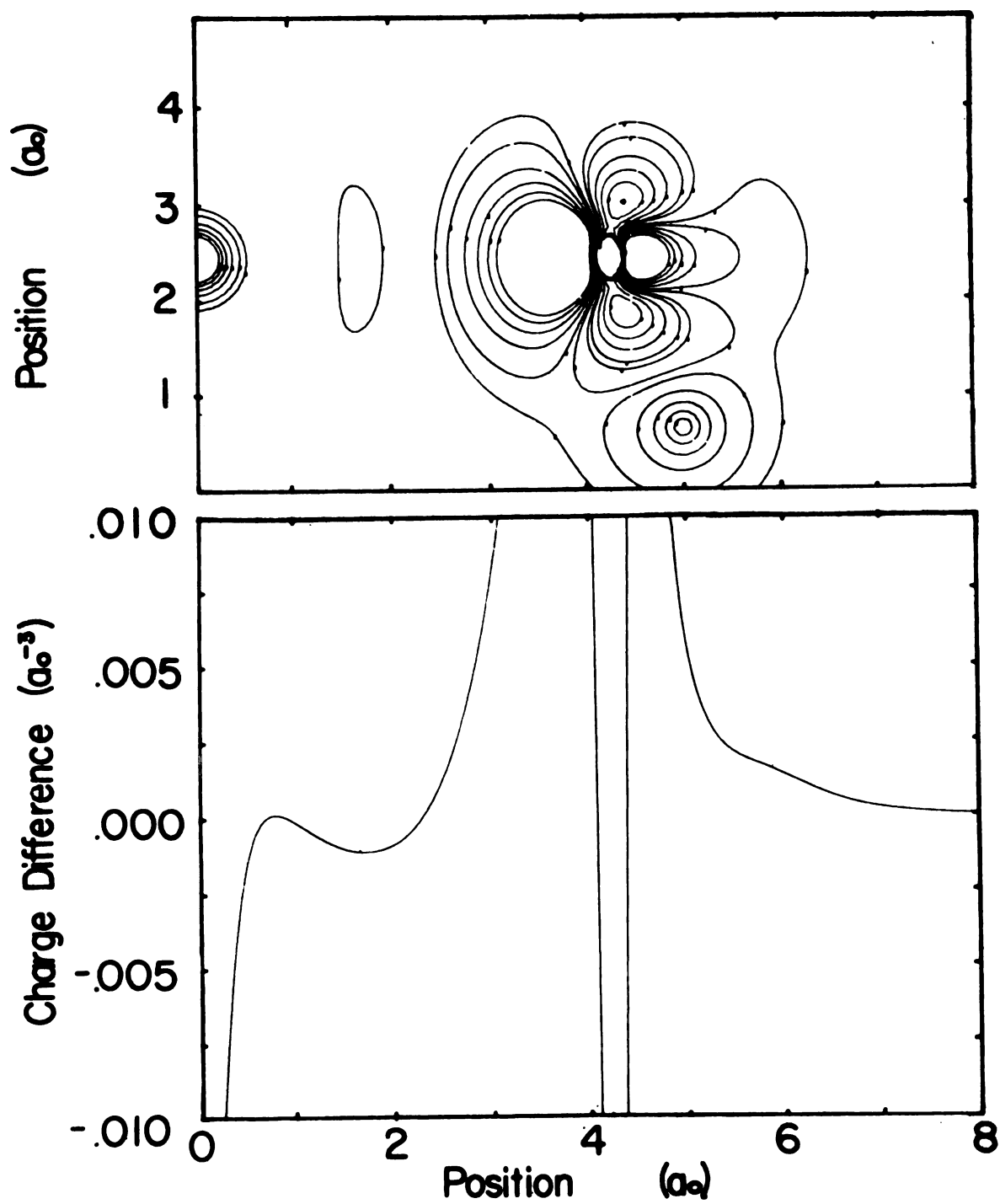


Figure 6

Figure 7. The unpaired electron charge density of the lithium atom. The contours in the upper graph are for 0.1136, 0.0599, 0.0316, 0.0167, 0.0088, 0.0046, 0.0024, 0.0013 and 0.0007 (a_0^{-3}). The upper graph is in a plane containing the lithium nucleus and the lower graph is along a line containing it.

