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# ELECTRON PARAMAGNETIC RESONANCE STUDIES OF UNPAIRED ELECTRON DISTRIBUTIONS IN ALKALIDES AND ELECTRIDES

presented by

Dae Ho Shin

has been accepted towards fulfillment of the requirements for

Ph. D. degree in Chemistry

James L. Dye Major professor

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#### ELECTRON PARAMAGNETIC RESONANCE STUDIES OF UNPAIRED ELECTRON DISTRIBUTIONS IN ALKALIDES AND ELECTRIDES

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by

Dae Ho Shin

#### A DISSERTATION

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Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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#### ABSTRACT

#### ELECTRON PARAMAGNETIC RESONANCE STUDIES OF UNPAIRED ELECTRON DISTRIBUTIONS IN ALKALIDES AND ELECTRIDES

by

Dae Ho Shin

The nature of the trapped electron in alkalides and electrides was explored by X-band EPR, G-band EPR, and pulsed EPR techniques. The EPR spectra of six compounds of known-structure reveal that excess electrons in these salts are trapped at vacant anionic sites and can be considered similar to F-centers. Hyperfine splitting is observed when the complexed cation is exposed to the anionic site, but not when the cation is well-shielded by inclusion in a sandwich structure formed by two crown ether molecules.

The g-values of the contact systems,  $K^+HMHCYNa^-$ , Rb<sup>+</sup>HMHCYNa<sup>-</sup>, and Cs<sup>+</sup>HMHCYNa<sup>-</sup> are 2.0029, 1.9983, and 1.9833, respectively. The g-values of the isolated systems, Cs<sup>+</sup>(18C6)<sub>2</sub>Na<sup>-</sup> and Cs<sup>+</sup>(15C5)<sub>2</sub>Na<sup>-</sup> are 2.0022 and 2.0020, respectively and are close to the free electron value. The % atomic character at the cations in K<sup>+</sup>HMHCYNa<sup>-</sup>, Rb<sup>+</sup>HMHCYNa<sup>-</sup>, and Cs<sup>+</sup>HMHCYNa<sup>-</sup> are 6.48, 10.5, and 11.9 %, respectively.

A new crystalline sodide, Na<sup>+</sup>HMHCYNa<sup>-</sup> was synthesized and characterized by EPR spectroscopy. The g-values of three sodides of

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unknown-structure, Na<sup>+</sup>HMHCYNa<sup>-</sup>, K<sup>+</sup>18C6Na<sup>-</sup>, and Rb<sup>+</sup>18C6Na<sup>-</sup> are 2.0010, 2.0023, and 1.9974, respectively. The % atomic characters of the cations in Na<sup>+</sup>HMHCYNa<sup>-</sup>, K<sup>+</sup>18C6Na<sup>-</sup>, and Rb<sup>+</sup>18C6Na<sup>-</sup> are 1.16, 18.9, and 16.3 %, respectively. The latter two compounds exhibit spin-pairing with spin-pairing energies of 1.94 x  $10^{-2}$ , 2.11 x  $10^{-2}$  eV, respectively.

Crystallized pure  $Cs^+(18C6)_2e^-$  has a nearly axially symmetric EPR signal, both at X-band (10 GHz) and at G-band (250 GHz). Crystallized pure  $Cs^+(18C6)_2Cs^-$  shows no evident separation of g-value at X-band but shows a separation at G-band. The increased resolution at 250 GHz completely separates the parallel and perpendicular components, and agrees with the results at X-band for  $Cs^+(18C6)_2e^-$ . The EPR pattern at 250 GHz for electrons trapped in  $Cs^+(18C6)_2Na^$ is similar that of  $Cs^+(18C6)_2e^-$ . These results show that the unpaired electron in pure electrides is localized on the EPR time scale at the same type of anionic site as is the F-center in alkalides.

Pulsed EPR studies of Cs<sup>+</sup>HMHCYNa<sup>-</sup> show two magnetically distinct groups of weakly coupled <sup>133</sup>Cs nuclei; one with an isotropic electron-nuclear hyperfine (Fermi contact) coupling of 0.34 MHz and the other with a contact coupling of less than 0.1 MHz. Analysis of these data by computer simulation shows that the number of Cs nuclei that give rise to these interactions and their distance from the paramagnetic center is consistent with the hypothesis that the trapped electrons occupy vacant anionic sites. The results indicate that the spread of the unpaired electron spin density along the axis formed by the "contact ion pair" may be greater than that in the plane perpendicular to this axis.

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# To my parents

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I would like to dedicate this thesis to my parents.

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#### CHAPTER I

#### INTRODUCTION

Alkalides and electrides are compounds in which the anions are alkali metal anions and trapped electrons respectively. This thesis will emphasize the characterization of the anionic site in alkalides and the electron locales in electrides. The primary techniques used to characterize the trapping site are X-band electron paramagnetic resonance (EPR), G-band EPR and pulsed EPR spectroscopy. This chapter will review background material about the trapped electron in liquids and solids. First, the solvated electron in liquids will be introduced and then the trapped electron (F-center) in ionic solids and localized electrons in aqueous frozen systems and in organic glassy solids will be discussed. The description of these systems will focus on their structures and on the magnetic properties of the electron.

Studies of solvated electrons originated with the investigation of active metals (alkali and alkaline earth metals plus Eu and Yb) dissolved in ammonia, amines and certain polyethers. These electrons show similar types of aggregate formation as do trapped electrons and ions in the solid state. These considerations may be expanded to the interpretation of the results obtained for polycrystalline alkalides and electrides. Finally, certain issues about the charge distribution for electrons trapped at anionic sites will be addressed in order to put the present work in perspective.

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#### I.A. Solvated Electrons in Solution

#### I.A.1 Metal-Ammonia Solutions

Since Weyl discovered that sodium and potassium metals form blue metal-ammonia solutions (MAS) when dilute and bronze colored solution when concentrated [1], this field has resulted in seven conferences named "Colloque Weyl" [2, 3, 4, 5, 6, 7, 8]. The most striking feature of metal-ammonia solutions are *electrons* in insulating liquids. The physical properties of these solutions change drastically with the concentration of electrons. The electrons in dilute solution are localized as solvated electrons, while in concentrated solutions they are delocalized to form a "Fermi gas". Many physical properties of alkali metal-ammonia solutions have been studied as a function of metal concentration, temperature and pressure. In this section the magnetic properties will be emphasized.

Hutchison and Pastor first reported the magnetic susceptibility of MAS by EPR in the nonmetallic region of sodium- and potassiumammonia solutions [9]. Essig and Schindewolf measured the magnetic susceptibility over a wide concentration range by EPR. The results from EPR [10, 11, 12] and static Gouy measurements [13, 14, 15, 16] are in good agreement. A comparison was made by Harris and Logowski, in describing their EPR data in the nonmetallic region of alkali metal-ammonia solutions [17]. The magnetic susceptibility is independent of the alkali metal used. The most important feature of the electronic susceptibility in MAS is strong reduction of the molar paramagnetism between 0.01 and 1 mole percent metal (MPM), which indicates formation of diamagnetic species usually designated as  $e_2^=$  or  $(e^- \cdot M^+ \cdot e^-)$ . EPR spectra of dilute MAS show an extremely narrow symmetrical line with only a few miligauss linewidth [18, 19]. Above 1.0 MPM the susceptibility reflects the progressive electron delocalization that leads to metallic behavior. Increasing the metal concentration to the region of the nonmetal to metal transition yields the highly asymmetrical EPR line shape that is known as Dysonian line shape [20]. This lineshape is characteristic of metallic samples whose thickness is comparable to or greater than the skin depth for electronic conductivity.

O'Reilly [21, 22] observed the Knight shifts [23] for all the nuclei in alkali MAS at 298 K in the region of 0.1 to 1.0 mole/l. All the nuclei except <sup>1</sup>H show positive values for the Knight shift. This indicates hyperfine interaction with the paramagnetic excess electrons because of  $M^+$ - e<sup>-</sup> interactions. Negative shifts for <sup>1</sup>H result from spinpolarization by the excess electrons on the electrons of N and H via N-H bonding [24].

In summary the electrons in very dilute MAS behave as noninteracting localized electrons, while the electrons at high concentrations exist as free electrons in normal liquid metal. The spin-pairing interaction between the dissolved electrons proceeds prior to the nonmetal to metal transition. The fundamental nature of the pair-wise interaction between solvated electrons to form the spinpaired species is not clear.

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I.A.2 Metals in Other Solvents: Amines, Ethers Amides, etc

The decrease in the dielectric constant and donicity of other solvents for the alkali metals (compared with ammonia) affects the solvation energy of the cation and the electron as well as the strength of the electron-cation interaction. As a result, the solubility decreases dramatically and the association of the solvated electron with the solvated cation is stronger than in MAS so that one no longer has a weakly interacting ion-pair species.

The optical absorption spectra of alkali metal-amine and -ether solutions depend on the alkali metal [25]. Generally there are two peaks, the solvated electron band and a higher energy peak which depends on the metal. Solutions of the alkali metals (except Li and Na) in ethylenediamine (EDA) showed absorption peaks due to both alkali anions and solvated electrons. Only the solvated electron band was observed in Li-EDA solutions and only the Na<sup>-</sup> band was observed in solutions of Na in EDA. The variations in intensities of the two peaks of optical spectra can be explained *via* the equilibrium

which lies far to the right for lithium and far to the left for sodium.

The EPR spectra of alkali metal solutions in amines depend on the metal and the solvent. Solutions of lithium in methylamine can be described as ammonia-like; a narrow singlet EPR signal was observed similar to the EPR signals of dilute MAS [26, 27]. Upon changing to ethylamine as the solvent, an eight-line EPR pattern was observed that arose from hyperfine coupling to four nitrogens [28]. Sodium and potassium in methylamine solutions showed no resolved hyperfine splitting and had nearly the free-electron g value (2.0023). By contrast, rubidium and cesium solutions in methylamine showed resolved hyperfine splitting due to coupling of the electron spin to a single alkali metal nucleus plus a central narrow peak of the solvated electron.

The assignment of the species M<sup>-</sup>, as a "genuine" alkali metal anion with two electrons in the outer s orbital in metal-amine and metal-ether solutions was verified by alkali metal NMR spectra [29,30]. These studies made it clear that it was not merely a cluster of solvated cations and solvated electrons. Recent NMR studies of solutions of alkali-metals in certain amides (Hexamethyl phosphoramide, DEA, DMP, DPA) showed a sharp signal (8 ~ 15 MHz at  $\delta \approx 62$  ppm) for only sodium solutions [31]. The sodium signal is caused by Na<sup>-</sup> in terms of the chemical shift, but no Na<sup>+</sup> NMR signal was observed. Solutions of alkali metals in hexamethylphosphoramide (HMPA), which has a high dielectric constant (29.6 at 298 K), showed a single EPR line [32] similar to the EPR signals of MAS. A single <sup>23</sup>Na NMR peak corresponding to Na<sup>-</sup> was observed in the Na-HMPA solution but the Na<sup>+</sup> peak was not observed [33]. When alkali metal-HMPA solutions were frozen, glassy blue solids were formed. EPR results of the frozen solutions were different from the unfrozen solutions [34]. These EPR results indicate the existence of several discrete localized excess electrons similar to those in amines or ethers.

A simple quantitative ion-pairing model for alkali metal solutions was first proposed by Dye [35], and also applied by Catterrall [32]. According to this model, the species formed in the ion-pairing equilibrium

$$M_s + e_s \longrightarrow M_s + e_s$$
 (1-2)

can vary from a solvent-separated or solvent-shared species at low temperatures or in high dielectric constant solvents to a contact ionpair in less polar solvents and/or at high temperature. This behavior is continuous as the center of electron charge density approaches that of the solvated cation. Collapse to a solvated atom would be an extreme case that leads to loss of ion-dipole solvation energy for both the cation and the electron. As a result, a compromise is reached that balances the Coulomb attraction between M<sup>+</sup> and e<sup>-</sup> and the ion-dipole interactions of both ions with the solvent. The lifetime of the monomeric species  $(M_s)$  is governed by the electron-nuclear correlation time,  $\boldsymbol{\tau}_{M}$  and the hyperfine coupling constant (HFC) corresponds to the electron density at the nucleus. In solvents of high dielectric constant (HMPA,  $NH_3$ ), the average lifetime of  $M_s$  is shorter than the inverse of the HFC. Thus, an averaged signal from  $e^-$  and  $M_s$ is observed as a single EPR line. In low dielectric media the lifetime is long enough to observe separate signals from  $e_{solv}$  and  $M^+ e^-$ . The gvalues of the solvated electron in metal solutions are close to the free electron value.

#### I.B. Trapped Electrons in Solid Systems

#### I.B.1 Glassy Systems

The mechanism for the solvation of the electron in fluids has been reviewed. In glassy or solid systems the trapped electron can be assumed to have a similar equilibrium structure after complete solvation. The theoretical ideas concerning electron localization should be applicable to liquids, glasses and solid. The most universally accepted model will be presented, even though Golden and Tuttle [36, 37] advocate a "solvated solvent anion model", with major reference to the interpretation of optical spectra.

An electron is trapped in a glass or solvent by two mechanisms. The first step is the localization of the itinerant electron at a preexisting site and the second step is the trapping into the lowest energy configuration. The first step is very fast (on the order of 10 to 40 picoseconds) in glasses. The amorphorous glassy structure has a number of sites created by random molecular orientation of the dipoles which can serve as initial traps for electrons. The time-scales of localization into pre-existing traps were obtained by picosecond pulse radiolysis experiments [38]. Recently, femtosecond studies on the birth of electrons in water showed that there are three welldefined states [39, 40, 41]: highly reactive dry electrons, initially localized but unsolvated wet electrons and fully solvated electrons.

The structure of the equilibrium solvation shell of a trapped electron in a glassy matrix has been studied by EPR techniques. Traditional EPR measurement showed only a broad line because of the weak couplings. Kevan [42] investigated the weak hyperfine interaction by using electron spin echo modulation (ESEEM) techniques which can provide such structural information as the distance between the electron and the interacting nucleus as well as the number of nuclei interacting with a trapped electron. The average geometric structure of the solvated electron in frozen 10 M NaOH solution and frozen ethanol solutions [43, 44] has been investigated by ESEEM. The structure of the frozen aqueous solution was independent of the nature of the cation; thus, the hyperfine coupling results from the protons on water. The structure proposed on the basis of ESEEM measurements is an octahedral arrangement of six water molecules oriented with an O-H bond directed toward the center of the electron cavity. The geometric structure of a trapped electron in ethanol showed that four molecules were arranged tetrahedrally to form the electron cavity. The results of ESEEM were interpreted on the basis of the semi-continuum model proposed by two groups [45, 46].

The semi-continuum model, an extension of the simple model of Jortner [47], assumes that the excess electron is trapped in a spherical cavity of radius  $r_c$  created by the finite number, z of first shell molecules. The first shell molecules are considered as ideal dipoles in their electrostatic interactions with the electron and are assigned a spatial radius,  $r_s$ . Outside the sum of these two radii the solvent is described as a dielectric continuum. The energy of the trapped electron is determined by long range interactions with the continuum via screened Coulombic polarization and short range interaction with the first solvation shell. Typical values of z and  $r_c$  are

4 - 8 and 1.7 - 2.2 Å, respectively. Recent EPR and ENDOR spectra of electrons in KCN showed 17 hyperfine features due to the coupling to the first shell of K<sup>+</sup> ions [48]. The <sup>14</sup>N ENDOR results showed a strong hyperfine coupling to nitrogen, with A = 38.6 MHz and Q = 0.9 MHz at 210 K, but below this temperature the <sup>14</sup>N coupling was lost. This result means that there is considerable delocalization into the first shell of CN<sup>-</sup> ions. This was expected because of the presence of low-lying empty orbitals.

The major improvements of this model are that the energy required to orient the first solvation shell can be explained and the strongest dipole attractions of the electron with the first solvation shell are explicitly included. The trapped electron at medium concentrations, in which the electron is localized at the cavity has been described. The trapped electron at low concentrations in solids, which reduces the Coulombic repulsions of cations bordering the cavity will be reviewed in the next section.

#### I.B.2 Color Centers

The trapped electron in solids was first reported 70 years ago. Alkali halides become colored when they are exposed to high energy radiation [49]. The radiation results in the formation of excitons, mobile excited state species which consist of an electron bound to a hole. The exciton can dissociate in the vicinity of an anion vacancy to give a localized electron (F-center) and a localized hole (V-center) species. The definition of an F-center is an electron trapped at an anion vacancy.

Several parameters have an effect on the stable formation of the localized electron state, including the radiation energy, the pressure and the temperature. These can affect the mechanism of the excitation and the nature of the excitonic species [50]. Color centers in alkali halides can be produced by exposure to UV radiation which strips the valence electron from the halide anion. The electron is initially weakly bound to the remaining halide atom at an energy just below the conduction band. The electron may subsequently be trapped at a pre-existing vacancy to form an F-center. Harder radiation can actually create the anionic vacancy by ejecting an anion from its lattice site. The electron can then be trapped at the vacant site to form an F-center. Typical color centers can have concentrations of  $10^{18}$  electrons/cm<sup>3</sup>.

The optical spectrum of F-centers [51] in an alkali halide crystal consists of a broad bell-shaped absorption band. The position of the band depends on temperature, pressure and the nature of the alkali halide. The breadth of the band increases with increasing temperature, while the oscillator strength remains constant. An empirical equation known as the Mollwo-Ivey relationship [47] roughly accounts for these phenomena

$$E = 17.7a^{-1.84}$$

in which E is the energy in eV of the absorption maximum and a is the interionic distance. According to this relationship, the interionic

distance will have a larger range of values for increased thermal vibration in the lattice [47].

The simplest wave function for the trapped electron can be approximated as that of a particle in a cubic box of length 2a. A more complex potential well similar to the Madelung energy, has also been used. The idea that the electron might interact with more than one shell of nearest neighbors is substantiated by EPR and ENDOR studies. Hyperfine interactions due to ions as far away as the eighth neighbor shell have been observed for F-centers in KBr [52]. These results indicate that the electron has long range interactions with the ionic lattice. The bulk of the electron density (63%) is, however, located inside the vacancy, and 90% of the electron density is found within the first two shells of ionic neighbors.

The F-center is similar to the trapped electron, which is weakly bound to its surroundings. The F-center concepts can be applied to explain the local structure of electrons trapped at anionic sites and the resulting electronic charge distribution in electrides and in electrons trapped at anion vacancies in alkalides.

#### I.C. Alkalides and Electrides

#### I.C.1 Alkalides

Since the discovery of the first salt of an alkali metal anion in 1974 [53, 54] the physical properties of alkalides and electrides have been extensively studied. The structures of 19 alkalides and 4 electrides were recently reported at Colloque Weyl VII [8]. The stabilization of alkali metal anions and trapped electrons in solids is due to complexation of the *cation* by cyclic or bicyclic polyethers or polyamines, which makes the synthesis of alkalides and electrides thermodynamically feasible.

The  $ns^2$  ground state of the alkali metal anion is intrinsically stable because of the positive electron affinities of gaseous alkali metal atoms that range from 0.62 eV (Li) to 0.47 eV (Cs) [55]. The transition  $ns^2 \rightarrow ns^1 np^1$  of the alkali metal anion dominates the spectrum since the ionization energy is higher than the excitation that is optically allowed. The wavenumber maximum depends on the metal anion and ranges from 15400  $\text{cm}^{-1}$  (1.9 eV) for Na<sup>-</sup> to 9600  $\text{cm}^{-1}$  (1.2 eV) for The excited state wave function is sensitive to the Cs<sup>-</sup> [56]. surroundings such as the host solvent or crystal and the spectra are similar to those of the charge-transfer-to-solvent spectra of halide ions [57]. A second absorbance at ~ 20000  $\text{cm}^{-1}$  (2.5 eV), which appears as a shoulder for a sodide might be due to a transition from the ground state to the conduction band. Recently several photophysical effects have been studied for Na<sup>+</sup>cryptand[2.2.2]Na<sup>-</sup> (Na<sup>+</sup>C222Na<sup>-</sup>) [58, 59, 60]. First, the excitons produced by 2.0 eV photons are extremely mobile and have the characteristics of exiton-polaritons [60]. Secondly, nearly reversible photobleaching of Na<sup>-</sup> can be induced by an intense laser pulse at 605 nm or at 302 nm [61].

The optical spectra alone did not prove the existence of genuine alkali metal anions with a spherical or nearly spherical charge distribution because of alternative possibilities formed by aggregation of the solvated or complexed cation and two solvated electrons or with an electron pair [62]. The nuclear magnetic resonance (NMR) technique was used to prove the existence of  $M^-$  in solution and in crystalline alkalides as "genuine" anions [63, 64, 65, 66]. Separate NMR signals were detected that corresponded to  $M^+$  and  $M^-$ . The former is observed at the chemical shift of Na<sup>+</sup> in model compounds and the latter agrees with the chemical shift of Na<sup>-</sup>(g) to within a few ppm and is insensitive to the host solvent or lattice [13, 16, 67]. These results indicate that the ground state of Na<sup>-</sup>, both in solution and in the solid state is not significantly perturbed by the surroundings. Larger shifts of the NMR peak from the gas phase for other alkali metal anions may result from the mixing of other states into the  $ns^2$  ground state [14, 68, 69, 70, 71, 72].

Even though most alkalides appear bright and metallic, none shows metallic conductivity. For  $Na^+C222Na^-$  [73], the temperature dependence of the conductivity is characteristic of an intrinsic semiconductor with a band gap of 2.4 to 2.5 eV. Other alkalides also show a logarithmic dependence of the resistance on 1/T but, in most cases, this temperature dependence of the conductivity is caused by defect electrons.

X-ray structure studies of alkalides prove that M<sup>-</sup> is present as a distinct anion and that there is essentially complete charge transfer to form the complexed cations and the alkali metal anion. The space occupied by the alkali metal anion is much larger than that of the alkali metal cation. Their large size and low surface charge density tend to make them polarizable so that they can deform upon contact with other atoms. The crystal structures of alkalides fall into three

categories: (1) structures with isolated anionic sites, (2) structures with anion dimers or chains and (3) structures with cation-anion pairs.

Because all alkali metal anions have the  $ns^2$  electron configuration, pure alkalides are diamagnetic. However, the magnetic susceptibilities of alkalides have been investigated [74] because alkalides are prepared from solutions that always contain some solvated electrons, which results in trapped electrons in the polycrystalline alkalides. These trapped electrons give rise to a small "Curie tail" at low temperature. The concentrations of trapped electrons in alkalides are high enough to detect, so the EPR technique has been recently used to study the nature of the trapping site or the electron charge distribution [22, 75, 76].

#### I.C.2 Electrides

Since the first electride,  $Cs^+(18C6)_2e^-$ , was isolated and identified in 1982 [77] the optical, electrical and magnetic properties of electrides have been investigated. Crystalline electrides are still more difficult to synthesize and work with than alkalides because trapped electrons are more reactive than alkali metal anions. The electrides have been classified as containing localized or delocalized electrons on the basis of the optical, electrical and magnetic properties.

The optical spectra of localized electrides show a distinct absorption in the near IR (6000 cm<sup>-1</sup> - 9000 cm<sup>-1</sup>) [78] indicating a minimum band gap of 0.5 to 1.1 eV. Most electrides fall into this category and have trapped electrons in potential wells of depth at least

0.5 eV. By contrast, the optical spectrum [25] of a delocalized electride,  $K^+C222e^-$ , is similar to the plasma absorption of metallic metal-ammonia solutions [79] with a rising absorbance across the visible and well into the IR.

Powder conductivities of localized electrides [80] show both ionic conductivity and semiconductor behavior. The observed resistance and nonohmic behavior result from concentration polarization and/or a resistive barrier at the sample-electrode interface as well as a Schottky barrier [81]. The activation energies for ionic conductivity are about 1.1 eV for  $Cs^+(18C6)_2e^-$  and 0.6 eV for  $Cs^+(15C5)_2e^-$  (both are localized electrides). Ionic conductivity could result from the transfer of  $Cs^+$  between anionic sites in the lattice. The delocalized electride  $K^+C222e^-$  shows high conductivity with an activation energy of 66 ~ 67 kJ/mole. This shows that the electron in this delocalized electride is more weakly bound than in localized electrides.

The magnetic susceptibilities of most localized electrides such as  $Cs^+(18C6)_2e^-$  [22] show only Curie-Weiss paramagnetism which indicates that the trapped electrons do not interact strongly with each other. The small negative Weiss constant of this compound indicates weak antiferromagnetic coupling, but it exhibits no magnetic transition. The localized electride,  $Cs^+(15C5)_2e^-$ , shows an antiferromagnetic transition with a Neel temperature of 4.6 K and a first-order phase transition at 295 K [82]. The magnetic behavior of  $Li^+C211e^-$  [83] and  $K^+C222e^-$  [84] indicates the existence of spinpaired singlet ground states. The temperature-dependence of the magnetic susceptibility yields a singlet-triplet splitting for the latter electride of 0.05 - 0.1 eV. This behavior shows that either there is a thermally accessible triplet state or temperature dependent electronpair dissociation [84].

The crystal structures of the localized electrides  $Cs^+(18C6)_2e^-$ [85, 86,87] and  $Cs^+(15C5)_2e^-$  [88], and the delocalized electride,  $K^+C222e^-$  [84, 89] provide information about their behavior by comparison with alkalides of similar structure. The former, the localized electrides, have anionic sites that are isolated from each other with constricted channels that join one site to its neighboring sites. The latter,  $K^+C222e^-$ , has anionic sites that are connected through short, open channels in two dimensions. The anionic sites in  $K^+C222e^-$  exist in pairs so that two trapped electrons are close enough to interact with one another. The structure and properties of this electride indicate that electron-pairs exist in a singlet ground state which has a thermally accessible triplet state and the electron mobility is high.

The electron locales cannot be determined by X-ray diffraction because of the extremely low scattering of a single electron. EPR spectroscopy has been used to investigate electron locales and the interactions between trapped electrons and their surroundings in electrides. Since exchange effects often dominate in pure electrides, EPR or ENDOR technique cannot give us information about local interactions. However, we can eliminate exchange effects by studying isostructural alkalides that contain low concentrations of trapped electrons. This subject will be introduced in detail in the following section. I.D Objectives of This Work

Since we cannot locate the electron in electrides by X-ray diffraction due to low scattering of an electron, much effort has been devoted in attempts to determine the locale of the trapped electron. Since we expect the complexant to be polarized with negative oxygens and positive  $-CH_2$ - groups, it is assumed that the trapped electron wavefunction will extend into  $-CH_2$ - framework of the complexant molecules. X-band and G-band EPR, ENDOR and ESEEM techniques are powerful tools for the investigation of paramagnetic species and electron charge distributions and hence have been brought to bear on this problem.

The objectives of the present work can be summarized as attempts to answer the following questions:

(1) What is the general location of the unpaired electron in electrides and alkalides ?

To probe the likely location location of trapped electrons in electrides we can take advantage of isostructural alkalides that correspond to electrides. The paramagnetic sites of isostructural alkalides and electrides will be compared with known-structure electrides and alkalides in Chapters IV and V. The anionic sites of the unknown-structure alkalides can be deduced from the comparison to the results of known-structure alkalides.

(2) What is the local charge distribution of the trapped electron in electrides and alkalides ?

To probe the local unpaired electron density of electrons trapped at anionic sites in alkalides, the ESEEM technique will be used, since we can obtain information about the distance between the trapped electron and the interacting nucleus and the number of interacting nuclei by using ESEEM. The results will be discussed in Chapter VI.

(3) What is the approximate wavefunction of the trapped electron ?

To obtain the approximate wavefunction of the trapped electron, alkalides that have contact ion-pairs and those that have isolated anions will be investigated to determine the hyperfine interactions and g values as well as their anisotropies. The results will be discussed in Chapters IV - VI.

(4) What is the interaction among these trapped electrons ? To probe the interaction among trapped electrons, the spin exchange and the temperature dependence of the intensity as well as the relaxation properties of alkalides and electrides will be investigated and discussed in Chapters IV and V.

The conclusions of this present work and suggestions for future work will be presented in Chapter VII.

#### CHAPTER II

#### EXPERIMENTAL METHODS

II.A Syntheses and Sample Handling

II.A.1 Purification of Metals, Complexants and Solvents

High purity metals and complexants are required for the reliable syntheses of alkalides and electrides. The solvents must be dry and free of oxygen and reducible impurities.

Sodium, potassium (99.95%) and rubidium (99.93%) were obtained from Johnson Matthey Inc. in 5 gram argon-filled glass ampoules. Cesium metal donated by the Dow Chemical company was used. The bulk metals were redistributed into small diameter tubes (2 - 5 mm I.D.) under high vacuum ( $< 10^{-5}$ torr) as described elsewhere [76, 90]. The number of moles of metal can be calculated from the length of the metal in a glass tube of known diameter.

15-crown-5 (98%), 18-crown-6 (98%), cryptand [2.2.2] (98%) were obtained from Aldrich Chemical Company. 12-crown-4 was bought from Sigma. The solid 18-crown-6 (18C6) and cryptand [2.2.2] (C222) were purified by sublimation under high vacuum (<  $10^{-5}$  torr) The liquids 12-crown-4 and 15-crown-5 were distilled at  $10^{-5}$  torr to remove impurities. Hexamethyl hexacyclen (HMHCY) was obtained by methylation of the precursor, hexacyclen [91], which was obtained

from Aldrich Chemical Company. HMHCY was purified as described elsewhere [92].

Dimethylether(Me<sub>2</sub>O, anhydrous) and trimethylamine (Me<sub>3</sub>N, anhydrous) were obtained from Matheson. Diethylether (DEE), 99.95%) was obtained from E. M. Science. The solvents were purified by first distilling them under vacuum over calcium hydride to remove most of the water. The solvents were then transferred into bottles containing Na films or NaK alloy, with benzophenone. The solvent was stirred until the solution was deep blue, which indicated that radical anions and/or dianions of benzophenone were stable in the solvent. The solvents were then transferred to cylindrical glass bottles in the cases of DEE and Me<sub>3</sub>N and to clean stainless steel tanks for Me<sub>2</sub>O. The solvents were repeatedly frozen in liquid nitrogen and pumped to remove soluble gases. DEE was stored over NaK alloy.

#### II.A.2 Syntheses of Alkalides and Electrides

A "K-cell" has been developed for the syntheses of alkalides and electrides as shown in Figure 2-1. All glassware was soaked in *aqua regia* overnight. The rinsed K-cell was dried in the oven for more than one day prior to use. The synthesis of alkalides and electrides is described in detail elsewhere [93, 94]. The reactions to form alkalides and electrides are given by the equations

$$M + N + nC \longrightarrow M^{+}C_{n}N^{-} \qquad (2-1)$$




and

 $M + nC \longrightarrow M^+C_ne^-$  (2-2)

in which M and N are the alkali metals Na, K, Rb and Cs (M can also be Li) C is a complexant, 12C4, 15C5, 18C6, C222, HMHCY etc. and n is 1 for a one-to-one cationic complex cation and 2 for a sandwich complex.

All handling of the solutions and products during synthesis is carried out at temperature below - 40°C after evacuation of the vessel to  $\approx 10^{-5}$  torr. The synthetic methods have been described in detail elsewhere [95]. The proper molar ratio of the metal(s) and complexants (usually about two millimoles of the compound) are introduced into a previously evacuated and degassed K-cell in a helium-filled dry box. Both arms are then sealed off under high vacuum. The metal is distilled under vacuum to make a film on the wall of bulb A in Figure 2-1 and then the arm is sealed off. The solvent,  $Me_2O$  is added to dissolve the complexant and then the solution is transferred from bulb B to A to dissolve the metal. The resulting blue solution is then transferred from bulb B to A after all metal has been dissolved. A less polar solvent (Me<sub>3</sub>N or DEE) is then distilled in as a co-solvent to yield polycrystalline salts. The solvent is removed and the powder is vacuum-dried. These poly-crystalline samples are then transferred into the storage fingers and sealed off. Fingers of alkalides are stored at -  $75^{\circ}$ C in a freezer and electrides are stored in a Dewar that contains liquid nitrogen.

The polycrystalline samples are transferred from the finger into an EPR tube while cold under a dry nitrogen atmosphere in a glove bag. The 4 mm commercial fused silica EPR tubes are then sealed off under high vacuum.

II.B Description of Instrumental Methods

## II.B.1 X-band EPR

EPR spectra were recorded on a Bruker 200 D spectrometer at 9.5 GHz. A rectangular  $TE_{102}$  cavity was used. An ER350 gaussmeter was used to measure the magnetic field strength with 1 mG resolution. Microwave frequencies were measured with a Hewlett-Packard 5425L frequency counter with 10 kHz resolution. The temperature was controlled either with flowing cold nitrogen or with a Varian 4540 temperature controller. The temperature of samples was calibrated with a copper-Constantan thermocouple inserted into the EPR sample Dewar and a Doric DS-350 digital readout system. Due to the thermal instability of the samples, the temperature was generally kept below -  $40^{\circ}$ C. Data were collected with an IBM-compatible Dell computer.

# II.B.2 G-band EPR

The high frequency EPR spectra were obtained at Cornell University with a G-band EPR spectrometer developed by the research group of J. H. Freed [96]. The block diagram of the far-IR EPR spectrometer used in this study is shown in Figure 2-2. The FIR source is a Millitech Corp. PLS-F phase locked solid state source which delivers 3-5 mW at 250 GHz (WR-4 waveguide). A semiconfocal Fabry-Perot resonator was used for the sample cavity; the cavity was tuned by controlling the distance between two mirrors. The modulation frequency was 65 kHz. The field was swept by using a superconducting solenoid ( $H_0 = 8.9$  T) driven by an HP6032A power supply that provided a point-to-point resolution of 0.188 G up to a sweep width of 560 G. The temperature was controlled in the range of - 120°C to - 40°C by using a heater and regulating the flow rate of cold nitrogen gas. The temperature stability was about  $\pm 3^{\circ}$ C.