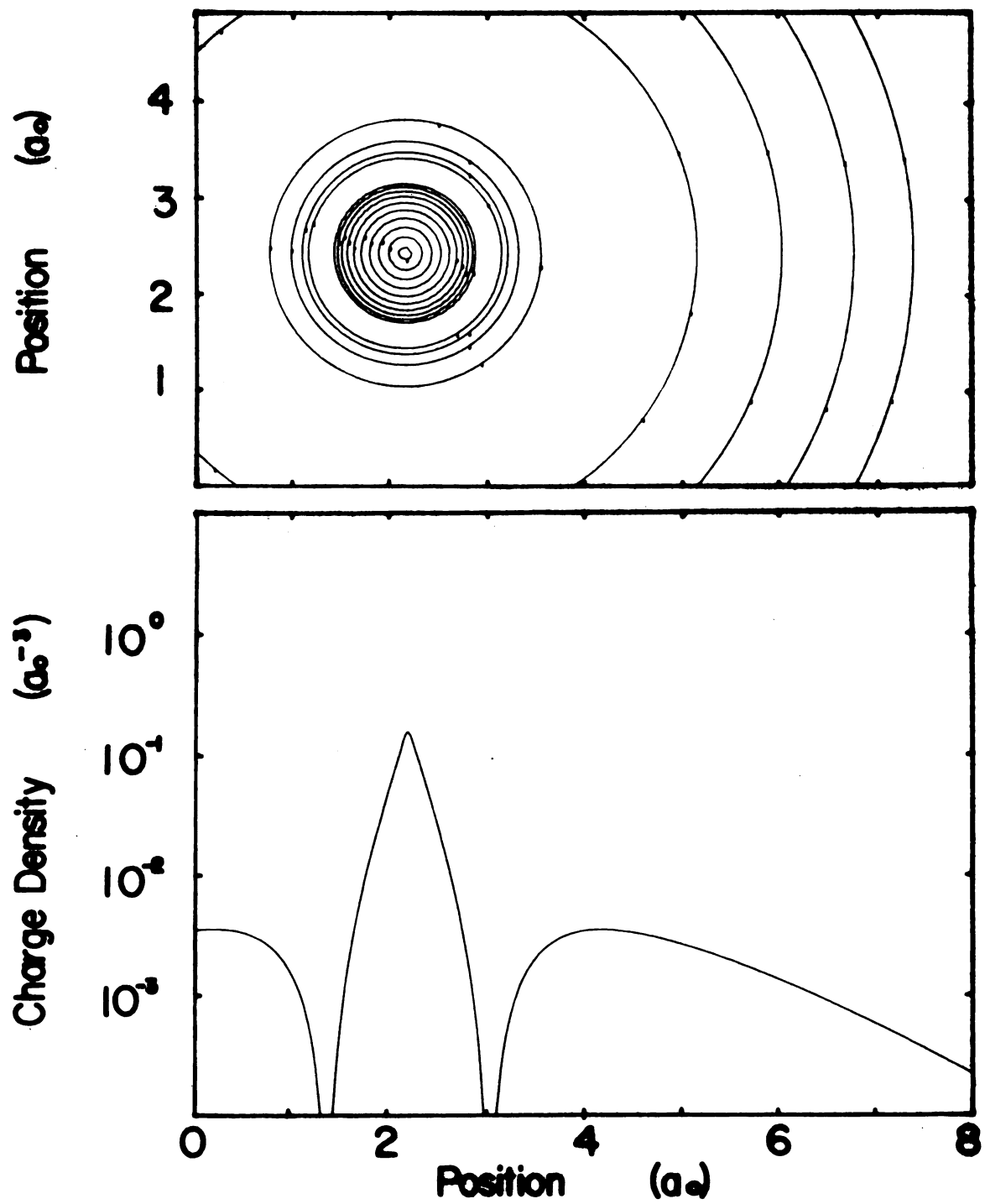


Figure 7

Figure 8. The unpaired electron charge density of the lithium-ammonia complex. The contours in the upper graph are for 0.1136, 0.0599, 0.0316, 0.0167, 0.0088, 0.0046, 0.0024, 0.0013 and 0.0007 (a_0^{-3}). The upper graph is for a reflection plane and the lower graph is along a C_3 axis of the molecule. The lithium is on the left.

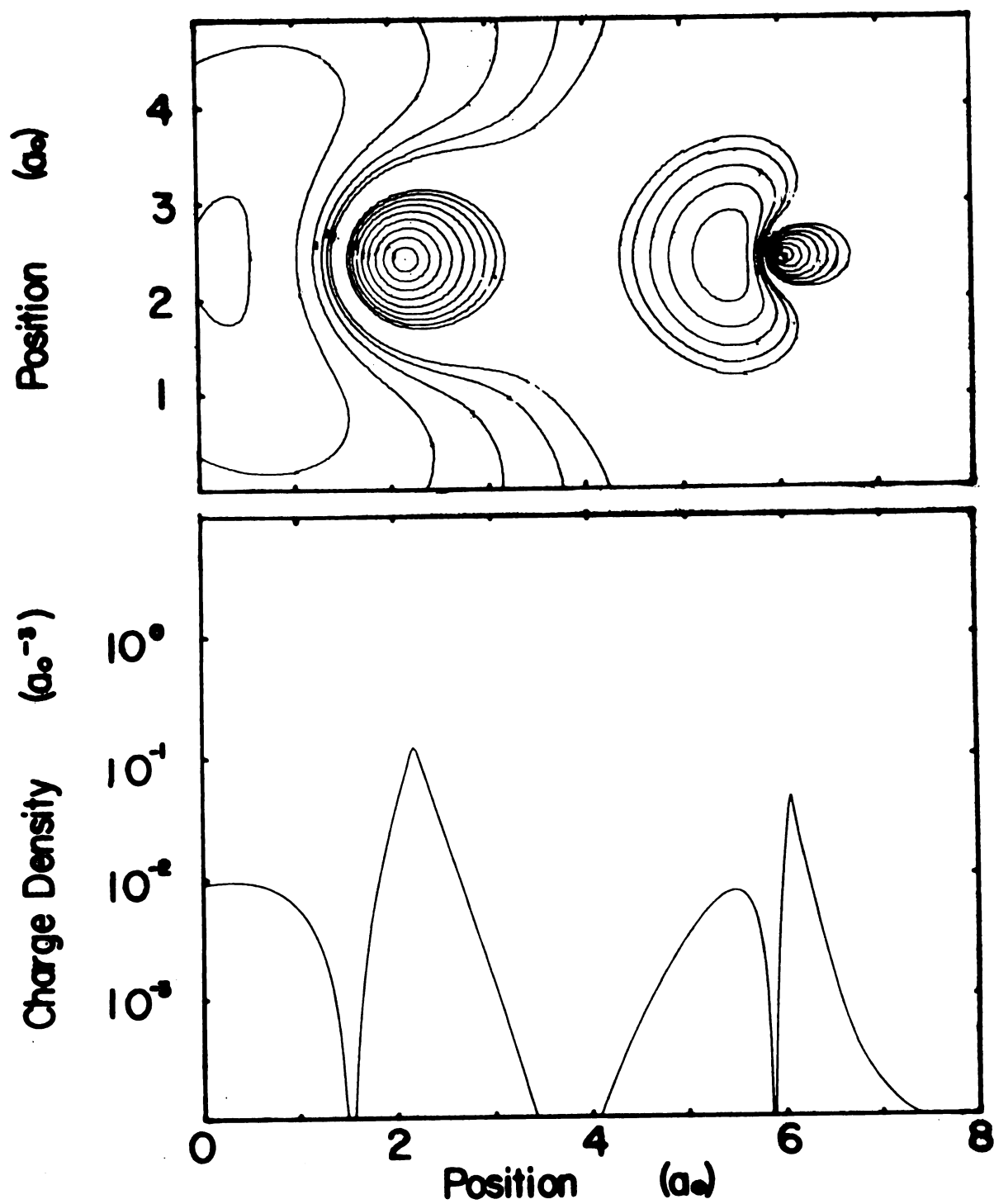


Figure 8

Figure 9. The unpaired electron charge density of the lithium diammonia complex. The contours in the upper graph are for 0.1136, 0.0599, 0.0316, 0.0167, 0.0088, 0.0046, 0.0024, 0.0013 and 0.0007 (a_0^{-3}). The upper graph is for a reflection plane of the molecule and the lower graph is along a C_3 axis of the molecule. Only one half of the complex is shown. The lithium is on the left edge of the graph.

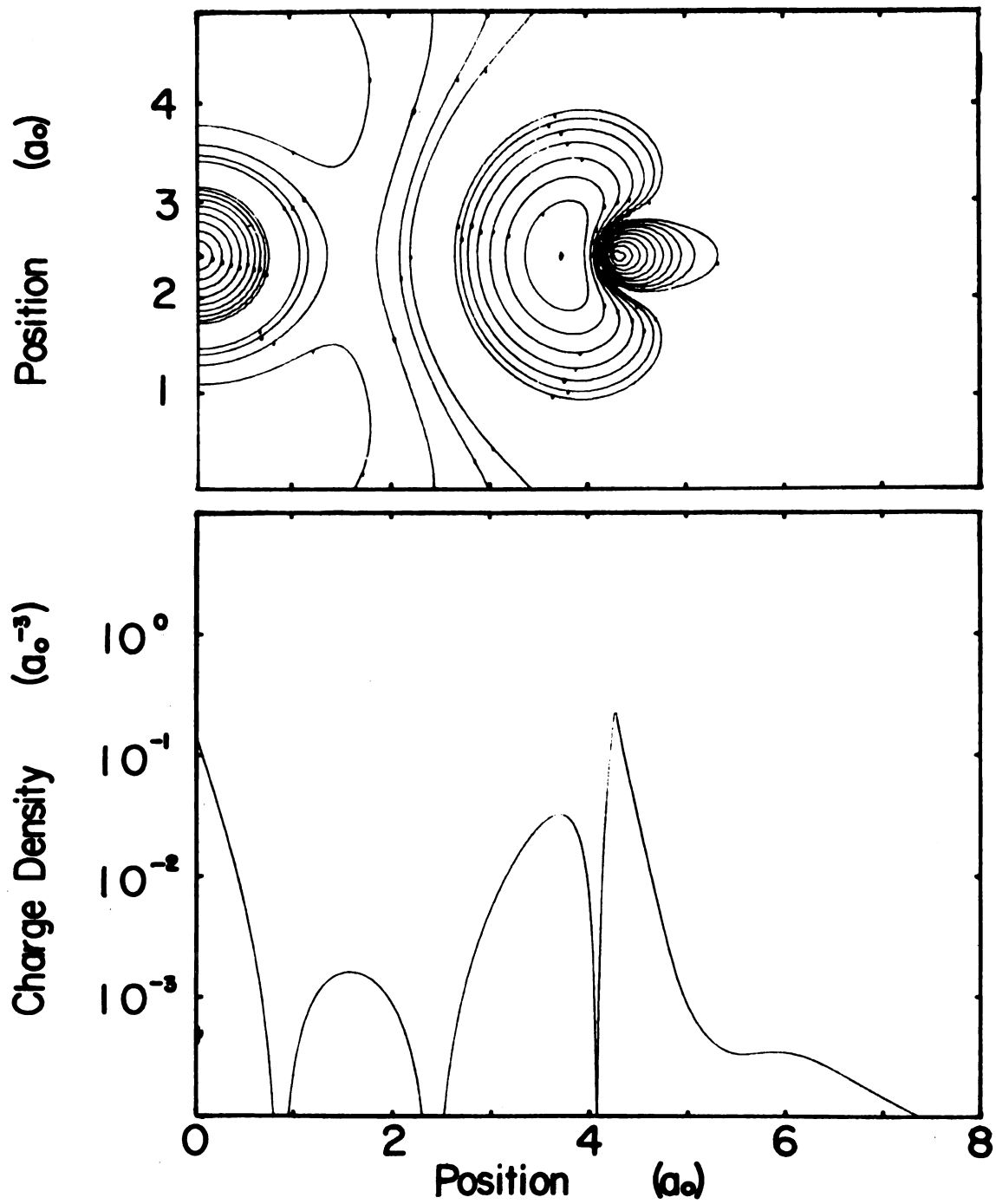


Figure 9

Figure 10. The charge density difference is for the unpaired electron density of the lithium ammonia complex. The values of the contours in the upper graph are 0.01, 0.008, 0.006, 0.004, 0.002, 0.001, -0.01, -0.008, -0.006, -0.004, -0.002, and -0.001 (a_0^{-3}). The upper graph is for a reflection plane of the molecule and the lower graph is along the C_3 axis of the molecule. For the lower graph the maximum has a value of 0.035 and the minimum has a value of 0.05. A positive difference shows a decrease in the charge density of the complex relative to the sum of the lithium atom and ammonia molecule densities.