The sample holder for the G-band EPR spectrometer is shown in Figure 2-3. Both Teflon and polymethylpentene (TPX) had been previously used as material for the construction of the sample holder. Teflon, TPX and Z-cut quartz had been used as windows for the sample holder because they have low absorbance in the FIR. Because Teflon would react with our sample, it was not used for the present study, and Z-cut quartz was chosen for the window. When the sample holder was put into the liquid nitrogen, however, the Z-cut quartz window popped out due to differential contraction of the sample holder with

popped out due to differential contraction of the sample holder with respect to the window. To overcome this problem Rexolite (crosslinked polystyrene) was chosen as a material of construction for both the sample holder and the window. The transmittance of far IR (FIR) radiation was such that Rexolite proved to be a satisfactory material; it was also stable with respect to both solvents and samples. Even though there were several tool marks apparent on the window, the optical performance was not compromised because the surface was flat to better that  $\lambda/8$ .



Figure 2-2. Block diagram of the G-band EPR spectrometer. A: Superconducting Solenoid and sweep coil, B: 250 GHz Source, C: 100 Hz reference oscillator, D: Detecto,r E: Cavity and field modulation coil, F: Quasi-optical beam guide, G: Main coil power supply H: current programmer, I: Sweep coil power supply, J: Computer, K: Lock-in amplifier, L: Field modualtion and lock-in reference oscillator, M: Tuning screw, N and O: Vapor-cooled leads, P: LHe indicator, Q: LHe transfer tube, R: Bath temperature and heater resistor, S: LHe blow-off Valves. [96]

For the 250 GHz EPR studies, the polycrystalline samples were ground in an agate mortar below -  $50^{\circ}$ C under a dry nitrogen atmosphere in a glove bag. The samples were loaded into the sample holder and then sealed with a Mylar tape. Since the radius of the FIR beam in the cavity is 2 mm, a larger sample volume could used than at X-band. The amount of sodide sample filled the sample cell up to half of its height but less sample was used for electrides and for Cs<sup>+</sup>(18C6)<sub>2</sub>Cs<sup>-</sup>.



Figure 2-3. Sample holder for G-band EPR [96]

# II.B.3 The Pulsed EPR Spectrometer

The sample preparation methods used were the same as for Xband EPR and samples were kept in the liquid nitrogen Dewar that contains liquid nitrogen. The pulsed EPR spectrometer used in this study was recently constructed at Michigan State University by Prof. J. L. McCracken. A block diagram of the pulsed EPR spectrometer is shown in Figure 2-4. A microwave synthesizer (Gigatronics Model 610), operating from 6 to 18 GHz, was used as a microwave source. The microwave bridge (capable of operating over 6 to 18 GHz) consists of three major components: the microwave transmitter, the cavity, and the microwave receiver. Microwave pulses are generated by pulse modulating a phase-locked, cw klystron with a fast PIN diode switch. The low power output pulses are passed through a  $0^{\circ}/180^{\circ}$  phase modulator (General Microwave Model F1938) and a coaxial attenuator and then amplified to the level of approximate 1 kW by a pulsed traveling wave tube. The high power pulses are then passed through an attenuator and delivered to the sample.

The cavity used in this work is of the reflection type and employs a folded half-wave resonator [97] and the X-band Gordon coupling arrangement developed by Britt and Klein [98]. A conventional 4 mm o.d. EPR tube can be used for this cavity and the sample can be introduced from the top of the Dewar without removing the header assembly.

The microwave receiver uses a double balanced mixer as a detection element (RHG Model DM1-18AB) in a homodyne arrangement. A low-noise GaAs FET amplifier (Avantek model AWT-18635) is used in the receiver, with a medium-power, high-speed PIN diode limiter (Innowave, model VPL-6018) and a fast PIN diode switch (General Microwave, model F9114) serving to protect it from damage by higher-power microwave pulses. A second PIN diode switch is used to attenuate the mixer input during microwave pulsing. An Apple Macintosh-Cx computer controls the pulse sequences and collects the ESE envelopes by using a modified version of the dead-time reconstruction protocol described by Mims [99]. Data collection and analysis software were written by using the C language.



Figure 2-4. Schematic Block Diagram of Pulsed EPR spectrometer

#### CHAPTER III

#### THEORY

III.A Solid State EPR

III.A.1 g-value

The isotropic g-value in EPR relates the transition frequency v to the magnetic field  $H via v = g\beta_e H$  in which  $\beta_e$  is the electronic Bohr magneton. The g-value depends on the wavefunction of the unpaired electrons in atoms or molecules and the difference in the magnetic properties and interactions of all electrons with spins  $\alpha$  and  $\beta$ . The deviation of the g-value from 2.0023 is determined by the contribution of orbital angular momentum (i.e., p-, d-character) to the wavefunction. If the spin-orbit interaction is small so that it may be considered as a perturbation of the Zeeman term [100] the spin Hamiltonian is

$$\mathcal{A}_{snin} = \beta_{\rho} H \cdot g \cdot S \tag{3-1}$$

where  $\mathbf{g}$  is now an effective  $\mathbf{g}$  tensor (no longer a g value because of molecular anisotropy) and  $\mathbf{S}$  is an operator corresponding to an effective spin. If we neglect any hyperfine interaction and the nuclear Zeeman term, the total Hamiltonian will be

$$\mathscr{I} = \beta_{e} \mathbf{H} \cdot (\mathbf{L} + \mathbf{g}_{e} \mathbf{S}) + \xi \mathbf{L} \cdot \mathbf{S}$$
(3-2)

where  $\beta_e$  is electron Bohr magneton and  $\xi$  is the spin-orbit interaction constant. In order to calculate the g tensor in Eq. 3-1 for an S = 1/2 system, it is instructive to proceed through the first order wavefunction obtained when the **L**-S term is considered as a small perturbation [101, 102]. If the zeroth order wavefunctions are the pure  $|0,\alpha\rangle$  and  $|0,\beta\rangle$  functions, where 0 indicates the ground state, the first order wavefunctions are

$$|+> = |0,\alpha> - S[/(E_n - E_0)]|n>$$

and

$$|-> = |0,\beta> - S[/(E_n - E_0)]|n>$$
 (3-3)

where n gives the number of the excited state. These wavefunctions are used to calculate the matrix elements of  $\beta_e H(L + g_e S)$  in the true Hamiltonian in Eq. 3-2 and they are compared with the corresponding matrix elements of the spin Hamiltonian Eq. 3-1. The effective spin operator **S** is defined as

$$S_z|+> = 1/2|+>, \qquad S_z|-> = 1/2|->$$
  
 $S_x|+> = 1/2|->, \qquad S_y|+> = 1/2|-> \text{ etc.}$ 

in analogy to S acting on  $|\alpha\rangle$  and  $|\beta\rangle$ .

For a linear molecule (or for any molecule with an axis of trigonal or higher symmetry) the principal components of the effective g tensor can be described as

$$g_{\parallel} = g_e - 2\xi S < 0 |L_z| n > < 0 |L_z| n > /(E_n - E_0)$$
 3-4

$$g_{\perp} = g_e - 2\xi S < 0 | L_x | n > < 0 | L_x | n > / (E_n - E_o)$$
 3-5

The expression for  $g_{\parallel}$  is simplified if  $|0\rangle$  is orbitally nondegenerate, since  $\langle 0|L_z|n\rangle = 0$  in Eq. 3-4, resulting in  $g_{\parallel} = g_e$ . Note however, that second order perturbation theory results in a nonvanishing term in Eq. 3-4, so  $g_{\parallel}$  could be slightly less than  $g_e$ . In any event,  $g_{\perp}$ obtained from Eq. 3-5 can vary considerably from  $g_e$  because of the ability of  $L_x(=L_y)$  to couple excited states with the ground state. The deviation of  $g_{\perp}$  from  $g_e$  will depend on whether the excited state has the properties of an electron in a p or  $\pi$ -orbital.

#### III.A.2 Nuclear Hyperfine Interaction

Hyperfine splittings of the energy level result from the interaction of a nucleus or nuclei with the electronic magnetic moment. The strength of the interaction depends on  $\mu_I/I$  and on the distribution of unpaired electron spin density at the nucleus. The Hamiltonian of the hyperfine interaction,  $\mathscr{I}_{hf}$  is the sum of Fermi contact and electron-nuclear magnetic-dipole interaction terms. For a hyperfine interaction with one magnetic nucleus, the Hamiltonian is given by

$$\mathcal{A}_{hf} = g_{\theta}\beta_{e}g_{n}\beta_{n}[(\boldsymbol{L} - \boldsymbol{S})\cdot\boldsymbol{I}/r^{3} + 3(\boldsymbol{S}\cdot\boldsymbol{r})(\boldsymbol{r}\cdot\boldsymbol{I})/r^{5} + 8\pi\delta(r)\boldsymbol{S}\cdot\boldsymbol{I}/3] \qquad 3-6$$

where  $\beta_n$  is nuclear Bohr magneton and  $g_n$  is nuclear g-factor. The third term is the *Fermi contact interaction* and contains the Dirac function,  $\delta$ , [103] to provide a nonzero value at the nucleus itself. Frosch and Foley [104] reduced this Hamiltonian to

$$\mathcal{A}_{hf} = aL_zS_z + bI \cdot S + cI_zS_z \qquad 3-7$$

where a =  $g_e \beta_e g_n \beta_n < 1/r^{-3} >$ 

$$b = g_{e}\beta_{e}g_{n}\beta_{n}[8\pi|\Psi(0)|^{2}/3 - \langle (3\cos^{2}\theta - 1)/2r^{-3} \rangle]$$

$$c = g_{\theta}\beta_{e}g_{n}\beta_{n} < (3\cos^{2}\theta - 1)/2r^{-3} >$$

 $|\Psi(0)|^2$  is the probability of finding the electron at the nucleus (depends on the s-orbital character), r is the distance between the electron and the nucleus, and  $\theta$  is the angle between r and the molecular axis.

The  $L \cdot I$  interaction is negligible so the contact term and the dipolar term can be expressed by

$$A_{iso} = g_{e}\beta_{e}g_{n}\beta_{n}|\Psi(0)|^{2}8\pi/3$$
 3-8

$$A_{dip} = (3\cos^2\theta - 1)/2r^{-3}$$
 3-9

With the *L*·*I* term neglected, the Hamiltonian can be written for one nucleus as

$$\mathcal{A}_{hf} = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$$
 3-10

For axial systems

$$\mathcal{A}_{hf} = A_{\parallel}S_{z}I_{z} + A_{\perp}(S_{x}I_{x} + S_{y}I_{y})$$
 3-11

so that from Eq. 3-8 and 3-9

$$A_{iso} = (A_{\parallel} + 2A_{\perp})/3 \text{ and } A_{dip} = (A_{\parallel} - A_{\perp})/3$$

These can be represented as A tensor referred to its principle axes.

$$\mathbf{A} = \mathbf{A}_{iso} \mathbf{1} + \mathbf{A}_{dip}$$
 3-12

where 1 is the unit matrix and  $\mathbf{A}_{dip}$  is a traceless tensor. The Hamiltonian of the hyperfine interaction between two or more nuclei and the electron is given by

$$H_{\rm hf} = \sum_{i} \mathbf{I}_{i} \mathbf{A}_{i} \mathbf{S}$$
 3-13

The experimentally determined values of  $|\Psi(0)|^2$  and  $\langle r^{-3} \rangle$  are characteristic of the electronic wavefunctions of atoms. Therefore

these can provide a test of any atomic wavefunction derived theoretically.

III.A.3 Lineshapes

The shapes of most lines in magnetic resonance are Gaussian or Lorentzian, or a combination of both The manner in which these shapes combine depends on whether the spin system is a gas, liquid or solid, and whether the line is homogeneous or inhomogeneous. Here only solid systems will be discussed.

# III.A.3.1 Gaussian and Lorentzian shapes

The analytical first derivative expression for a Gaussian absorption lineshape as a function of the magnetic field H is

$$\dot{Y}_{G} = 1.649 \ y'_{m} \frac{(H - H_{o})}{0.5\Delta H_{pp}} \exp \left\{-0.5\left[\frac{(H - H_{o})}{0.5\Delta H_{pp}}\right]^{2}\right\}$$
 3-14

and the corresponding expression for a Lorentzian is

$$Y'_{G} = \frac{16Y'_{m}\frac{(H - H_{o})}{0.5\Delta H_{pp}}}{\left[3 + \frac{(H - H_{o})}{0.5\Delta H_{pp}}\right]^{2}}$$
3-15

where  $y'_m$  denotes the maximum amplitude and  $\Delta H$  is the peak-topeak width. These lineshapes are normalized in terms of amplitude. The number of spins in the sample is proportional to the area.

$$A = \int_{0}^{\infty} Y_{(H-H_{o})} = \int_{0}^{\infty} (H - H_{o}) Y_{(H-H_{o})}^{'} dH \qquad 3-16$$

The various linebroadening mechanisms are characterized by the moments of the line  $\langle (H - H_0)^n \rangle$ ,  $n = 2, 3 \cdots$ 

$$<(H - H_o)^n > \frac{1}{(n+1)} \int_0^\infty (H - H_o^{n+1}) Y'_{(H-H_o)} dH$$
 3-17

The relation of the area and moments to other parameters has been reviewed elsewhere [105, 106].

A combination of Lorentzian and Gaussian lines can result from an exchange-narrowed line and from an inhomogeneously broadened line. The former is Lorentzian in the center, and Gaussian in the wing and the latter is a superposition of many narrow Lorenztians compromising a Gaussian envelope. The Voigt convolution lineshape is obtained for the inhomogeneous case.

$$Y_{(H-H_{a})} = \frac{\sqrt{\ln 2}}{\pi} \left( \frac{\Delta H_{1/2}^{L}}{\Delta H_{1/2}^{G}} \right) \int_{-\infty}^{\infty} \frac{e^{-x^{2}} dx}{\left( \frac{\Delta H_{1/2}^{L}}{\Delta H_{1/2}^{G}} \right) \ln 2 + \left[ 2\sqrt{\ln 2} \left\{ \frac{(H-H_{0})}{\Delta H_{1/2}^{G}} - x \right]^{2}}$$
 3-18

where the subscript G denotes Gaussian, and L signifies Lorentzian.

#### III.A.3.2 Relaxation

There are two principal types of resonance lines in solids. They arise from homogeneous and inhomogeneous linebroadening respectively [107,108,106]. Homogeneous broadening may be caused by dipolar interactions, the spin-lattice interaction, diffusion of the spin excitation, and motional narrowing. Inhomogeneous broadening arises from anisotropic effects, unresolved hyperfine structures, and inhomogeneities in the magnetic field. The linewidth of a homogeneously broadened line is proportional to the inverse of the spin-spin relaxation time,  $T_2$ . In many solids the principal mechanism of homogeneous broadening is the dipolar interaction between all neighboring spins, and this produces a Gaussian lineshape. When exchange effects become pronounced, the spin-lattice  $(T_1)$  and spinspin relaxation  $(T_2)$  times become equal. The spin-lattice relaxation of solids may be caused by a direct process that involves one lattice vibration phonon, or an indirect Raman process that involves two phonons.

Two methods have been used to measure relaxation times: the saturation method [108 109] and the pulse method [105, 106, 110]. In the saturation method, one observes spectra at a number of power levels up to and beyond the oneset of saturation. The pulse method entails the excitation of the sample with appropriate pulses of radiofrequency energy, after which one monitors the recovery to equilibrium. Here, only the saturation method will be discussed. It uses the following simplified equation

$$\dot{y_m} = s^{3/2} \dot{y_m} = \dot{y_m} \frac{\sqrt{P}}{\left(1 + \frac{Pg^2T_1T_2}{4}\right)^2}$$
 3-19

where P is the microwave power,  $y_m$  is peak-to-peak amplitude,  $y_m^{o}$  denotes the maximum amplitude below saturation, and s is the saturation factor. Equation 3-19 is used for saturation curve fitting. The peak-to-peak width is given by

$$\Delta H_{pp} = \Delta H_{pp}^{0} \left( 1 + \frac{Pg^2 T_1 T_2}{4} \right)^{1/2}$$
 3-20

 $T_2$  can be determined from the homogeneous linewidth below saturation.

$$T_2 = \frac{2}{\sqrt{3}g\Delta H_{pp}^0}$$
 3-21

and  $T_1$  can be obtained from the value of microwave power at maximum as shown in Figure 3-1.

$$T_{1} = \frac{1.97 \times 10^{-7} \Delta H_{pp}^{0}}{4g P_{max}}$$
 3-21

The peak-to-peak first derivative amplitude  $y'_m$  can be plotted as a function of the square root of the microwave power P, and  $P_{max}$  is the microwave power at the maximum of the saturation curve.. The dashed line is an extrapolation of the linear dependence at low powers [106].

.



Figure 3-1. The saturation curve for a homogeneously broadened line (solid line) and an inhomogeneous line (lashed line).

Since systematic investigations with high frequency EPR were first reported in 1976 [111], several general reviews on EPR studies from the radio frequency region to the far infrared have appeared [112, 113,114]. The magnetic field at resonance is determined by  $\mathbf{H} =$ hv/g $\beta$ . If paramagnetic centers with different g values are present, the difference in the field positions of the resonances is proportional to v:

$$\Delta H = \frac{hv}{\beta} \left( \frac{1}{g_1} - \frac{1}{g_2} \right)$$
 3-22

This illustrates the fundamental reason for high frequency EPR; to get an enhanced spectral resolution. For most organic radicals, the relative differences  $\Delta g/g$  do not exceed 10<sup>-4</sup> to 10<sup>-3</sup> corresponding to line separations  $\Delta H$  of 0.3 to 3 G at 10 GHz, which can be difficult to detect. If the linewidth does not increase with frequency, we need a frequency of v > 100 GHz to get satisfactory resolution.