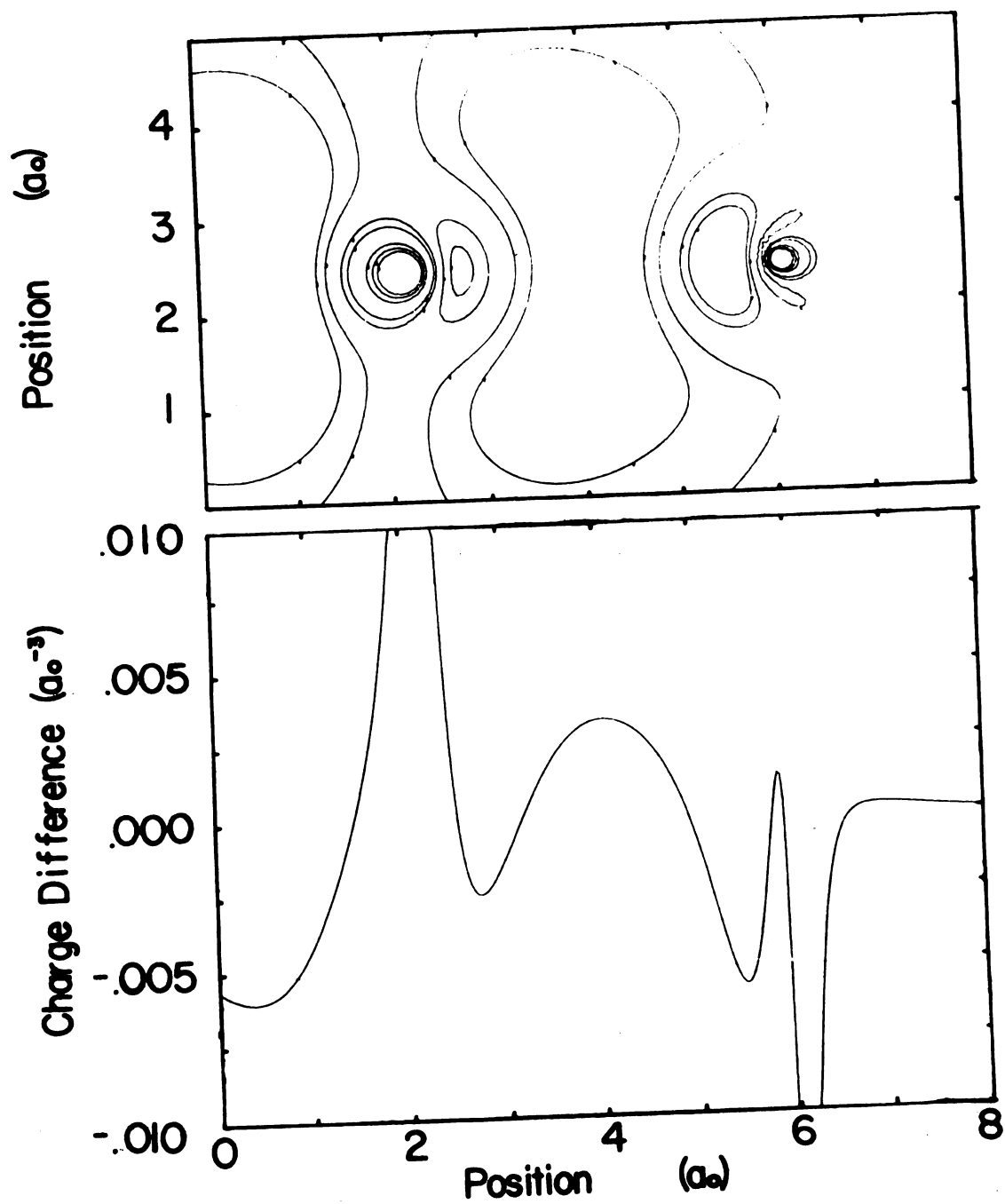


Figure 10

Figure 11. The charge density difference is for the unpaired electron density of the lithium diammonia complex. The values of the contours in the upper graph are 0.01, 0.009, 0.006, 0.004, 0.002, 0.001, -0.01, -0.008, -0.006, -0.004, -0.002, and -0.001 (a_0^{-3}). The upper graph is for a reflection plane and the lower graph is along a C_3 axis of the molecule. The maximum not shown in the lower graph has a value of 0.017 and the minima have values of -0.032 and -0.22. A positive difference shows a decrease in charge density in the complex relative to the sum of charge densities of the lithium atom and ammonia molecules.

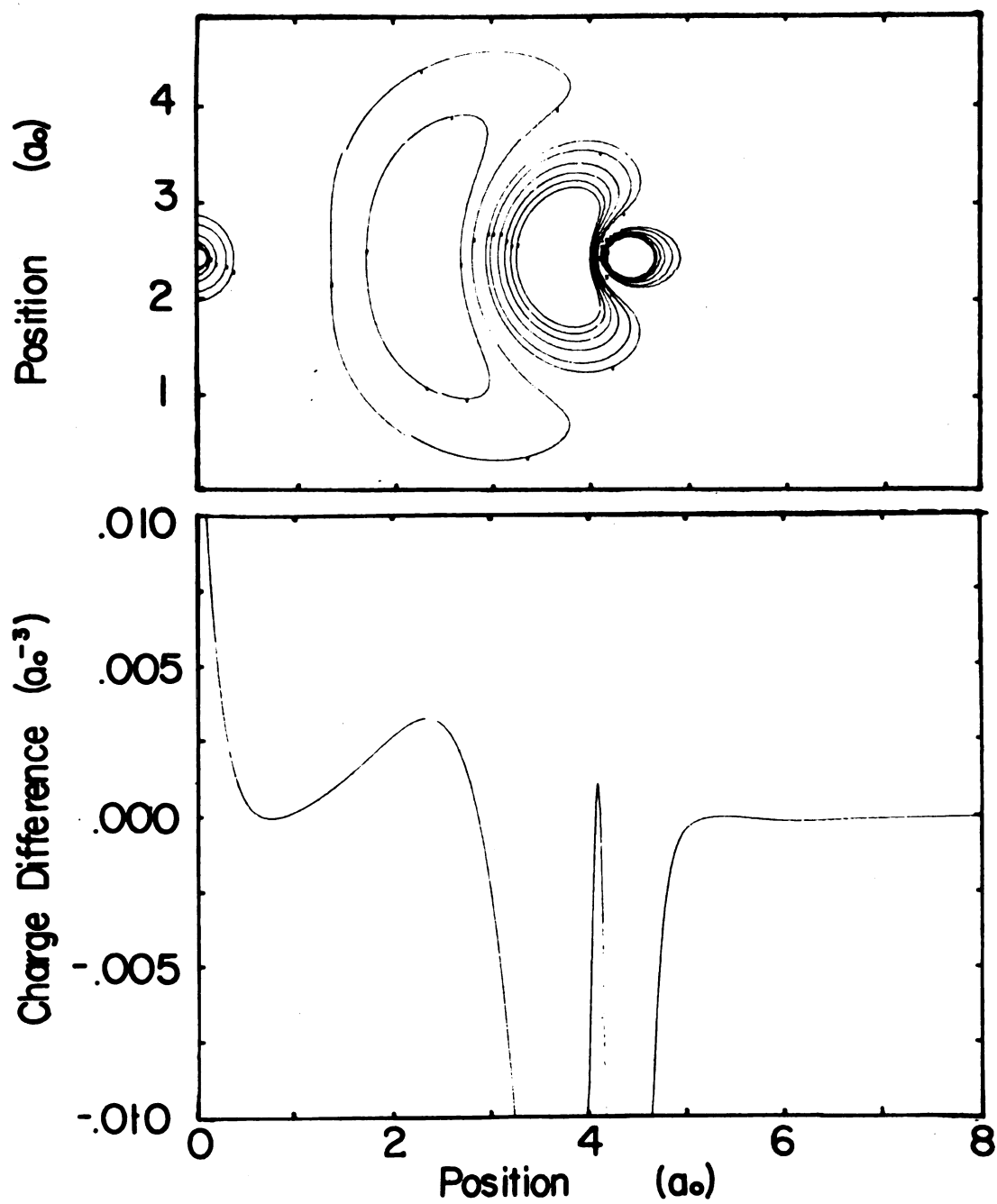


Figure 11

Figure 12. This is a comparison of the unpaired electron distribution in the lithium atom (...), the lithium ammonia complex in a minimum basis (---), and the lithium ammonia complex in the extended basis (—). The charge density is taken on a line passing through the lithium and nitrogen nuclei.

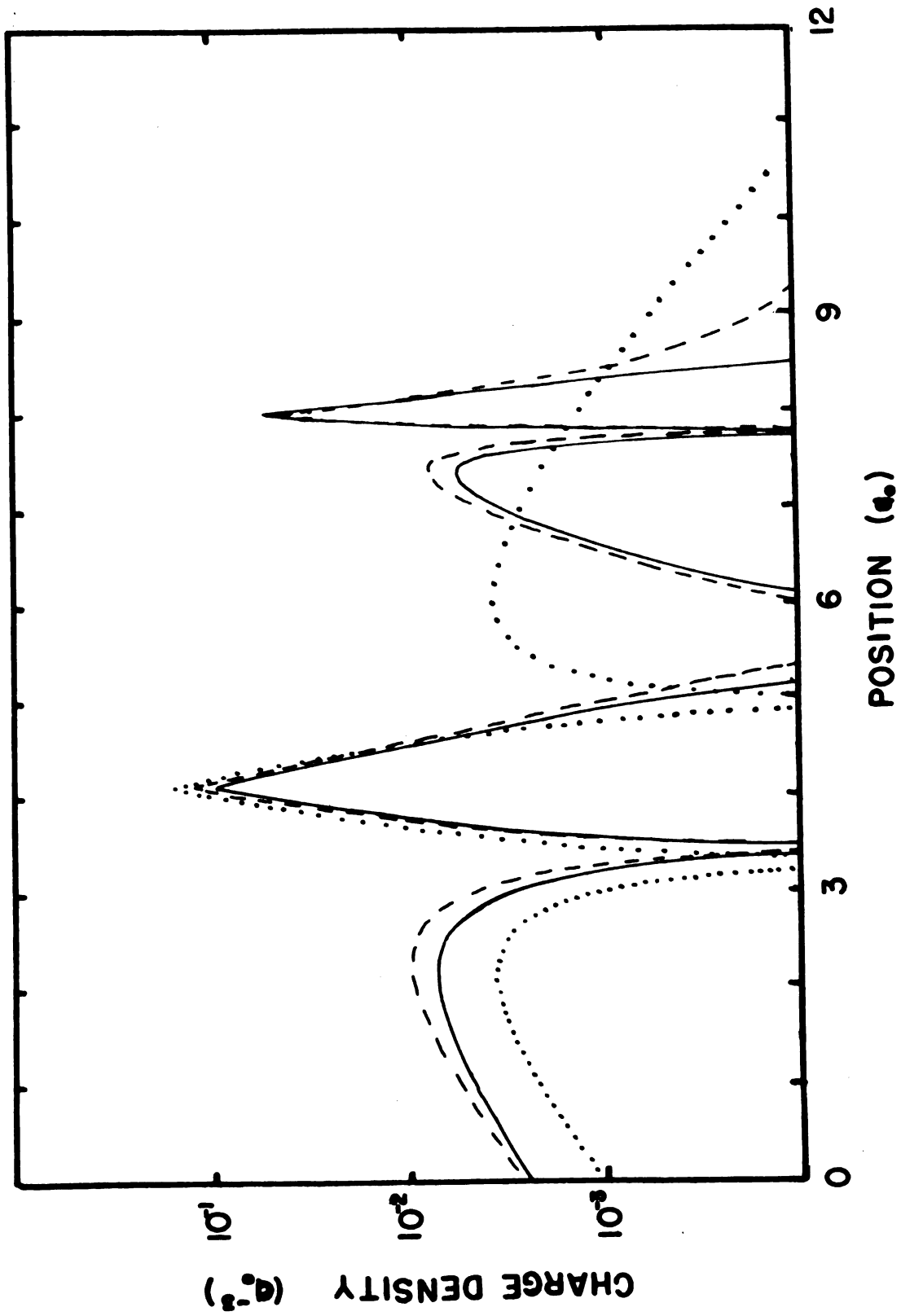


Figure 12

Discussion

The meaning of the various quantities which have been calculated and their probable relation to physical systems are related in this section. First, the reliability of the quantities will be examined and then their chemical significance will be considered.

Energy

The energy shown in Table I and certain energy differences shown in Table II are the result of the single determinant, small basis representation of the electronic wave function for the system of nuclei and electrons. The differences of this method from experiment can be listed as: 1) errors due to the limited basis, 2) errors due to the inability of a single determinant to describe the exact solution, and 3) errors due to neglected effects. Ritchie and King (59) have obtained near Hartree-Fock (best single determinant) solutions for ammonia and other molecules. From their results, they have estimated the correlation energy (contribution not represented by a best single determinant) in ammonia to be -0.33 a.u. (207 kcal/mole). Thus, one can see that if an energy difference is obtained (as in Table II), it will only be meaningful if the correlation energy changes are small compared to the total correlation energy. Ritchie and King also estimated the Hartree-Fock energy of ammonia to be -56.201 a.u. which means that the minimum basis

calculation of ammonia listed in Table I is high by 0.059 a.u. (37 kcal/mole); a substantial amount of energy on a chemical scale. Therefore, the errors due to basis limitations must cancel if energy differences for reactions are to be meaningful.