A homogeneous EPR line is dependent on spin-lattice and phase relaxation and on spin-spin dipolar and spin exchange interactions. The spin-lattice relaxation rate depends on the Zeeman frequency  $\omega$  in different ways [113] given by

$$1/T_{1} \sim \omega^{n}$$
 3-23

with a power factor, n, that ranges from 0 (modulation of anisotropy hyperfine interaction, HFI) to 4 (direct relaxation process). The

homogeneous line width arising by phase relaxation frequently is related to the average anisotropic magnetic interaction and can be described by

$$1/T_2 \sim r_e (\Delta g_{an} \omega/g + \Delta A_{an})^2 \tau_c \qquad 3-24$$

where  $\Delta g_{an}$  is the anisotropy of the g value,  $\Delta A_{an}$  is the anisotropy of the HFI and  $\tau_c$  is the correlation time for motional averaging. As for inhomogeneous broadening, it does not depend on  $\omega$  when it is caused by unresolved HFI or spin-spin interaction, but it depends on  $\omega$  when it comes from a dispersion of g values. We can expect that the theoretical prediction of the frequency dependence of the line width will be difficult and only experiment can give an answer at present. At moderate temperatures the line width can determined by Eq. 3-24, but the increased anisotropy at high frequency can be compensated for by a slight temperature increase since  $\tau_c$  is exponentially dependent on 1/T. This also allows one to measure shorter  $\tau_c$  than can be done at X-band.

For powdered samples, the EPR spectrum results from signals from all possible orientations as in Figure 3-2a. The line shape may be obtained as the convolution of the individual line shapes  $f_0(H)$  and the distribution function,  $f_g(H)$ , that describes the angular dependence of the g value according to [115]

 $f_g(H) \sim 1/|\nabla H|$  3-25



Figure 3-2. Approximate shape of a high frequency EPR spectrum with an anisotropic g factor (a) and 150 GHz spectrum (first derivative) of perdeuterated nitroxide radical (b) compared to a 10 GHz spectrum (c), both in the solid state [113].

where  $\nabla H = [(\delta H / \delta \theta)^2 + (\delta H / \delta \phi)^2]^{1/2}$ ,  $\theta$  and  $\phi$  are the polar and azimuthal angles determining the orientation of the molecule in the laboratory frame. At the turning points, at which  $\theta = 0$ ,  $\phi = 0$  ( $g = g_x$ ) and  $\theta = 90^\circ$  ( $g = g_z$ ), the line shape is close to a stepwise  $\theta$  function, while for  $\theta = 0$ ,  $\phi = 90^\circ$  ( $g = g_y$ ) it is close to a  $\delta$  function. When the first derivative of f(H) is detected in the regions of  $g = g_x$ ,  $g = g_z$  we observe an almost pure absorption function  $f_o(H)$  and at  $g = g_y$  an almost pure first derivative  $f_o(H)$  as shown Figure 3-2b. This is true only if the intrinsic line width  $\Delta H_o$  is small compared to the field shifts  $H_x - H_y$  and  $H_y - H_z$ . When anisotropic hyperfine structure is present (Figure 3-2b), single-crystal-like spectra are observed if the following relations are valid:

$$A_y + A_z < (|g_z - g_y| / \beta g^2)hv$$
 3-26

$$A_x + A_z < (|g_x - g_y| / \beta g^2)hv$$
 3-27

Adding the line width, these equations may be given by

$$\beta g^{2} (\Delta H_{oy} + \Delta H_{oz} + |A_{y}| + |A_{z}|) < |g_{y} - g_{z}|hv \qquad 3-28$$

where  $\Delta H_{oy}$  and  $\Delta H_{oz}$  are the intrinsic linewidths of the y and z components. This is considered as the high resolution condition for solid state EPR spectra, and is fulfilled only at high enough frequency.

Since high frequency EPR studies are performed with strong magnetic fields, the relation between the values of the external magnetic field and the local field of the electron is dramatically changed, resulting in a change in the axis direction of nuclear spin quantization. A nucleus feels the electronic magnetic field  $H_e \sim 10 \text{ kG}$  for an electron-nuclear distance of 1 Å, so the nuclear spin is quantized along  $H_e$  at X-band EPR; however, it is nearly along the external field at 250 GHz ( $H_o = 89 \text{ kG}$ ). For a paramagnetic center with I = 1/2 and S = 1/2 the EPR spectrum in the z direction of  $H_o$  will consist of four lines [115,116].

For the transitions with  $\Delta I_z = 0$  the splitting is given by

 $\Delta H(\Delta I_z = 0) = 2(R_+ - R_-)$ 

$$R_{\pm} = \frac{1}{4} \sqrt{A_{zx}^2 + A_{zy}^2 + (A_{zz} \pm \frac{\gamma_n}{\gamma_0} H_0)^2}$$

and intensities equal to

$$J(\Delta I_z=0) = \frac{1}{2} - \frac{1}{32} \frac{A_{zx}^2 + A_{zy}^2 + (A_{zz} - 4\frac{\gamma_n}{\gamma_0}H_0)^2}{R_+ - R_-}$$
 3-29

For the  $\Delta I_z = \pm 1$  transitions,

 $\Delta H(\Delta I_z = 1) = 2(R_+ - R_-)$  and  $J(\Delta I_z = \pm 1) = 1 - J(\Delta I_z = 0)$ 

### **III.C** Electron Spin Echo Modulation

#### III.C.1 Nature of Electron Spin Echo Modulation

After spin echoes were discovered in nuclear magnetic resonance by Hahn, modulation phenomena in electron spin echoes were also found and were first reported in 1961. The basic theory of the modulation effect was described by Rowan. Hahn, and Mims [117]. The physical origin of electron spin echo modulation can be described in either classical or quantum mechanical terms. Figure 3-3 shows the classical picture of spin echo envelope modulation. The amplitude of the echo modulation depends on the orientation of  $H_{eff}$ , on the electron-nuclear distance r and on the number of an equivalent nuclei at r. An analysis of an echo modulation pattern gives information about the number and distance of weak dipolarly interacting nuclei as well as their indentity from the modulation frequency.

The quantum-mechanical picture of echo modulation can be explained in terms of a spin level energy diagram. For I = 1/2, S = 1/2, there are two allowed EPR transitions and two forbidden EPR transitions. If the microwave pulse has sufficient magnitude to excite both transitions, it produces a branching of nuclear frequencies that modulate a single electron spin level. The two sets of electrons precess at two different frequencies that are separated by the nuclear frequency. Interference between these two precession frequencies generates a modulation of the electron magnetization at the nuclear frequency. Electron spins from upper levels that are excited into lower levels generate modulation of the nuclear frequency. If a second microwave pulse is applied before these induced nuclear modulations have decayed, the electron magnetization will show the additional sum and difference modulation frequencies. Thus the two-pulse spin echo is modulated by these four nuclear frequencies  $\omega_{\alpha}$ .  $\omega_{\beta}$ .  $\omega_{\alpha}$ -  $\omega_{\beta}$ .  $\omega_{\alpha}$  +  $\omega_{\beta}$ .



Figure 3-3. Diagram showing the origin of electron spin-echo modulation. (a) A nucleus of spin I at distance r from the electron precesses around an effective magnetic field  $H_{eff(1)}$  due to the vector sum of  $H_0$  and the electron dipolar field at the nucleus  $H_e$ . The precession of I produces a time-dependent magnetic field of amplitude  $\Delta H_{n(1)}(t)$  at the electron. (b) Some I nuclei at the right precession position in (a) can follow the sudden field change by a microwave pulse and begin to precess about  $H_{eff(2)}$  to produce a different amplitude magnetic field  $\Delta H_{n(2)}(t)$  at the electron. The interference between the modulation of the electron at both  $\gamma_n H_{eff(1)}$ and  $\gamma_n H_{eff(2)}$  produces modulation beats in the electron precession at the nuclear frequencies. After a second microwave pulse this modulation appears in the electron spin-echo signal.

This is simplified when weak nuclear coupling to the electrons exists (r > 0.3 nm) so that the nuclear frequencies  $\omega_n$  in the upper and lower electron spin manifolds are about same  $(\omega_{\alpha} \sim \omega_{\beta} = \omega_n)$ . Therefore the observed frequencies are at  $\omega_n$  and  $2\omega_n$ , with the the latter also weak for even longer distance interactions.

Figure 3-4 shows the pulse sequences for a two-pulse echo  $(90^{\circ} \tau$ -180°) and a three-pulse echo (90°- $\tau$ -90°-T-90°). The three-pulse sequence is sometimes called a stimulated echo, because the second  $90^{\circ}$  pulse puts the spins into a holding pattern in the z-direction until the third  $90^{\circ}$  pulse generates the rephasing in the xy plane to stimulate the echo modulation. Generally the interpulse time  $\tau$  is fixed and T is varied to generate the echo decay curve for a three-pulse experiment. The three-pulse echo as a function of T decays as the spin-lattice time  $T_1$  since during time T the electron spins are oriented along the z-direction. Thus the three-pulse echo decays more slowly than the two-pulse echo. The three-pulse echo may be modulated only by the nuclear frequencies and not by the sum and difference frequencies. The first pulse generates modulation at the nuclear frequencies; the second pulse incorporates the sum and difference frequencies; the third pulse causes interference of the sum and difference frequencies to leave only the nuclear frequencies. In the three-pulse echo experiment the first two pulses generate a weak two-pulse echo at time  $\tau$  after the second pulse. Therefore, at T =  $\tau$ this two-pulse echo interferes with the three-pulse echo detection. This can be minimized by selecting  $\tau$  to correspond to a minimum in the two-pulse echo modulation and can be nearly eliminated by appropriate phase cycling [118].





Three-pulse

Figure 3-4. Illustration of modulation of a Two-pulse (a) and a Threepulse (b) Spin Echo Decay Envelope.

### III.C.2 Analysis of Echo Modulation

To obtain explicit hyperfine information from spin-echo modulation it is necessary to calculate the expected modulation pattern for a certain assumed hyperfine interaction or electronnuclear geometry. Rowan, Hahn, and Mims [117] first presented a density matrix formalism for simulating echo modulation patterns and obtained explicit expressions for the I =1/2, S = 1/2 case. Later Mims rewrote the formalism and discussed the approximations and limitations involved for both two-pulse and three-pulse echo modulation [119, 120]

# III.C.2.1 Two-pulse spin echo modulation pattern

The total time dependence of the spin echo intensity  $V_{echo}$  can be described as

$$V_{echo} = V_{decay} V_{mod}$$
 3-30

To calculate  $V_{mod}$  it is easier to use variant density matrix formalism [121]. Any wavefunction for a system can be expanded in terms of a complete set of orthonormal functions

$$\Psi(q,t) = \Sigma C_n(q,t)U_n(q) \qquad 3-31$$

with the time dependence all in the coefficients  $C_n$ . The energy of a real system that consists of many spins can be found by the ensemble average of the energy operator H, as in the following equation:

$$E = \psi \mathbf{H} \psi = \sum_{n,m} \overline{C_m^* C_n} \langle U_m | \mathbf{H} | U_n \rangle$$
 3-32

where we used Eq. 3-31 to replace the wavefunction  $\Psi$  and the bar represents an ensemble average. the density matrix  $\rho^*$  is define as the matrix of the coefficient products  $\overline{C_m^*C_n}$ . The energy is given by

$$E = Trace (\rho H)$$
 3-33

The matrix elements of  $\rho$  are calculated from the equation of motion for the density matrix

$$\partial \rho / \partial t = 2\pi i / h [\rho, H]$$
 3-34

in which the brackets represent the commutator of  $\rho$  and **H**.

To apply Eq. 3-33 the appropriate Hamiltonian and an expression for g must be obtained. Here we do not include any relaxation terms in the spin Hamiltonian because these will affect  $V_{decay}$  but not  $V_{mod}$ . Therefore the appropriate Hamiltonian for echo modulation alone is

$$H = H_0 + H_t 3-35$$

where  $H_0$  is the ordinary static Hamiltonian in the absence of a microwave pulse and  $H_t$  is the time-dependent part associated with a pulse. By assuming that the high field and point dipole approximations are valid for the anisotropic hyperfine interaction, the static Hamiltonian  $H_0$  becomes

$$H_0 = \beta_e g_e H_0 S_z - \beta_n g_n H_0 I_z + a S_z I_z + [(3\cos^2\theta - 1)I_z + 2\sin\theta\cos\theta I_x]S_z$$
$$x \frac{\beta_e g_e \beta_n g_n}{r^3} \qquad 3-36$$

where  $H_0$  is the external field, **a** is the hyperfine coupling, r is the distance between the electron and nucleus and  $\theta$  is the angle between  $H_0$  and the position vector **r** joining the electron and nucleus. The time-dependent Hamiltonian  $H_t$  is given by

$$H_{t} = 2g\beta H_{1}S_{y} \cos(\omega_{e}t)$$
 3-37

 $H_1$  is the rotating component of the microwave field at frequency  $\omega_e$ .

Let us return to the application of Eq. 3-33 to calculate the echo modulation. The density matrix  $\rho(2\tau)$  is time-dependent so that Trace( $\rho H$ ) will depend only the time dependent part of H given by Eq. 3-37. The normalized echo modulation  $V_{mod}(2\tau)$  is given by

$$V_{mod}(2\tau) = \frac{\text{Tr}[\rho(2\tau)S_y]}{\text{Tr}[\rho(0)S_y]}$$
3-38

where the denominator is the normalization factor and  $\rho(0)$  is the time dependent equilibrium density matrix in the high-temperature approximation that exists prior to the first pulse. Since the electron Zeeman interaction dominates  $H_0$  in the high-temperature approximation the thermal equilibrium density matrix is given by [117]

$$\rho(0) = \frac{1}{2S+1} \left(1 - \frac{g\beta H_0 S_z}{kT}\right)$$
 3-39

Now from Eq. 3-34 a formal solution is obtained when H is independent of time

$$\rho(t) = \exp(-iHt/h)\rho(0)\exp(iHt/h) \qquad 3-40$$

To apply Eq. 3-40 the time dependence in **H** is eliminated by transforming the Hamiltonian to the electron rotating frame. This is equivalent to subtracting the electron Zeeman term **H**  $H_r = H - g\beta H_0 S_z$  3-41

$$H_{\rm r}({\rm off}) = H - g\beta H_0 S_{\rm z}$$
 3-42

$$H_{r}(on) = H_{r}(off) + 2g\beta H_{1}S_{y} \sim 2g\beta H_{1}S_{y} \qquad 3-43$$

The density matrix  $\rho(t)$  is obtained from Eq. 3-40 by successively applying the appropriate time-independent Hamiltonians. Let  $R_i = \exp(-iH_it/h)$  then

$$R_1 = \exp\left(-ig\beta H_1 S_y \pi/h\right) \qquad 3-44$$

$$R_2 = \exp\left(-iH_r(off)\tau/h\right) \qquad 3-45$$

$$R_3 = \exp(-i2g\beta H_1 S_V \pi/h)$$
 3-46

therefore

$$\rho(2\tau) = R_2 R_3 R_2 R_1 \rho(0) R_2 R_3 R_2 R_1^*$$
 3-47

Using Eq. 3-47 and 3-39,  $V_{mod}(2\tau)$  is evaluated [117, 119].

Here the simplest case (I = 1/2 and S = 1/2) which has an isotropic g value and no quadrupole interaction will be discussed. For a S = 1/2, I = 1/2 system the result is

$$V_{mod}(2\tau) = 1 - 2k\sin^2(\omega_{\alpha}/2)\sin^2(\omega_{\beta}/2) \qquad 3-48$$

where  $k = [\omega_{\alpha}B/\omega_{\alpha}\omega_{\beta}]^2$ ,  $\omega_{\rm I} = g_{\rm I}\beta_{\rm I}H_{\rm O}/h$ 

$$\omega_{\alpha} = [(A/2 + \omega_{I})^{2} + (B/2)^{2}]^{1/2}$$

$$\omega_{\rm B} = [(A/2 - \omega_{\rm I})^2 + (B/2)^2]^{1/2}$$

$$A = \frac{\mu_e \mu_n}{r^3} (3\cos\theta^2 - 1) + 2\pi a$$

$$B = \frac{\mu_e \mu_n}{r^3} (3\cos\theta \sin\theta)$$

Eq. 3-48 can be rewritten in the equivalent form [122]

$$V_{mod} = 1 - k[2 - 2\cos(\omega_{\alpha}\tau) - 2\cos(\omega_{\beta}\tau) + \cos(\omega_{\alpha} - \omega_{\beta})\tau + \cos(\omega_{\alpha} + \omega_{\beta})\tau]$$

$$3-49$$

which clearly shows that the nuclear frequencies and their sum and difference occur in the modulation pattern.