Recently, Snyder and Basch (62) have investigated the calculation of reaction energies by the SCF method. For the systems investigated, they found a root mean square deviation of the calculated reaction energy from experiment of 6.5 kcal/mole. However, several points must be made concerning the differences between this work and the work of Snyder and Basch. First, they were using comparable (but slightly better) basis sets (their NH_3 energy is -56.1714). Most of the reactions they investigated involved systems with multiple bonding going to systems with different bonding (in a number of cases having no multiple bonding). Thus, the changes in bonding in their calculation are much greater than those in these calculations (see later). Most of the systems they investigated were substantially larger than the $\text{Li}-\text{NH}_3$ calculations reported here. Therefore, equal fractional changes in correlation energy, or changes due to basis incompleteness would be more pronounced in their calculations. The one further difference between this work and the other is that the present calculations have an open shell involved in some cases. Since the unpaired electron is reasonably localized in the lithium orbitals and because

the calculation is on the same level as Snyder and Basch's calculation, one can probably conclude that the presence of the open shell is not significant. Taking all of these arguments into account, one can probably conclude that the error shown by the calculations of Snyder and Basch are expected to be outer limits for the energy calculation of LiNH_3 , Li , and NH_3 .

Based upon the calculated energy one can conclude the following; although the absolute values of the energies calculated are significantly in error (i.e., they have relatively large known errors), the differences are probably accurate enough to permit the conclusion that the complex of lithium and ammonia would be stable with respect to dissociation into the (gas phase) atom plus an ammonia molecule by about 20 kcal/mole. As is to be expected, it is also very stable with respect to ionization. The process of adding a second ammonia molecule (in a D_{3h} configuration) does not appear favored but two things must be considered. The C_{2v} configuration has not been considered. This geometric arrangement might be more suitable, but the increased repulsion of the ammonia molecules would make it seem unlikely. Secondly, the energy differences are smaller in this case and the overall energy is larger, leading to greater uncertainty in the result.

Population Analysis

At the outset it was decided not to alter the NH_3 internal geometry since it was thought that the bonding in this structure would not be significantly perturbed by the presence of the lithium atom. The population analysis provides the first opportunity to examine this assumption. A comparison of the N-H parameters given in Tables III to V shows, using the same basis, they are changed very little by the presence of lithium.

In Table III the net overlap between atoms is given. The interpretation of this quantity is that two atoms are bonded, non-bonded or anti-bonded to each other depending on whether this quantity is positive, zero, or negative. The minimum basis calculation shows a positive overlap between lithium and nitrogen orbitals but the extended calculation shows the opposite. This result cannot be explained but is not to be accepted since it is in disagreement with the observable, i.e., the expectation value of the binding energy.

Table IV contains the gross populations of the orbitals on an atom. From this quantity one desires to learn how the charge is rearranged on forming a molecule. One can, in M O. theory, assign electron pairs to orbitals and this population breakdown is supposed to inform about which electrons are in which regions of the molecule. Only the valence shells are included since the lower lying orbitals are primarily confined as they are in the constituents.

The result of primary interest here is the location of the unpaired electron, but one also obtains insight into the mechanism of the bonding of the lithium to the ammonia.

Using the data in Table IV we can conclude that the unpaired electron remains with 99.4% of its population, in the lithium orbitals. Notice that the sixth orbital in the LiNH_3 has an 8.8% population in the lithium orbitals, also. This orbital corresponds essentially to the lone pair of the ammonia molecule and populates the lithium orbitals by overlap with the P_z orbital of lithium. It is primarily through this mechanism that the lithium gains the excess population of 0.067 electrons which is shown in Table V for the LiNH_3 . The extended basis calculations show the same basic effects. The negative population on nitrogen given in Table VI is similar to those attributed by Mulliken to imperfections in the definitions of the orbital populations.

Table IV also shows that for the complex with two ammonias, each nitrogen gains about 2.6% of the unpaired electron, or equivalently the unpaired electron has a population of 94.4% in the lithium orbitals. Notice also in Table V that the lithium again obtains a significant increase in gross charge.

Change Densities

Charge density as a function of position has been calculated for some of those species for which the wave function was obtained. Two quantities have been calculated; the

unpaired electron density at a nucleus (related to the hyperfine splitting) and both the total and unpaired electron density in planes of symmetry. They will be discussed separately.

Density of Unpaired Electron at an Atom. Before considering the results obtained, a discussion of the general accuracy of the method in predicting the observed value is needed. Here, as with the energy calculation, one needs to know how errors are likely to enter and what their magnitude is likely to be. This method has two predominant sources of error. First, the Hartree-Fock method may not give the exact solution and second, the functions which have been used as a basis for the expansion may not behave "properly" at the nucleus. Using lithium atoms as an example of the accuracy available, one finds that the Hartree-Fock solution yields a value of 2.09 (atomic units) (41) with an experimental value of 2.906 (atomic units) (41) for the value of the square of the wave function (ψ^2) at the nucleus. Therefore, it can be concluded that the Hartree-Fock method itself is deficient with respect to this expectation value. Using Whitten's gaussian expansion of the Hartree-Fock solution (70) gives a value of ψ^2 at the nucleus of 1.55 (Table I). This happens because the gaussian function differs from the natural solution in the region of the nucleus because it approaches the origin with a slope tending toward zero whereas the natural solutions approach the origin with

a finite slope. Addition of more functions to the expansion can improve this to the point of the HF solution. Thus, the small size of the value calculated from Whitten's function is a result of the limited basis. These inaccuracies will also be present in other numbers calculated with a similar basis. Even though the absolute magnitude of the result is expected to be in error, the trends observed due to the formation of a complex are probably correct.

The results are listed in Table I. First, the L_1NH_3 results will be considered. The most obvious trend is that the formation of the complex significantly lowers the contact at the lithium nucleus. It is also to be noticed that the value of the unpaired density at lithium is a rather sensitive function of the position of the ammonia. Note that a significant decrease in contact density occurs even though the population analysis indicates small decrease in the population of the lithium orbitals. Notice also that the unpaired spin density at the nitrogen is large, even though the unpaired electron transfer to the ammonia orbitals is small (Table IV). This is not a contradiction and will be commented on further when the contour maps of density are presented.

Examination of the values for the diammonia complex shows different results. The value of the density at lithium is smaller than for the atom but larger than for the one ammonia complex. Note, however, that the value of

the spin density at nitrogen has increased about an order of magnitude over the value for the one ammonia complex. This increase at nitrogen is consistent with the increase in unpaired electron density in the nitrogen orbitals as shown by the population analysis (Table IV). The value at hydrogen has also increased by about the same factor even though it is still very small.

Charge Densities in General. Although the value of the contact density is not well-represented by the basis used, one would expect the charge density in other regions to be much better represented. In Whitten's earlier work (69,70) he has shown how well the gaussian lobe expansion represents the atomic orbitals. One might expect similar representation of the molecular charge density; especially in this case where little rearrangement is seen.

The figures have been ordered so that Figures 1 through 4 show the total charge density for the constituents and for the complexes at the geometry of their lowest energy. However, because the shifts in charge density on forming the complex are small, a plot of the shifts has been created by forming a difference density of the reactants minus the product. This is shown in Figure 5 for LiNH_3 and Figure 6 for $\text{Li}^+(\text{NH}_3)_2$. A word of caution is due here: the changes in charge density are a small fraction of the total charge density. Note the magnitude of the changes are less than 0.3 a_0^{-3} while in some regions the total density may be as high as 180.0 a_0^{-3} .

Figures 5 and 6 show that in both the one-to-one and the one-to-two complexes of lithium and ammonia, the total charge in the region of the lithium nucleus increases. In both cases, one can also see that near the nitrogen nucleus the density changes oscillate in sign along a line connecting the two nuclei. The upper half of the figures shows that what is happening is a decrease of charge density in the region of the lone pair of electrons on the ammonia and an increase in the plane perpendicular to the axis of the lone pair. This charge shift probably results from two causes. First, the lithium atom could act repulsively toward these electrons and second, some of the charge could be transferred into the orbitals on the lithium. The transfer to lithium is consistent with the population analysis, and also provides an explanation of the increase of charge behind the lithium atom (relative to the ammonia position).

Figures 7 through 11 are similar plots except that the density of the unpaired electron is shown. The changes in this density are a much larger fractional change than with the total charge density since the unpaired electron density is initially much smaller. The line plots of density versus position along the C_3 axis show clearly that the presence of the ammonia molecule changes the number and location of nodes in the unpaired electron wave function. Comparison of Figures 7 and 8 also shows that the unpaired electron density peaks sharply in the region of the nitrogen

nucleus, even as the bulk of the orbital tends to avoid the region of the ammonia molecule. This results from the requirement that the unpaired electron orbital remain orthogonal to the other occupied orbitals and that the region close to the nitrogen has a large density of electrons. The peak arises from the mixing of a small amount of nitrogen orbitals to achieve this orthogonal condition but the total electron transfer to nitrogen is very small as is shown by the population analysis (Table IV). One can see by comparison of Figures 8 and 9 that the fraction of unpaired electron in the region of the ammonia is greater in the two-ammonia complex than in the one-ammonia complex. The peak in the region of the nitrogen is also higher in the two-ammonia complex. Figure 9 shows that the unpaired electron avoids the ammonia when only one is present by obtaining a higher density "behind" the lithium. Since this is not possible in the two-ammonia complex, one should not be surprised to find increased occupancy of the nitrogen orbitals by this electron.

Figures 10 and 11 are difference density maps of the unpaired electron density. The changes in density are about the same magnitude as the changes in total charge density (Figures 5 and 6) but a comparison shows that the changes in a given region of space are of opposite sign to the changes in total density; that is, where the total density increases, the unpaired density increases and vice versa, with the magnitudes of the changes being similar.

Influence of the Basis on the Charge Distribution. As mentioned earlier, there was concern about the need for a larger basis set to describe the gross features of the problem. If the unpaired electron shows any tendency to transfer to the ammonia molecule, it would probably transfer into what would be essentially a 3s orbital of nitrogen. On the other hand, if hybridization arguments are used, one might expect the lithium to form an sp hybrid resulting in promotion of the unpaired electron to a 3s of lithium, followed by donation of the lone pair of ammonia into the sp hybrid to form the bond. Either of these schemes would change the charge distribution from that given by the minimum basis calculations because the 3s orbitals for either atomic system are poorly represented in this basis.

Figure 12 represents the charge distribution calculated using different basis sets. We can see once again how the ammonia perturbs the unpaired electron distribution by comparison with the lithium atom, but we can also see that the effects of extending the basis are rather minor. From this we conclude that the 3s orbitals of nitrogen and lithium are rather unimportant in the description of this complex.

Implications for Monomer Models

These calculations show that a lithium atom transfers little charge to ammonia molecules which are near it and that ammonia bonds to a lithium atom by a coordinate covalent bond. Because alkyl groups are electron donating groups,

the aliphatic amines would be expected to have a charge density at the NH_2 group at least as large as in ammonia. Therefore, the charge transfer to ammonia is expected to be at least as large as in the amines. The predominant effect of the neighbor molecules is repulsion of the metal electrons; particularly the unpaired electron.

These calculations indicate that any model of the monomer which treats it as an expanded atom should consider the repulsion of the individual solvent molecules for the unpaired electron. The charge density maps from this calculation of the unpaired electron orbital show it to have a pronounced angular dependence. Therefore, if the short range interactions of the ammonia molecules with the unpaired electron are correctly described by a model which treats the ammonias as an array of electrostatic point dipoles, the angular dependence of the unpaired electron orbital which is shown in the ab initio calculations implies that the electrostatic potential terms with angular dependence are important.

If a lithium atom were inserted into the solvent lattice, these calculations indicate that the value of some properties such as the hyperfine contact density at various nuclei would be sensitive to the number and position of neighboring solvent molecules. Furthermore, the values of the observables might be significantly different from the free atom values.

The experimental hyperfine contact in lithium-ethylamine solutions is very much smaller than the free atom and that at the nitrogen is larger than at the lithium. It has been

suggested (3) that this occurs because of a spherically symmetric redistribution of the unpaired electron from lithium onto nearby solvent molecules. These calculations do not show any mechanisms by which such behavior can be explained. In particular, if the long range solvent interactions are predominant in the reduction of contact at the atom, a similar reduction in contact at the nitrogen should be expected.