## III.C.2.2 Three-pulse Echo Modulation Pattern

Three-pulse echo modulation usually occurs over a longer time scale than two-pulse modulation because of the longer interval time T. This may be sensitive to weaker hyperfine interactions than two-pulse echo modulation. The simulation of three-pulse echo modulation is a straightforward extension of the formalism used for the two-pulse case [119, 120]. Mims showed that the three-pulse modulation expression can obtained simply from the two-pulse modulation expression without using density matrix methods by following the procedures given below:

1. Write the two-pulse expression with  $\cos(\omega_{\alpha}\tau)$  or  $\sin(\omega_{\alpha}\tau)$  replaced by  $\cos[\omega_{\alpha}(\tau + T)]$  or  $\sin[\omega_{\alpha}(\tau + T)]$ .

2. Write the two-pulse expression with  $\cos(\omega_{\beta}\tau)$  or  $\sin(\omega_{\beta}\tau)$  replaced by  $\cos[\omega_{\beta}(\tau + T)]$  or  $\sin[\omega_{\beta}(\tau + T)]$ .

3. Add the expressions (1) and (2) and divided by two to normalize.

III.D. Simulation in Disordered Systems

If the nuclear spin-spin interaction is neglected, the amplitude of the spin-echo modulation  $V^n_{mod}$  for n nuclei is

$$V_{mod}^{n} = \sum_{i=1}^{n} V_{mod}^{i}$$
 3-50

This equation holds for both identical and nonidentical nuclei, so the modulation depth increases as the number of interacting nuclei increases for identical nuclei.

In disordered systems the echo modulation pattern is obtained by averaging over all orientations. Kevan et al. [122] suggested a spherical model in which an effective interaction distance is used for the closest shell of nuclei. The amplitude of the echo modulation is

$$\overline{V_{\text{mod}}^{n}} = [\langle V_{\text{mod}}(\mathbf{r}, \mathbf{a}) \rangle_{\theta}]^{n}$$
 3-51

which is a function of r (distance between electron and the interacting nucleus),  $\mathbf{a}$  (hyperfine coupling constant), and n (the number of interacting nuclei with an electron).

### CHAPTER IV

## EPR STUDIES OF ELECTRONS TRAPPED IN SODIDES

This chapter is in the form of a paper that has been published in the Journal of Physical Chemistry, and which is entitled "EPR Studies of Electrons Trapped in Sodides". Supplementary materials and the results for sodides of unknown-structure are added. This chapter includes some work by Dr. Ahmed Ellaboudy and Dr. Marc DeBacker.

The EPR spectra of six sodides of known structure reveal that excess electrons in these salts are trapped at vacant anionic sites and can be considered similar to F-centers. Hyperfine splitting is observed when the complexed cation is exposed to the anionic site, but not when the cation is well-shielded by inclusion in a sandwich structure formed by two crown ether molecules. The g-values,  $T_{1e}$  relaxation times, hyperfine splittings, and dependence of intensities on temperature are reported and discussed.

### **IV.A** Introduction

It is now well established that alkali metal ions can have the oxidation number - 1 as well as the usual + 1 value. <sup>1-6</sup> A number of ionic salts that contain alkali metal anions have been crystallized and have had their structures determined by single crystal X-ray diffraction methods. <sup>7-13</sup> In these compounds, called *alkalides*, the

thermodynamics is driven by the trapping of an alkali cation by a complexant such as a crown ether or a cryptand. These compounds may be represented by  $M_a^+(C)_n M_b^-$ , in which  $M_a$  and  $M_b$  are the same or different alkali metals, C is the complexant, and n is 1 or 2.

It is also possible to synthesize *electrides*; salts in which the anion has been replaced by an electron.  $^{14-20}$  The X-ray structures of these materials show large vacancies or "empty" regions where anions were located in alkalides.  $^{11, 13, 15, 17, 21}$  The electron density in these cavities is, however too small to be detected by X-ray crystallography. Electron trapping at all of the anionic sites is inferred from the physical properties and the similarity of the structures to those of alkalides having the same complexed cation.

Isolated trapped electrons are paramagnetic so that EPR spectroscopy can sometimes be used to probe the charge distribution around the trapping sites. In many cases, however, rapid electron exchange occurs to yield only a single exchange-narrowed line, in which case little information can be gained from the EPR spectrum of the pure electride (The same thing occurs for the solvated electron in liquid ammonia). Pure alkalides are intrinsically diamagnetic with an  $ns^2$  structure that gives rise to a  ${}^1S_0$  state, but they usually contain defect electrons that can be studied by EPR methods. Electron trapping occurs in crystalline alkalides because they are synthesized from solutions the majority anions, M<sup>-</sup>, are in equilibrium with solvated electrons that may become trapped in the alkalide crystals.<sup>4</sup> In the case of sodides the equilibrium strongly favors Na<sup>-</sup> vs e<sup>- 22,23</sup>; thus among the alkalides, sodides contain the smallest concentrations

of defect electrons. The crystal structures show that, in all sodides studied to date, the anions are separated from one another. Trapped electrons, present in small concentration, are therefore isolated from one another, which avoids the problem of exchange-narrowing of the EPR spectrum.

The EPR spectra of a number of alkalides and electrides prepared by solvent evaporation  $^{24.25}$  or crystallization  $^{14.26-30}$  show that many complications can arise. Electrons can be trapped at several sites, temperature-dependent spin-pairing can occur, exchange rates can vary depending on the preparation method, and observable hyperfine coupling to cations can occur. In general, when the cations are well-shielded from the anions by inclusion in a crown ether sandwich or in a cryptand cage, no hyperfine splitting occurs, indicating that the electrons are not trapped by individual alkali cations to form, for example, an "expanded atom" within the cage. When, however, the crystal structure shows or the composition suggests, that the alkali cation is exposed to the anionic site, hyperfine splitting by interaction with a single alkali cation is frequently observed.<sup>27</sup>

The present study was undertaken to verify these general observations and to study in detail the EPR behavior of two classes of sodides of known crystal structure. In one type, each Cs<sup>+</sup> ion is sandwiched between two crown ether molecules and each Na<sup>-</sup> ion is surrounded by eight such complexed cations at roughly equal distances. In the other class of sodides, each complexed K<sup>+</sup>, Rb<sup>+</sup> or Cs<sup>+</sup> ion is in contact (or nearly so) with one Na<sup>-</sup> and at a much larger distance from other anionic sites as determined from the X-ray crystal


Figure 4-1. Representations of the ionic packing in (A)  $Cs^+(HMHCY)\cdot Na^-$  and (B)  $Cs^+(18C6)_2\cdot Na^-$ . Each Na<sup>-</sup> ions is surrounded by eight complexed cations, four of which are shown here.

structure.<sup>10</sup> In this class, the cation is complexed by the fully methylated aza-crown analog, hexamethyl hexacyclen (HMHCY). <sup>31, 32</sup> The packing of the complexed cations and Na <sup>-</sup> anions is shown in Figure 4-1 for Cs<sup>+</sup>(HMHCY)·Na<sup>-</sup> and Cs<sup>+</sup>(18C6)<sub>2</sub>·Na<sup>-</sup>.

## **IV.B** Experimental Section

All sodides were synthesized according to previously described procedures. <sup>10,27</sup> The compounds were precipitated or recrystallized from trimethylamine or dimethyl ether solutions. The purification of solvents and complexants and the handling of alkali metals have been described in detail elsewhere. 3,10,27,33 All steps in the preparation processes were carried out at temperatures below - 40 °C. The samples were kept in sealed tubes at low temperatures. The sodide samples were loaded into EPR tubes (4 mm o.d. clear fused TO8 commercial quartz tubes) under dry nitrogen. After loading the sample, the EPR tube was sealed off under vacuum  $(1x10^{-5} \text{ torr})$ . The EPR spectra were obtained by using a  $TE_{102}$  rectangular cavity in a Bruker 200D EPR Spectrometer operating at 9.4 GHz (X-band). The temperature was controlled by a Varian 4540 temperature controller or by adjusting the flow rate of cold nitrogen. An ER350 NMR Gaussmeter was used to measure the magnetic field with 1 mG resolution. The microwave frequency was measured to 0.01 MHz by an HP5245 Frequency Counter. The g-values were obtained directly by measuring the magnetic field strength and the microwave frequency. The data were collected with an IBM-AT microcomputer. The nonlinear least-squares curve fitting program, KINFIT <sup>34</sup> was used to

fit the saturation curves with equations given by Poole  $^{35}$  and the powder EPR spectra were simulated with a program developed by M.J. Nilges.  $^{36-39}$ 

IV.C Results and Discussion for Known-structure Sodides

## IV.C.1 Results

The sodides can be divided into two kinds of systems in terms of their single crystal structures. One type (contact systems) has the sodide anion in contact or nearly in contact with the metal cation (Fig. 4-1a). Electrons trapped in such sodides show distinct hyperfine patterns. The other type (isolated systems) has trapped electrons isolated from the metal cation (Fig. 4-1b). Such systems show no resolved hyperfine interactions.

## The EPR spectra of contact systems

The EPR spectra of electrons trapped in  $M^+(HMHCY) \cdot Na^-$  with  $M^+ = K^+$ ,  $Rb^+$ ,  $Cs^+$ , are shown in Figure 4-2. A hyperfine structure consisting of 2I+1 lines is observed. From these spectra, it is possible to measure the isotropic part of the hyperfine coupling constant  $A_{1SO}$  and to calculate the electron density according to

$$A_{iso} = (8\pi/3)g\beta g_N^{\beta} |\Psi_s(0)|^2$$
<sup>(1)</sup>

where  $\beta$  is the electronic Bohr magneton and  $|\Psi_{g}(0)|^{2}$  is the probability distribution function for the electron evaluated at the



Figure 4-2. EPR spectra of (A) K<sup>+</sup>(HMHCY)·Na<sup>-</sup>.(B) Rb<sup>+</sup>(HMHCY)·Na<sup>-</sup> (C), Cs<sup>+</sup>(HMHCY)·Na<sup>-</sup> and (D) simulated EPR spectrum of Rb<sup>+</sup>(HMHCY)·Na<sup>-</sup>. nucleus. The subscript N refers to the nuclear values of g and  $\beta$ . The electron densities at the cations K<sup>+</sup>, Rb<sup>+</sup>and Cs<sup>+</sup> are 0.49, 1.60 and 3.13 x10<sup>30</sup> m<sup>-3</sup> respectively. From these values, the percent atomic character of each of these cations was calculated (Table 4-1).

Each hyperfine component of  $Rb^+(HMHCY) \cdot Na^-$  and  $Cs^+(HMHCY) \cdot Na^-$  shows a first derivative powder pattern that can be described by axially symmetric g and A tensors. The EPR spectrum of  $K^+(HMHCY) \cdot Na^-$  shows a more nearly isotropic hyperfine pattern and a "broad-wing" EPR peak. Satisfactory representations of these spectra could be simulated by using the spin Hamiltonian. <sup>40</sup>

$$H_{\mathbf{g}} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - \beta_{N} \mathbf{I} \cdot \mathbf{g}_{N} \cdot \mathbf{H}$$
(2)

where **H** is the applied Zeeman field vector, **S** and **I** are the electron and nuclear spin operators, **A** is the hyperfine tensor and **D** is the dipolar operator. The g tensors of  $Rb^+(HMHCY) \cdot Na^-$  and  $Cs^+(HMHCY) \cdot Na^-$ , obtained by simulation, show that  $g_{\parallel}$  values are 2.0083 and 1.996, and  $g_{\perp}$  values are 1.9933 and 1.977, respectively. The g-tensor of K<sup>+</sup>(HMHCY) \cdot Na^- yields an isotropic g-value of 2.0029. The perpendicular components,  $A_{\perp}$  of the hyperfine coupling tensors due to the isotopes <sup>85</sup>Rb and <sup>87</sup>Rb are 100 and 349 MHz respectively and the corresponding parallel components,  $A_{\parallel}$ , are 109 and 362 MHz. The  $A_{\perp}$  value for Cs<sup>+</sup>(HMHCY) \cdot Na<sup>-</sup> is 266 MHz and  $A_{\parallel}$  is 302 MHz. The isotropic hyperfine coupling constants,  $A_{iso}$  of M<sup>+</sup>(HMHCY) \cdot Na<sup>-</sup>, are given in Table 4-1. Table 4-1 Magnetic parameters calculated from the EPR spectra of sodides

Sodides	g-value	ΔH <sub>pp</sub> (G)	% atomic character	10 <sup>4</sup> T <sub>1</sub> (s) <sup>b</sup>	с <sub>е <u>у</u> Т</sub>
Cs(18C6) <sub>2</sub> Na	2.0023 <sup>a</sup> 2.0022	0.97 2.43		< 6 x 10 <sup>-2</sup>	Curie
K(18C6)Na	2.0023	3.85 <sup>c</sup> 5.02 <sup>h</sup>	18.9	1.24	0.01 <b>94 cV</b>
Rb18C6Na	2.0023 <sup>c</sup> 1.9974 <sup>f</sup>	5 <sup>c</sup> 13/16 <sup>c,f</sup>	16.3	2.3	0.0211 cV
Cs(15C5) <sub>2</sub> Na	2.0020	2.21		5.16(7)x10 <sup>-2</sup>	
Cs(12C4) <sub>2</sub> Na	2.0025	4.40		2.2(3)	
NaHMHCYNa	2.0010 <sup>f</sup> 2.0018 <sup>c</sup>	1.6 1.2	1.16	2.73x10 <sup>-3</sup>	Curie
KHMHCYNa	2.0029	2.85	6.48	12(2)	<b>(d)</b>
RbHMHCYNa	1.9983	5.25/13 <sup>8</sup>	10.5	4.5(3)	Curie
CsHMHCYNa <sup>c</sup>	1.9833	8.8	11.9	3.3(3)	Curie

a. Two lines observed, the first is the narrower central line.

b. Standard deviation estimates of the last digit are given in parentheses.

c. Values are given for the central peak.

d. Nearly independent of temperature - see text. e. The data for CsHMHCYNa are for the methyl deuterated compound.

f. Values are given for hyperfine peaks.
 g. Values are given for <sup>85</sup>Rb and <sup>87</sup>Rb.

EPR spectra of isolated systems

The EPR spectrum of  $Cs^+(18C6)_2 \cdot Na^-$  (Figure 4-3) shows two signals, a broad line and a narrow central line. The intensity ratio of the two peaks depends on the synthesis. No resolved hyperfine splitting is observed; however, the line broadening probably results from super-hyperfine coupling to a number of surrounding nuclei rather than to a distribution of g-values. The results of high frequency EPR studies of  $Cs^+(18C6)_2 \cdot Na^-$  agree with this conclusion. <sup>41</sup> The spectra of  $Cs^+(15C5)_2 \cdot Na^-$  and  $Cs^+(12C4)_2 \cdot Na^-$  show only a single line. The g-values of  $Cs^+(15C5)_2 \cdot Na^-$  and  $Cs^+(12C4)_2 \cdot Na^-$  are close to the free electron value. The peak-to-peak widths and g-values are given in Table 4-1.

## Power saturation studies

The saturation curves of most sodides (first derivative amplitude plotted as a function of the square root of the microwave power) demonstrate homogeneous line broadening characteristic of a single type of environment. For example, the saturation curves of  $K^+(HMHCY) \cdot Na^-$ ,  $Rb^+(HMHCY) \cdot Na^-$  and methyl deuterated  $Cs^+(HMHCY) \cdot Na^-$  are characteristic of such Lorenztian line broadening. A fit of the saturation curve for methyl deuterated  $Cs^+(HMHCY) \cdot Na^-$  is shown in Figure 4-4. The nonlinear least squares program KINFTT <sup>34</sup> was used to fit the saturation curve by the equation: <sup>35</sup>

$$\dot{y_m} = \dot{y_m} \frac{H_1}{\left(1 + \frac{H_1^2 g^2 T_1 T_2}{4}\right)^2}$$
 (3)







Figure 4-4. Power saturation curve of  $Cs^+(HMHCY) \cdot Na^-$ . The solid line is the least-squares best fit of the data for a Lorentzian line shape.

The best fit values of  $T_{1e}$  and the estimated standard deviations are given in Table 4-1. The EPR spectrum of trapped electrons in  $Cs^+(18C6)_2 \cdot Na^-$  could not be saturated in the range 0 to 0.1 W, permitting only an upper bound estimate of  $T_{1e}$ .

## Temperature behavior

The EPR intensities in these systems generally follow the 1/T dependence characteristic of Curie law behavior. Although pure sodides are diamagnetic, the magnetic susceptibility data show a "Curie law tail" that is characteristic of a small concentration of trapped electrons. There is no significant variation in the g-value with temperature. The EPR intensities of Rb<sup>+</sup>(HMHCY)·Na<sup>-</sup> and Cs<sup>+</sup>(18C6)<sub>2</sub>·Na<sup>-</sup> are shown as a function of 1/T in Figure 4-5. The spin susceptibilities of trapped electrons in Cs<sup>+</sup>(18C6)<sub>2</sub>·Na<sup>-</sup>,

Cs<sup>+</sup>(HMHCY)·Na<sup>-</sup> and Rb<sup>+</sup>(HMHCY)·Na<sup>-</sup> follow the Curie law; that is, the concentration of unpaired spins is constant in this temperature range and the trapped electrons do not strongly interact with each other. The peak-to-peak width of the EPR signal is independent of temperature in the range 130 K to 250 K. The magnetic parameters of the sodides are summarized in Table 1. It should be noted that one of sodides studied, K<sup>+</sup>(HMHCY)·Na<sup>-</sup>, did not show any temperature dependence of the signal intensity in the range of 190 K to 240 K. However, the intensity increased between 240 K and 260 K. This phenomenon is similar to that observed for Li<sup>+</sup>C211·e<sup>- 24</sup>, Rb<sup>+</sup>(18C6)·Na<sup>-</sup> and K<sup>+</sup>(18C6)·Na<sup>-</sup> systems. <sup>30</sup> This might result from spin pairing or antiferromagnetic coupling between electrons with different temperature dependences in the two sites.



Figure 4-5. Temperature dependence of intensities of EPR spectral lines of (A)  $Rb^+(HMHCY)\cdot Na^-$  and (B)  $Cs^+(18C6)_2\cdot Na^-$ .

The temperature dependence of the intensity was not measured for  $Cs^{+}(15C5)_{2} \cdot Na^{-}$  and  $Cs^{+}(12C4)_{2} \cdot Na^{-}$ .

## IV.C.2 Discussion

The differences in the structures of the two families of compounds studied readily explains the fact that a hyperfine EPR pattern is observed in the case of the HMHCY complexes, while none is seen for the sandwich complexes. The number of peaks in the pattern in the former case corresponds to the interaction of each electron with a single nucleus with spin number 7/2, 5/2 or 3/2 as appropriate. In the case of Rb<sup>+</sup>(HMHCY)·Na<sup>-</sup>, patterns for both rubidium isotopes are observed. Hyperfine patterns have already been reported for other complexes that contain only one crown ether molecule per cation, such as Rb<sup>+</sup>(18C6)·Na<sup>-</sup> where unpaired electrons apparently have easy access to the rubidium nuclei. <sup>18, 28</sup> Such cases are not considered here because of the lack of structural information.

In most of these systems, anisotropy is observed as expected from the structure. The isotropic part of the hyperfine coupling constant can be used to determine the percent atomic character of the cation in contact with the electron. The values reported in Table 4-1 show that the charge transfer becomes more favorable when the cation becomes less shielded by the complexant. As the size of the cation increases, it moves further out of the "pocket" of the complexant, thus permitting greater overlap with the wavefunction of the trapped electron. The 11.9 % atomic character in the cesium case is similar to that of cesium in ethylamine at room temperature. <sup>42</sup> The crown-ether sandwich complexes of cesium do not show any resolved hyperfine splitting, indicating that the electron density at the nucleus is small. This agrees with the independent determination of 0.033 % atomic character that was obtained for  $Cs^+(18C6)_2.e^-$ (which is isostructural with  $Cs^+(18C6)_2.Na^-$ ) by susceptibility and cesium Knight shift measurements. <sup>43</sup>

As Table 4-1 shows, except for the last two salts, the g-values are close to that of the free electron, in agreement with the view that the electron is trapped in a large anionic site with little spin-orbit coupling. The last two compounds have much bulkier cations that are not as well shielded by the complexant. The significantly lower g-values obtained in these cases indicate that the Rb<sup>+</sup>.e<sup>-</sup> and Cs<sup>+</sup>.e<sup>-</sup> systems are not spherical, but rather have significant spin-orbit contributions. Similar g-values were observed for the corresponding "monomers" in ethylamine solutions <sup>42</sup> which have been described as contact ion-pairs between solvated electrons and solvated metal ions. <sup>44</sup> The significance of the negative g-shift was previously discussed by M.C.R. Symons <sup>45</sup> who observed that when silver cations solvated in a rigid matrix gained one electron to form trapped *atoms*, there was a positive g-shift, whereas a negative g-shift implies that the electron density is not spherically distributed about the cation.

The results described in this chapter are in complete accord with the "F-center model" of trapped electrons in alkalides and electrides. According to this picture, electrons are trapped at normal anionic sites, but the electron density can penetrate somewhat into the surroundings, resulting in Fermi contact density at nearby nuclei. When the alkali cations are well shielded by the complexant and

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rather uniformly distributed around the anionic site, the contact density at  $M^+$  is small and no hyperfine splitting is observed. When, however, the anionic site is in contact (or close) to a single alkali cation, considerable overlap occurs, resulting in a distinct hyperfine pattern. The decrease in the g-value and the anisotropy of the hyperfine coupling show that the unpaired electron density is not spherically symmetric about the alkali cation in these cases.

The temperature dependences of the EPR intensities for various sodide systems show two different kinds of behavior; Curie law and spin-pairing. The former result indicates that the trapped electrons are rather isolated from each other while the latter implies the presence of spin pairing or antiferromagnetic coupling between trapped electrons, which must therefore be relatively close to one another.

ENDOR studies of the interactions of the unpaired spins of electrons trapped in  $Cs^+(HMHCY) \cdot Na^-$  with protons and with neighboring  $Cs^+$  and  $Na^-$  ions were reported. <sup>31</sup>

IV.D Results and Discussion for Sodides of Three Unknown-Structure

### EPR spectra

The EPR parameters of sodides of unknown-structure are summarized in Table 4-1. The EPR spectrum of Na<sup>+</sup>HMHCYNa<sup>-</sup> shows four hyperfine peaks due to Na<sup>+</sup> (I = 3/2) in Figure 4-6. The hyperfine coupling constant is isotropic, 10.3 MHz, corresponding to 1.16 % atomic character. The g-value is 2.0010, close to the free electron value. The hyperfine interaction results from Fermi contact interaction



Figure 4-6. X-band EPR spectrum of Na<sup>+</sup>HMHCYNa<sup>-</sup>.

between the trapped electron and the sodium cation as with the other M<sup>+</sup>HMHCYNa<sup>-</sup> systems. This indicates that the structure of Na<sup>+</sup>HMHCYNa<sup>-</sup> is probably similar to those of the other M<sup>+</sup>HMHCYNa<sup>-</sup> salts.<sup>10</sup> The g-value indicates that the spin-orbit interaction is small.

The EPR spectrum of K+18C6Na<sup>-</sup> shown in Figure 4-7 has a single central peak with a 3.9 G linewidth and four hyperfine peaks as for dilute metal-amine solutions. 42 The hyperfine splitting due to potassium in metal-amine solution increase with temperature in the range of -80 °C to 80 °C and the g-values of alkali metal-amine solutions decrease with higher atomic weight (from K to Cs) at given temperature. The hyperfine coupling constant for polycrystalline K+18C6Na<sup>-</sup> is 43.7 MHz which corresponds to 18.9 % atomic character. This % atomic character is close to that given by the hyperfine coupling at about 60 °C in ethylamine. The g-value is 2.0023 for both peaks and is isotropic. The isotropic hyperfine interaction of K<sup>+</sup>18C6Na<sup>-</sup> is due to Fermi contact interaction between the trapped electron and the potassium cation (I = 3/2). The isotropies of both parameters suggest that the charge distribution of an electron in the vacant anionic site of K<sup>+</sup>18C6Na<sup>-</sup> might be symmetric. The g-value indicates negligible spin-orbit interaction. The central single peak might arise from the electron trapped at an interstitial site that interacts weakly with its surroundings.

The EPR spectrum of Rb+18C6Na<sup>-</sup> shown in Figure 4-8 has a strong central single line and 10 hyperfine peaks due to the two isotopes  $^{87}$ Rb (I = 3/2) and  $^{85}$ Rb (I=5/2) as is the case for metal-amine solutions. Both the hyperfine interaction and the g- value are isotrpic. The isotropic hyperfine coupling constants are 58.8 G ( $^{85}$ Rb) and



Figure 4-7. X-band EPR spectrum of K<sup>+</sup>(18C6)Na<sup>-</sup>





199.6 ( $^{87}$ Rb) G, which corresponds to 16.3 % atomic character. The anisotropic hyperfine coupling constant can arise from both the Fermi contact interaction and the dipolar interaction between the trapped electron and the rubidium cation. The g-value of the hyperfine peak is 1.9974 which indicates the presence of spin-orbit interactions. The spin-orbit interaction might arise from the mixing of unoccupied *p*-states into the valence state. The intensity of a central peak with a g-value of 2.0023 varied with the synthesis. Therefore, there are two types of trapped electrons: One type is in contact with the rubidium cation and the other might be trapped at an interstitial site. The interaction between trapped electrons in both types of sites to yield spin-pairing is indicated by the temperature dependence, as shown in Figures 4-12 and 4-13. The axial symmetries of the g-value and the hyperfine coupling constant of the hyperfine signal indicate that the electron charge distribution might be non-spherical.

## Power saturation studies

The saturation curve of Na<sup>+</sup>HMHCYNa<sup>-</sup> is shown in Figure 4-9. The saturation curve corresponds to homogeneous line broadening. The spin-lattice relaxation time,  $T_1$ , of Na<sup>+</sup>HMHCYNa<sup>-</sup> obtained by the saturation method, is  $1 \times 10^{-3}$  s. The saturation curve of K<sup>+</sup>18C6Na<sup>-</sup> also indicates a Lorenztian line shape as shown in Figure 4-10. The spin-lattice relaxation time is  $1.24 \times 10^{-4}$  s at 183 K. The saturation curve of K<sup>+</sup>18C6Na<sup>-</sup> was observed as a function of the temperature as shown in Figure 4-10. As the temperature is increased, the maximum position of the saturation curve moves to higher microwave power, which means the spin-lattice relaxation time decreases. This result indicates that the spin-lattice relaxation might arise from diploar



Figure 4-9. Power saturation curve of Na<sup>+</sup>HMHCYNa<sup>-</sup>.



Figure 4-10. Temperature dependence of power saturation curve of K<sup>+</sup>18C6Na<sup>-</sup>. Symbol **=**: -40 °C, **c**: -80 °C, **o**: -100 °C, **x**: -120 °C.

interactions or direct spin-phonon interactions. The saturation curve of the central peak for  $Rb^+18C6Na^-$  corresponds a Gaussian line shape as shown in Figure 4-11. This indicates the presence of unresolved hyperfine coupling to hydrogen or sodium nuclei. The saturation curve of the hyperfine peak for  $Rb^+18C6Na^-$  corresponds to mixing of Lorenztian and Gaussian line shapes. An approximate spin-lattice relaxation time of 2.3 x  $10^{-4}$  s was obtained from the maximum of the saturation curve.

## Temperature behavior

As mentioned earlier, most alkalides follow the Curie law. The temperature dependence of the intensity for Na<sup>+</sup>HMHCYNa<sup>-</sup> also shows Curie law behavior. The intensity decreases as the temperature is increased. This implies that the trapped electron is isolated and that there is no significant interaction between spins. The total number of unpaired spins is constant in this temperature range. The area of the EPR signals for K<sup>+</sup>18C6Na<sup>-</sup> and Rb<sup>+</sup>18C6Na<sup>-</sup> was studied as a function of temperature for both the hyperfine and the central peak. The log of the area is a decreasing linear function of the inverse of the temperature as shown in Figures 4-12 and 4-13. This implies an equilibrium between unpaired spins and paired spins that shifts to the unpaired side as the temperature is increased. This phenomenon is similar to that of  $Li^+(C211)e^{-24}$  and indicates antiferromagnetic coupling between electrons in two different sites. A possible explanation is given by the equation,



Figure 4-11. Power saturation curve of Rb<sup>+</sup>(18C6)Na<sup>-</sup>.



Figure 4-12. Temperature dependence of areas of EPR spectra of Rb<sup>+</sup>(18C6)Na<sup>-</sup>.



Figure 4-13. Temperature dependence of areas of EPR spectra of K<sup>+</sup>(18C6)Na<sup>-</sup>.

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$$e_2 = e_a + e_1$$

Where  $e_a$  represents the electron at the anionic site and  $e_i$  is the electron at the interstitial site. The spin pairing energies obtained from the initial slope are 1.94 x10<sup>-2</sup> and 2.11 x10<sup>-2</sup> eV for K<sup>+</sup>18C6Na<sup>-</sup> and Rb<sup>+</sup>18C6Na<sup>-</sup>, respectively.

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#### CHAPTER V

# HIGH FIELD AND LOW FIELD EPR STUDIES OF AN ELECTRIDE AND TWO ALKALIDES

This chapter is the form of the draft that will be submitted to the *Journal of Physical Chemistry*. Dr. David E. Budil and Dr. Keith A. Earle at Cornell University helped me to obtain and discuss the G-band spectra.

The EPR spectra of polycrystalline samples of Cs+(18-crown- $6)_2X^-$ , in which  $X^- = e^-$ . Na<sup>-</sup> or Cs<sup>-</sup>, were studied at both X-band (9 GHz and G-band (250 GHz). The spectra of the electride at both frequencies, and the temperature and saturation behavior at X-band, correspond to electron localization on the EPR time scale at a single type of asymmetric site with weak coupling to surrounding nuclei. The results are in agreement with the "F-center" model, in which electrons serve to balance the charge of the complexed cations with the center of charge of each electron at an anionic site. Defect electrons in the alkalides  $Cs^{+}(18C6)_2Na^{-}$  and  $Cs^{+}(18C6)_2Cs^{-}$  show EPR signals from several sites in each case, with the strongest signal originating from electrons trapped at anionic vacancies. This signal in  $Cs^{+}(18C6)_2Na^{-}$ , and that of isostructural electride,  $Cs^{+}(18C6)_2e^{-}$ , have nearly the same g-anisotropy, indicating similar electron-trapping sites. The intensities of two EPR signals from Cs<sup>+</sup>(18C6)<sub>2</sub>Cs<sup>-</sup> decrease in the same manner as the temperature is reduced, suggesting the presence of a common spin-paired precursor that dissociates to populate both types of sites.

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## V.A Introduction

Since the isolation of the first salt of an alkali metal anion in 1974  $^{1,2}$ , we have characterized many of the physical properties of alkalides and electrides. Polycrystalline alkalides and electrides are synthesized from solutions that contain the alkali cation, complexed by a crown ether, cryptand or aza-analog, and an equal concentration of either alkali metal anions or solvated electrons. However, no solution contains exclusively M<sup>-</sup> or e<sup>-</sup>. Rather, a dissociation equilibrium is present as given by

$$M^+$$
 complexant  $\longrightarrow M^+$  complexant +  $2e_{solv}$  (1)

As a result, electrons are always trapped in crystalline alkalides. The concentration of trapped electrons depends on the synthesis method used. For example, slow crystallization and an excess of alkali metal tend to produce lower concentrations of trapped electrons.

A major goal of EPR studies of alkalides and electrides is to determine the nature of the electron trapping site(s) and the degree of overlap of the trapped electron wavefunction with nearby nuclei. In most electrides studied to date, the concentrations and exchange rates are so high that only a single exchange-narrowed EPR line is seen at X-band. (The electride described in this chapter is an exception:) Electron-trapping in alkalides provides an opportunity to study the nature of trapped electrons in the absence of exchange.

The electronic wavefunction of the trapped electron in an alkalide can have a significant spatial extent, which leads to hyperfine interactions with nearby nuclei. The electron density at the alkali cation due to the trapped electron changes with the structure of the anionic site for both alkalides and electrides. The most obvious indication of this electronic charge distribution is the EPR line broadening and hyperfine splitting due to Fermi contact and/or electron nuclear dipolar interaction. Generally, when the cation is well-shielded within a cryptand cage or in a sandwich crown-ether complex, the contact electron density at the cation due to the trapped electron is small.<sup>3</sup> By contrast, if the alkali cation is exposed to the anionic site, as in a one-to-one crown ether complex, or when a methylated aza-crown is used 3.4 the contact electron density of the trapped electron at the cation can be large. For the former case, no hyperfine splitting is observed due to the low contact electron density at the cation and the interaction of the electron with a number of nuclei. The latter case shows hyperfine splitting due to a relatively strong interaction between each trapped electron and a single cation.

The X-band EPR spectrum of  $Cs^+(18C6)_2Na^-$  showed at least two signals, a strong broad line and a narrow central line with much smaller integrated intensity. <sup>3</sup> The intensity ratio of the two peaks depended on the synthesis. No resolved hyperfine splitting or ganisotropy were observed; the line broadening could have resulted from either super-hyperfine coupling to a number of surrounding nuclei or to a distribution of g-values. <sup>3</sup> The use of high field EPR in the present study was initiated to resolve this uncertainty. Previous EPR studies of  $Cs^+(18C6)_2Cs^-$  showed the presence of at least two electron trapping sites with complex temperature behavior. <sup>5</sup> Rotation of a single crystal demonstrated the presence of g-anisotropy. No identification of the sites responsible for the EPR peaks was made at the time.

Electrides are crystalline compounds in which trapped or intinerant electrons are present in amounts equal to those of the complexed cations. 5-13 Thus, electrons serve in place of the anions of alkalides to balance the cationic charge. The physical properties of electrides and their structural similarity to corresponding alkalides strongly suggest that electrons are trapped stoichiometrically at all of the anionic sites. The crystal structures of electrides show large vacancies at the locations of the anionic sites, but the trapped electrons cannot be directly detected because of the low electron density.