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APPENDICES

APPENDIX I

A DIFFERENTIALLY PUMPED, GREASELESS HIGH VACUUM VALVE AND END JOINT

Greaseless high vacuum valves and joints often leak small quantities of gas, especially when they are opened or closed or parts are moved relative to one another. In this appendix a modification of commercially available valves and joints which stops this leakage is described.

Figure 1 shows how to construct the valve from commercially available valves. A new Teflon plug must be machined to fit the longer barrel and should have "O" rings above and below the intermediate pumping chamber. When the valve is used, the bottom parts are used as with a normal valve and the top part is pumped by an auxiliary system. Both 4 and 10 mm valves have been constructed using Delmer-Urry valves.

Figure 2 shows the arrangement of parts used to construct a rotatable joint. The outer chamber formed when two of these parts are joined is pumped by the same auxiliary pumping system as the valves. When constructing this joint, the two individual joints must be made coplanar and concentric. Although 5mm and 15mm joints have been used, 5mm and 20mm joints would be better.

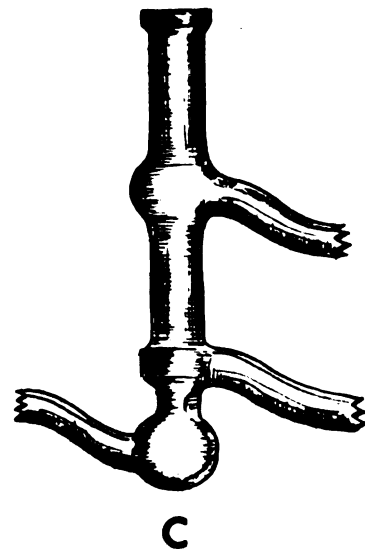
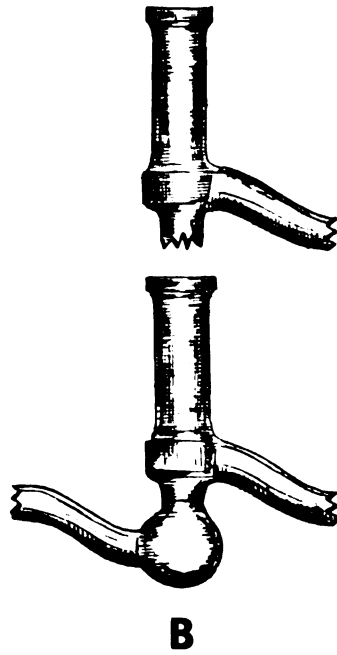
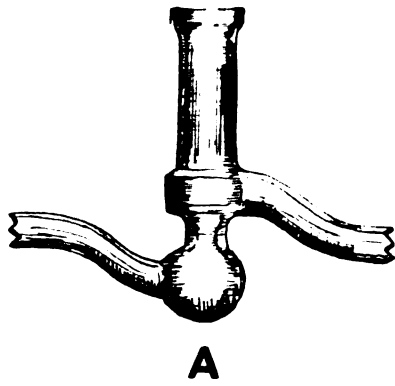


Figure 1

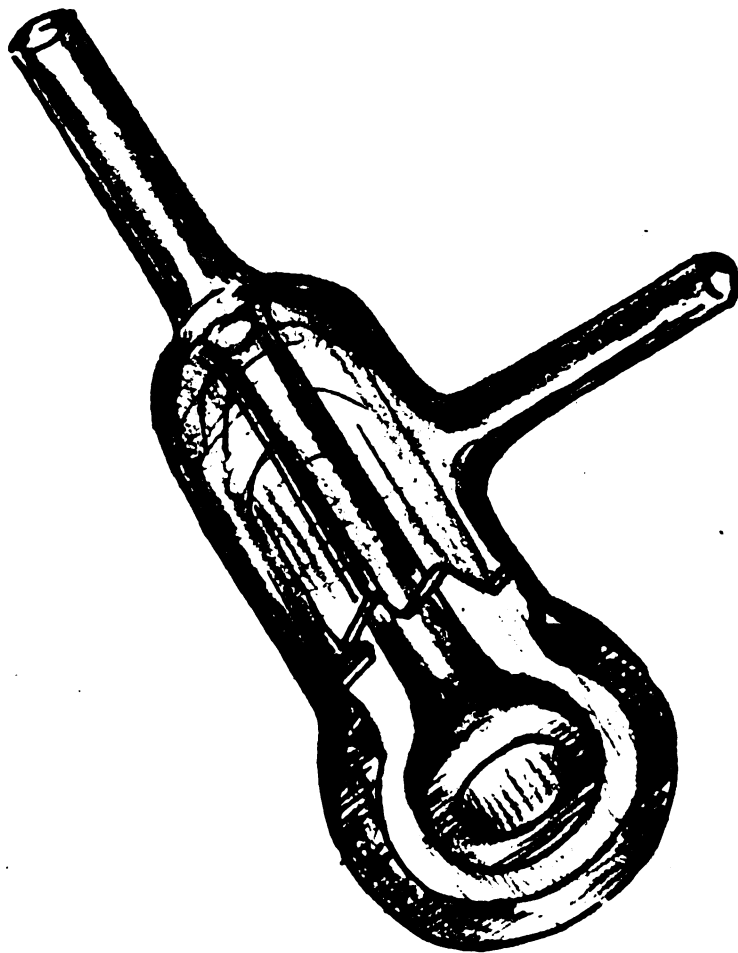


Figure 2

APPENDIX II

LIST OF PROGRAMS

This appendix lists several computer programs for data handling and analysis which were developed during the course of this work. The names and functions of these programs will be listed here. All of these programs were written in FORTRAN for the CDC-3600 computer.

A G VALUE--The program calculates the best least square value of the A and g constants for an isotropic ESR spectrum with hyperfine splitting from a single nucleus.

LINSEP--This program separates overlapping first derivative ESR lines by least squares fitting a set of shape functions to the magnitude versus field data. The data from CAT is used as described in Chapter II.

LINWID--This program calculates linewidth as a function of m_I using the formalism described in Chapter II. It fits by the criterion of least squares the fluctuation constants. The version used assumed a two-state model, but could be easily modified for more general cases.

CONPLT--This is a subroutine which calculates and plots the contour maps shown in Chapter III. The input data give the magnitude of the function to be plotted at a rectangular array of points in the plane of interest.

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