Previous studies of the X-band EPR spectra of  $Cs^+(18C6)_2e^-$  at temperatures as low as 2.9 K showed only a single narrow (0.5 G) line whose width was independent of temperature. The lineshape became Dysonian at higher temperatures, indicative of high microwave conductivity. The activation energy for this conductivity was only 0.05 eV, much lower than the apparent d.c. activation energy of 0.45 eV. These results indicated rapid electron exchange, even at the lowest temperatures measured. <sup>5</sup>

Recent d.c. and a.c. powder conductivity studies of electrides  $^{14}$  have revealed that contamination of the electride  $Cs^+(18C6)_2e^-$  with  $Cs^-$  drastically affects the conductivity, increasing the electronic contribution by several orders of magnitude. Apparently, the presence

of small amounts of excess cesium provides a mechanism for electron migration and exchange that is not present in the pure electride. The effect on the EPR spectrum is also dramatic as described in this chapter.

The present study of the X-band and G-band EPR spectra of three compounds that contain the complexed cesium cation,  $Cs^+(18C6)_2$ , was initiated in attempt to separate the effects of multiple trapping sites, hyperfine broadening and g-anisotropy on the EPR spectra of  $Cs^+(18C6)_2e^-$ ,  $Cs^+(18C6)_2Na^-$  and  $Cs^+(18C6)_2Cs^-$ .

## V.B Experimental Methods

## V.B.1 Sample Preparation

The sample preparation methods used for X-band EPR studies have been described elsewhere.<sup>15</sup> For 250 GHz EPR (G-band) studies, polycrystalline samples of  $Cs^+(18C6)_2Na^-$  and  $Cs^+(18C6)_2e^-$ , and single crystals of  $Cs^+(18C6)_2Cs^-$  were ground with a mortar and pestle below -50 °C under a dry nitrogen atmosphere in a glove bag. The samples for the high field studies were loaded into the sample holder described below under cold nitrogen, and then sealed with a Mylar film. A larger sample volume could be used than at X-band. An amount of sample was used that filled about half of the sample holder.

## V.B.2 Sample holder

The sample holder has been previously described. <sup>16</sup> It is cylindrical in shape with a diameter of 3.8 mm and depth of 10.2 mm. Polymethylpentene(TPX), Teflon and Z-cut quartz had been previously used as window materials for the sample holder, because they have

low absorbance in the FIR. Because Teflon might react with our samples, Z-cut quartz was first chosen as the window material. When the sample holder was put into liquid nitrogen, however, the quartz window tended to pop out because of differential contraction of the sample holder and the window. Finally, Rexolite (cross-linked polystyrene) was chosen for the window. Transmittance of FIR radiation showed that the Rexolite is sufficiently transparent in the FIR to use as a sample holder. It is also stable with respect to the solvent and samples. Even though the windows had some tool marks, the optical performance was not compromised because the surface was flat to better than  $\lambda/8$ . The samples were stored under liquid nitrogen in a Dewar.

## V.B.3 Instrumentation

X-band EPR spectra were obtained with a Bruker 200D EPR spectrometer with a  $TE_{102}$  rectangular cavity. An ER350 NMR gaussmeter was used to measure the field to  $\pm 1$  mG resolution. The microwave frequency was measured to 0.01 MHz with an HP5245 frequency counter. The g-values of X-band spectra were obtained directly from the magnetic field strength and the microwave frequency. The temperature was controlled by adjusting the flow rate of cold nitrogen.

The FIR EPR spectrometer developed by J.H. Freed *et al.* <sup>16</sup> was used to obtain the high frequency EPR spectra. The FIR source was a Millitech Corp. PLS-3F phase-locked solid state source that delivered 3-5 mW at 250 GHz (via a WR-4 waveguide). A semiconfocal Fabry-Perot resonator was used for the sample cavity; the cavity was tuned by controlling the distance between two mirrors. The modulation frequency was 65 kHz. The field was swept by using a superconducting solenoid driven by an HP6032A power supply that provided point-to-point resolution of 0.188G. The temperature was controlled in the range -120 °C to -40 °C by using a heater and regulating the flow rate of cold nitrogen gas. The temperature drift was about  $\pm 3$  °C. The sweep width was about 50 G.

## V.C Results and Discussion

## V.C.1 $Cs^{+}(18C6)_2e^{-}$

The compounds  $Cs^+(18C6)_2e^-$  and  $Cs^+(18C6)_2Na^-$  are isostructural with the metal cation and the metal anion or trapped electron rather isolated from one another. <sup>7</sup> Presumably, electrons are trapped at anionic vacancies, although the presence of interstitial electrons and ions cannot be ruled out. Ceside-free  $Cs^+(18C6)_2e^$ appears to be primarily an ionic conductor with an activation energy of about 1.1 eV; the conduction mechanism is probably closely related to that of  $Cs^+(15C5)_2e^-$ . <sup>14</sup>

As shown in Figure 5-1, the EPR spectrum of  $Cs^+(18C6)_2e^-$  that is free of contamination by  $Cs^-$  is not exchange-narrowed, but rather shows axially symmetric g-anisotropy that is only partially resolved at 9.5 GHz. There is no observable hyperfine splitting. The perpendicular component  $(g_{\perp})$  is 2.0021 and the parallel component  $(g_{\parallel})$  is 2.0024. At 250 GHz, as shown in Figure 5-2, the extremes of the spectrum are spread out by about 26 times relative to those of the X-band spectrum. At high resolution, however, the rhombic symmetry


Figure 5-1. (A) X-band spectrum (solid line) and (B) the simulation spectrum (dotted line) of  $Cs^+(18C6)_2e^-$ .



Figure 5-2. G-band EPR spectra of (A)  $Cs^+(18C6)_2e^-$  and (B)  $Cs^+(18C6)_2Na^-$ .

of the g-anisotropy is evident, although it is nearly axial. This rhombic symmetry is consistent with the shape of the cavity as shown by the single crystal structure; that is, the electron distribution is not expected to be spherical in the anion vacancy. The isotropic g-value of the trapped electron in  $Cs^+(18C6)_2e^-$  is close to the free electron gvalue and indicates that contributions due to spin-orbit interactions are small.

The X-band EPR spectra were simulated by using the Hamiltonian. <sup>17-19</sup>

$$H_{s} = \beta_{e} \mathbf{S} \mathbf{g} \mathbf{H} + \sum_{i}^{n} \mathbf{I}_{i} \mathbf{A}_{i} \mathbf{S} - \beta_{N} \mathbf{I}_{i} \mathbf{g}_{i} \mathbf{H}$$
(2)

are also shown in Figure 5-1. The simulations confirm that there is negligible hyperfine interaction (0.06 MHz) between cesium cations and an electron trapped in the anionic vacancy.

The temperature dependences of the linewidth, lineshape, and intensity were studied at X-band and the temperature dependences of the linewidth and lineshape were studied at G-band. The intensity of the X-band EPR spectrum is plotted as a function of inverse temperature in Figure 5-3 and shows that the spin susceptibility of the trapped electron follows the Curie law, indicating that the trapped electrons are not spin-paired at these temperature.

The high-field EPR spectrum at low modulation amplitude and at the higher temperatures showed some fine-structure between the major broad peaks. This was attributed to the presence of a few crystals that had not been ground finely enough to yield a powder



Figure 5-3. Temperature dependence of the intensity of the X-band EPR spectrum of  $Cs^+(18C6)_2e^-$ .

pattern. The line separation of the high field EPR spectrum increased from 15.3 G to 19 G as the temperature was decreased in the range of -43 °C to -129 °C. The separation between  $g_{\perp}$  and  $g_{\parallel}$  was 0.65 G at 9.5 GHz, while the corresponding separation was 17G at 250 GHz. This agrees with the expected resolution enhancement of a factor of 26 at 250 GHz.

The saturation curve at X-band for  $Cs^+(18C6)_2e^-$  shows that the line shape is nearly Lorenztian. A fit of the saturation curve is shown in Figure 5-4a. The nonlinear least squares program KINFIT <sup>20</sup> was used to fit the saturation curve by the equation. <sup>21</sup>

$$\dot{y_m} = \dot{y_m} \frac{H_1}{\left(1 + \frac{H_1^2 g^2 T_1 T_2}{4}\right)^2}$$
 (3)

The presence of a single Lorenztian line is indicative of a single type of trapping site in the electride.

Attempts to obtain the electron spin echo envelope modulation (ESEEM) spectrum of  $Cs^+(18C6)_2e^-$  resulted in a pronounced free induction decay signal (FID) with no well-defined echo modulation signal, indicating a rather long value of T<sub>2</sub>. When the field was varied across the resonance field, the off-resonance FID signal collapsed. This also indicates that the EPR spectrum of  $Cs^+(18C6)_2e^-$  is homogeneous.

The results are all in accord with the assumption that most of the unpaired electrons in  $Cs^+(18C6)_2e^-$  are localized in the anionic cavities. The nearly axially symmetric g-anisotropy of the trapped electron is in agreement with the structure of the cavity (diameter  $\sim 4$  Å and length  $\sim 6$ Å). Of course, the electron density can spread onto atoms in the vicinity of the cavity, but the overlap with Cs<sup>+</sup> and with neighboring trapped electrons is small.

## V.C.2 Cs<sup>+</sup>(18C6)<sub>2</sub>Na<sup>-</sup>

As indicated above,  $Cs^+(18C6)_2Na^-$  is isostructural with  $Cs^{+}(18C6)_{2}e^{-}$ ; each anion is surrounded by eight nearest-neighbor complexed cations. The X-band EPR spectrum of Cs<sup>+</sup>(18C6)<sub>2</sub>Na<sup>-</sup> shows three signals, a main broad peak, a minor broad peak, and a narrow central peak.<sup>3</sup> The intensities of these three peaks at X-band change from sample to sample . In this work, the intensity ratio of the narrow peak to the main broad peak was very small, both at X-band and at G-band, and the minor broad peak was nearly absent. No resolved hyperfine splitting was observed. The g-values of the broad peak and the narrow peak at X-band are 2.0022 and 2.0023 respectively. The narrow peak probably arises from exchangenarrowing due to itinerant electrons. The broader peak results from trapped electrons that interact with surrounding hydrogens and complexed cesium cations. The broadening results from superhyperfine coupling to a number of surrounding nuclei and also yields a small negative g shift. The presence of three signals shows that several different trapping sites are present in  $Cs^+(18C6)_2Na^-$  and that the trapped electrons are isolated from each other. The g-values are all close to the free electron value, which suggests that the spinorbit interaction is very small.

The X-band EPR intensity of the major signal in  $Cs^+(18C6)_2.Na^$ increases linearly with the inverse temperature, showing that the spin susceptibility of the trapped electron in  $Cs^+(18C6)_2Na^-$  follows the Curie law. <sup>3</sup> This indicates that the concentration of unpaired electrons is constant in this temperature range. The linewidth is independent of temperature in the range 130 K to 250 K.

The g-anisotropy of the  $Cs^+(18C6)_2Na^-$  EPR spectrum at G-band is basically similar to that of the  $Cs^+(18C6)_2e^-$  spectrum as shown in Figure 5-2. This suggests that the major signal arises from F-center electrons trapped at anionic vacancies.

As indicated above, several sites were observed at X-band. However, only a single major signal was evident at the high field. The spin concentration responsible for the central narrow peak was probably too small to yield a detectable peak at G-band in the sample used. It should be noted that the integrated central peak at X-band varied from sample to sample and was always much smaller than that of the broad peak. The broad peak observed at X-band would have masked any anisotropy of the g-value.

The saturation curve at X-band for  $Cs^+(18C6)_2Na^-$  shown in Figure 5-4b, does not reach a maximum in the range 0 to 0.1 W. This permits only an upper bound estimate of  $T_{1e}$  (< 6 x 10<sup>-6</sup> sec) and supports the assumption that the linewidth originates from unresolved hyperfine spin packets.

## V.C.3 $Cs^{+}(18C6)_2Cs^{-}$

The crystal structure of  $Cs^+(18C6)_2Cs^-$  shows that there are seven complexed cesium cations around each  $Cs^-$  ion at distances of



Figure 5-4. Power saturation curve of (A)  $Cs^+(18C6)_2e^-$  and (B)  $Cs^+(18C6)_2Na^-$ .

8.09 to 9.65 Å. <sup>22</sup> Both cations and anions form zigzag chains parallel to the b-axis with uniform interionic distances of 8.78 and 8.86 Å, respectively. Each cesium anion is 8.12 Å from another cesium anion in an adjacent chain. Thus, the cesium anions are relatively isolated from one another and from the cesium cations.

Previous X-band EPR spectra of polycrystalline  $Cs^+(18C6)_2Cs^$ showed two overlapping signals. <sup>5</sup> One was a narrow peak (0.62 G) at the free electron g-value. The other was a smaller and broader peak that had g-anisotropy, as demonstrated by the spectrum of a single crystal at different orientations. In the present work, the X-band EPR spectrum of polycrystalline  $Cs^+(18C6)_2Cs^-$  shown in Figure 5-5 also shows a broad peak and a central narrow peak, similar to the X-band EPR spectrum of  $Cs^+(18C6)_2Na^-$ .

The line widths of the broad peak and the narrow peak at Xband are 15.1 G and 0.64 G, and the g-values are 1.9987 and 2.0020, respectively. Cs+(18C6)<sub>2</sub>Cs<sup>-</sup> samples obtained from different syntheses were used for the X-band and G-band studies. Rather large crystals were grown and crushed to prepare the sample for G-band EPR, while a polycrystalline sample was used for the X-band studies. The G-band EPR spectrum of Cs+(18C6)<sub>2</sub>Cs<sup>-</sup> shown in Figure 5-6 has a strong peak and a weak peak, each with an axially symmetric g-value. The signals correspond to the broad peak and the narrow peak observed at Xband. The separations of  $g_{\parallel}$  and  $g_{\perp}$  for the strong peak and the weak peak are 17.6 G and 16.8 G at G-band, which would correspond to 0.68 G and 0.64 G at X-band, respectively. The g-anisotropy of the broad peak would be unobservable, while that of the narrow peak could be masked by broad peak or by exchange narrowing. If the latter



Figure 5-5. X-band EPR spectrum of Cs+(18C6)<sub>2</sub>Cs<sup>-</sup>.



Figure 5-6. G-band EPR spectrum of Cs+(18C6)<sub>2</sub>Cs<sup>-</sup>.

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explanation is correct, the exchange rate would be faster than 1.9  $x10^{6}$  sec<sup>-1</sup> but slower than 5  $x10^{7}$  sec<sup>-1</sup>.

The temperature dependence of the X-band intensities of the two EPR peaks of  $Cs^+(18C6)_2Cs^-$  is shown in Figure 5-7. The intensity increases with increasing temperature from - 70 °C to - 24 °C, while below - 70 °C the temperature dependence follows Curie-law behavior. The temperature dependence could result from the presence of spin-paired electrons that can dissociate to populate both sites above -70 °C according to

$$e_2$$
  $e_a$   $+ e_i$  (4)

where  $e_a^-$  and  $e_i^-$  represent trapped electrons at F-center and interstitial sites, respectively. At lower temperatures, the rate of this process might be too slow to affect the unpaired electron concentration. Another explanation is that there might be a composition change from Cs+(18C6)<sub>2</sub>Cs<sup>-</sup> to Cs+(18C6)e<sup>-</sup> as the temperature is increased above - 70 °C, according to.

 $Cs^{+}(18C6)_{2}Cs^{-} \longrightarrow Cs^{+}(18C6)_{2}e^{-} + Cs$  (5)

This phenomenon would result in an increase in the EPR intensity at higher temperature.



Figure 5-7. Temperature dependence of the intensity of the X-band EPR spectrum of  $Cs^{+}(18C6)_2Cs^{-}$ .

#### V.D Conclusion

The only EPR signal from  $Cs^+(18C6)_2e^-$  and the major signal from  $Cs^+(18C6)_2Na^-$  and  $Cs^+(18C6)_2Cs^-$  result from electrons trapped at anion vacancies. In the electride, the resulting g-anisotropy is observed at both G-band and X-band, while in the alkalides the ganisotropy can only be resolved at G-band. In all case, there is evidence for superhyperfine interaction of the trapped electron with a number of surrounding nuclei, but, as anticipated for trapped electron in the rather isolated anion vacancies, there is no strong coupling to one, or a few nuclei. The anisotropy of the g-value results from the non-spherical shape of the cavity and suggests that the ground state of the trapped electron is not strictly describable as an s state.

In the alkalides, there are other trapping sites than the Fcenter, but their nature cannot be deduced from the EPR spectra. The temperature dependence of the EPR intensities for  $Cs+(18C6)_2Cs^$ shows that a common spin-paired species can dissociate as the temperature is raised to increase the EPR intensities of both signals.

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#### CHAPTER VI

# PULSED EPR STUDIES OF POLYCRYSTALLINE CESIUM HEXAMETHYL HEXACYCLEN SODIDE

This chapter is in the form of a paper that has been submitted to the Journal of Applied Magnetic Resonance. The final version was written with the assistance of Professor John L. McCracken.

## Abstract

The electron spin echo envelope modulation (ESEEM) technique of pulsed EPR spectroscopy has been used to measure weak <sup>133</sup>Cs hyperfine couplings to trapped electrons in polycrystalline cesium hexamethyl hexacyclen sodide. Two magnetically distinct groups of weakly coupled <sup>133</sup>Cs nuclei were found; one with an isotropic electron-nuclear hyperfine (Fermi contact) coupling of 0.34 MHz and the other with a contact coupling less than 0.1 MHz. Analysis of these data by computer simulation shows that the number of Cs nuclei that give rise to these interactions and their distance from the paramagnetic center is consistent with the hypothesis that the trapped electrons occupy vacant anion sites. The results indicate that the spread of unpaired electron spin density, along the axis formed by the "contact ion pair," may be greater than that in the plane perpendicular to this axis.

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#### VI.A Introduction

Electrides are a class of solids that consist of complexed metal cations and trapped electrons in a well-defined structural arrangement. As a class, electrides represent extremes, in which trapped electrons are localized at one limit and are able to move from site to site at the other. The degree of localization of trapped electrons depends markedly on the metal cation and complexant used for the synthesis. For cesium 18-crown-6 electride,  $Cs^+(18C6)_2e^-$ , cesium cations are complexed by two 18C6 crown ethers, and the trapped electrons are localized with separation distances of 8-10 Å. <sup>1,2</sup> A much different situation is found for K<sup>+</sup>(C222)e<sup>-</sup>, where strong interelectron interactions have been observed. <sup>3</sup> Possible uses of these compounds for the doping of organic semiconductors, <sup>4</sup> and as chemical reagents for the preparation of small metal particles, <sup>5</sup> have Because their chemical and physical properties been reported. depend on the nature of their trapped electrons, it is important that the details of these trapping sites be understood.

EPR spectroscopy provides an ideal vehicle for the study of electron-trapping sites in these materials. The ability of EPR methods to focus on the immediate environment of the unpaired electron spin and measure the amount of unpaired spin density that is distributed over the molecular framework of a material gives it advantages over other spectroscopic techniques for the study of these sites. Unfortunately, attempts to use cw-EPR and ENDOR methods for such studies on electrides have met with little success, most likely because of the high concentration of paramagnetic centers in these materials. Alkalides are a closely related group of compounds, in which alkali metal anions serve as the "counterions" to the complexed metal cations. <sup>6</sup> Trapped electrons are also found in these materials as a result of dissociation of electrons from alkali metal anions during their formation. The concentration of trapped electrons can be controlled for alkalides by varying the concentration of metal relative to complexant during synthesis. Because the concentration of paramagnetic centers can be kept low and X-ray crystallographic studies have shown that alkalides and their corresponding electrides are isostructural, <sup>7</sup> these materials provide an ideal system for the study of electron-trapping sites using EPR methods.

In the present study, we have used the electron spin echo envelope modulation (ESEEM) technique of pulsed EPR spectroscopy to study electron-trapping sites in the thermally stable alkalide, cesium hexamethyl hexacyclen sodide (Cs+(HMHCY)Na-).<sup>8</sup> A computer simulation of the cation-anion packing in this compound, generated using X-ray crystallographic data, <sup>9</sup> is shown in Fig. 6-1. The cesium cations in this material are complexed by HMHCY, a methylated nitrogen analog of 18-crown-6. X-ray data show that nitrogens 4, 7, 13, and 16 of the complexant are coplanar, and that the Cs<sup>+</sup> ion is located 0.9 Å above the center of this plane (Fig. 6-1A). Nitrogens 1 and 10 are located 1.1 Å below this plane with their methyl groups closing off the bottom of the cation "cup." The cesium cations are coordinated to all six HMHCY nitrogens with Cs-N distances that range from 3.2 - 3.35 Å. The closest Na<sup>-</sup> ion is located 4.26 Å above the Cs<sup>+</sup> ion, forming a contact-ion pair. In the unit cell, these ions are held in a staggered arrangement, yielding a distorted



Figure 6-1. Computer simulation of the cation-anion packing in  $Cs^+(HMHCY)Na^-$  from x-ray crystallographic data: (A) the molecular unit, (B) cutaway view down the *b* axis, and (C) cutaway view down the *a* axis.

octahedral coordination geometry between Na<sup>-</sup> and its six nearest complexed Cs<sup>+</sup> neighbors. The Na<sup>-</sup>-Cs<sup>+</sup> distances in this distorted octahedral arrangement range from 7.2 - 8.6 Å for the five more distant cations and 4.26 Å for the contact pair. <sup>9</sup> It has been proposed that the trapped electrons in this material occupy vacant Na<sup>-</sup> sites.

The chief goal of EPR studies on alkalides has been to precisely determine electron locales. Previous cw-EPR and cw-ENDOR studies of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> have provided valuable information toward reaching this goal. <sup>10</sup> The X-band cw-EPR spectrum of this material shows a large hyperfine splitting to a single Cs<sup>+</sup> ion with the isotropic, or Fermi contact portion of the coupling being 98G. Parallel ENDOR studies showed additional magnetic couplings between the unpaired electron spin and protons of the complexant, <sup>23</sup>Na and <sup>133</sup>Cs nuclei. These observations are supportive of the current picture of the electron-trapping site, as described above, in that a single, large  $^{133}Cs$ hyperfine coupling is observed due to the trapped electron spin being "in contact" with one complexed Cs<sup>+</sup> cation and that additional couplings to  $^{23}$ Na and  $^{133}$ Cs, as seen by using ENDOR, were small. These small couplings are consistent with the 8-10 Å distance between adjacent Na<sup>-</sup> sites, and the distances between the trapped electron spin and five of its Cs<sup>+</sup> nearest neighbors. For the purpose of defining electron locales, one also needs information concerning the number of nuclei involved in a particular coupling. Unfortunately, this information is lost in a standard ENDOR measurement. In an attempt to measure hyperfine coupling constants and obtain quantitative information regarding the number of interactions, we have studied Cs+(HMHCY)Na<sup>-</sup> by using the ESEEM method of pulsed EPR

spectroscopy. Because ESEEM techniques are best suited for the study of weakly coupled nuclei with small magnetic moments and large nuclear spins, they may be ideal for the characterization of paramagnetic centers in alkalides. In this chapter, the results of Xband ESEEM studies on Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> are presented. Evidence for hyperfine coupling between trapped electrons and two magnetically distinct sets of Cs<sup>+</sup> ions was obtained. These data are analyzed and yield results in agreement with the current picture regarding the location of trapped electrons in this material.

## VI.B Materials and Methods

Polycrystalline samples of  $Cs^+(HMHCY)Na^-$  were prepared according to literature procedures. <sup>8,11</sup> The complexant, hexacyclen, was purchased as the sulfate salt (Aldrich Chemical) and methylated, using published methods. <sup>12</sup>

Pulsed EPR studies were performed with a home-built spectrometer recently constructed at Michigan State University. The microwave bridge is capable of operation over a bandwidth of 6 to 18 GHz and has a transmitter that employs two microwave pulse channels for the implementation of different phase-cycling or pulse-swapping schemes.  $^{13,14}$  A microwave synthesizer (Gigatronics, model 610) serves as the source for this instrument, and each pulse channel consists of a low-power, high-speed PIN diode switch (General Microwave model FM864-BH), a high-speed 0°/180° wideband phase modulator (General Microwave model F 1938) and an isolator. The low-power pulses from these arms are combined and fed into a medium-power GaAs FET amplifier (Avantek model SWL-89-0437) and a 1KW pulsed travelling wave tube amplifier (Applied Systems Engineering, model 117). The cavity used in these measurements was of the reflection type and employed a folded half-wave resonator <sup>15</sup> and the X-band Gordon coupling arrangement developed by Britt and Klein<sup>16</sup>. Experiments were carried out at 4.2K, using a home-built liquid helium immersion dewar. The microwave receiver utilizes wideband components and a double balanced mixer (RHG model DM2-18 AB) in a conventional homodyne arrangement. A low-noise GaAs FET amplifier (Avantek model AWT-18635) is used in the receiver, with a medium-power, high-speed PIN diode limiter (Innowave, model VPL-6018) and a fast PIN diode switch (General Microwave, model F9114) serving to protect it from damage by higher-power microwave pulses.

The spectrometer is controlled by a McIntosh IIx microcomputer (Apple Computer) via an IEEE-488 interface (National Instruments) to a four-channel digital delay and gate generator (Stanford Research, Model DG535) and a Stanford Research SR245 "computer interface" module. The digital delay and gate generator is used to supply the accurate pulse delays required for ESEEM measurements, as a programmable clock for controlling the overall repetition rate of our measurements, and supplies trigger pulses to a gated integrator (Stanford Research model 250) responsible for measuring spin echo intensities. The SR245 computer interface module serves to digitize the gated integrator output signal, count the number of pulse sequences repeated at a given set of microwave pulse spacings, and to clear the gated integrator after its analog output has been read. Data collection and analysis software was written using the C language (Symantec). ESEEM spectra were obtained from time domain data, using a modified version of the dead-time reconstruction protocol described by Mims. <sup>17</sup> Simulations of <sup>133</sup>Cs ESEEM functions were performed on a Microvax II computer (Digital Equipment) using a published theoretical treatment. <sup>18,19</sup>

#### VI.C Results and Discussion

The cw-EPR spectrum of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> has been reported. <sup>10</sup> The spectrum has eight major peaks split about g = 1.98 that have been attributed to hyperfine coupling between the trapped electron and its complexed Cs<sup>+</sup> counterion 4.26 Å away. Analysis of this spectrum by computer simulation showed a nearly isotropic g matrix  $(g_{\parallel} = 1.996, g_{\perp} = 1.977)$  and an axial Cs hyperfine tensor with  $A_{\perp} =$ 93.7 and  $A_{\parallel}$  = 106.3 gauss. ESEEM data were collected at three different field positions across the low field Cs hyperfine component at g = 2.25 and at a higher field where the EPR signal is maximized (g = 1.78). Because the anisotropy in the resolved Cs hyperfine splitting is small and the spectral width sampled with our 15 nsec hard microwave pulses is greater than ten gauss, no orientation selection effects were observed in the data. <sup>20,21</sup> Three-pulse, stimulated echo ESEEM data collected at g = 2.21 are shown in Fig. 6-2. The time domain data were taken using a tau value (spacing between the first two microwave pulses) of 225 nsec. 1024 data points were taken with the first 1000 spaced at 15 nsec increments, starting at  $\tau$ +T = 270 nsec. The last 24 points were used to record the baseline and were



Frequency (MHz)

Figure 6-2. Stimulated echo ESEEM data and associated frequency spectrum obtained for Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>. Conditions for this measurement were: microwave frequency, 9.412 GHz; magnetic field strength, 3043G; microwave pulse power, 80W (15 nsec FWHM); tau value, 225 nsec; starting T, 30 nsec.; sample temperature, 4.2; pulse sequence repetition rate, 5 Hz; 12 events were averaged for each time point with 1024 pts being collected at 15 nsec increments.

collected with the gated integrator trigger pulse set to a value 100 nsec after the echo. Figure 6-2A shows that the ESEEM observed for Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> is fairly shallow, with modulation depths being < 20% of the overall spin echo amplitude. The frequency spectrum for these data (Fig. 6-2B) shows a large, broad component centered at 0.5 MHz and two pairs of narrow lines centered at the <sup>133</sup>Cs Larmor frequency of 1.7 MHz. This pattern of four lines was observed at all of the field positions examined in this study. Three-pulse ESEEM spectra collected at g = 2.25 and g = 1.78 are shown in Fig. 6-3. The set of lines centered at 1.68 MHz at 2980 G (Fig. 6-3A) shift to a center frequency of 2.1 MHz at 3770 G (Fig. 6-3B), consistent with their assignment to weakly coupled <sup>133</sup>Cs nuclei.

The broad, lower-frequency peaks observed in the spectra shown in Figs. 6-2 and 6-3 most likely arise from magnetically coupled <sup>14</sup>N nuclei. Because a large amount of unpaired electron spin density is present at the Cs cation closest to the proposed Na<sup>-</sup> vacancy, it is reasonable to assume that couplings to the nitrogen nuclei of the HMHCY complexant should be observed. This idea is supported by previous ENDOR studies <sup>10</sup> where proton hyperfine couplings as large as 4.0 MHz were assigned to the methyl protons of the HMHCY complexant based on isotopic substitution work. Additional, weak ESEEM frequency components were observed at 3.4, 4.2, and 4.6 MHz and may arise from hyperfine coupling to <sup>14</sup>N or <sup>23</sup>Na nuclei. These components were best observed at short tau values (< 150 nsec) in stimulated echo experiments. Multifrequency ESEEM studies aimed



Figure 6-3. ESEEM spectra obtained for  $Cs^+(HMHCY)Na^-$  at two different magnetic field positions within the EPR absorption envelope. Measurement conditions were as in Fig. 6-2 except for (a) magnetic field strength, 2980G; tau value, 220 nsec, and for (b) magnetic field strength, 3770G; tau value, 190 nsec. Time domain data points were collected at 10 nsec intervals for both spectra.

at enhancing the modulations arising from these couplings and determining their origin are planned.

Computer simulations of the  $^{133}$ Cs ESEEM data shown in Figures 2 and 3 were undertaken to test our current hypothesis regarding the location of trapped electrons in these materials. Our calculations made use of the theoretical treatment of Shubin and Dikanov,  $^{18}$  where analytical expressions for two- and three-pulse ESEEM functions were derived for I > 1/2 nuclei. This formalism was developed using perturbation methods and applies to conditions where anisotropic hyperfine and nuclear quadrupole interactions are small compared to the nuclear Zeeman splitting. According to the above assumption, the primary ESEEM is described by the expression:

$$V_{I}^{Q}(\tau) = 1 - \frac{2}{3} I(I+1) \frac{B^{2}}{v_{I}^{2}} [1 - 2 \cos 2\pi \gamma_{I} \cos 2\pi (\frac{A}{2}\tau) G(\gamma \tau) + \frac{1}{2} \cos 2\pi (2v_{I}\tau) G(\gamma \tau) + \frac{1}{2} \cos 2\pi (A\tau)]$$
(6-1)

where

$$\gamma = \frac{3}{4} \frac{eQV_{zz}}{hI(2I-1)}$$

$$G(\mathbf{x}) = \frac{3}{2I(I+1)(2I+1)} \sum_{m=-I}^{I-1} [I(I+1) - m(m+1)] \cos 2\pi (2m+1)\mathbf{x}$$

eQ is the nuclear quadrupole moment and  $V_{zz}$  is a component of the electric field gradient tensor.  $\tau$  is the pulse width and  $v_I$  is the modulation harmonic of nucleus I. Because multiple <sup>133</sup>Cs nuclei are involved in the observed coupling, individual three-pulse ESEEM

simulations were combined using the spherical model approximation to the product rule. <sup>22</sup> Our analysis was guided by the x-ray crystal structure of Cs<sup>+</sup>(HMHCY)Na<sup>-9</sup> and the hypothesis that the trapped electrons in these materials occupy vacant anion sites. The complexed Cs<sup>+</sup> ions would then be positioned about this vacant anion site in a distorted octahedral arrangement. Figure 6-1B shows that there are four complexed Cs<sup>+</sup> ions that are nearly coplanar with the proposed trapping sites, with the cations positioned at distances of 7.5, 8.1, 8.2, and 8.6 Å. The remaining two complexed Cs<sup>+</sup> ions are perpendicular to this plane. One is centered at a distance of 4.25 Å from the proposed vacant  $Na^{-}$  site (Fig. 6-1A) and is the ion that strongly interacts with the trapped electron giving rise to the observed splitting in the cw-EPR spectrum. The second is located directly opposite to this, at a distance of 7.2 Å, and is shielded from the trapping site by complexant (Fig. 6-1C).

Because the cesium ESEEM data provide evidence for two magnetically distinct sets of coupled nuclei, our modeling was done using two sets of coupling parameters. One set considered the Fermi contact portion of the hyperfine coupling to be 0.34 MHz, as measured from the ESEEM spectra, while the second set considered the contact interaction to be < 0.1 MHz. For both parameter sets, the dipoledipole distances and number of contributing nuclei were varied within limits defined by the x-ray structure of the material. To simplify our calculations further, the Cs<sup>+</sup> nuclear quadrupole coupling constants were set to zero. The effects of a weak nuclear quadrupole interaction, within the framework of the pereturbation treatment used here, are to enhance the damping of the observed modulations. <sup>23</sup> Because the damping is also affected by a background decay function of unknown form  $^{24}$  and nuclear quadrupole interactions are expected to be the same for all of the complexed Cs<sup>+</sup> ions, this assumption will not affect our analysis. The implications of ignoring nuclear quadrupole interactions will be discussed in greater detail below.

To facilitate comparison between calculated ESEEM functions and those obtained experimentally, the ESEEM spectrum of Fig. 6-3A was treated with a windowing function to isolate the four peaks centered at 1.7 MHz and the component at 0 MHz. The resulting frequency spectrum was then backtransformed to give the result shown in Fig. 6-4A. Our best simulation results are shown in Figs. 6-4B and 6-4C. This simulation was obtained by using a model that considered one cesium nucleus at 5.8 Å with a contact coupling of 0.34 MHz, and a second set of four cesium nuclei at a dipole-dipole distance of 8.1 Å with a contact coupling of 0.07 MHz. Because the amplitudes of both sets of modulation components are comparable, the set of four cations must be at the longer distance and were assigned the smaller isotropic hyperfine coupling constant. The idea that the four "in-plane" cesium ions couple to the trapped electron in a similar manner and are distinct from the "axial" Cs cations is in good agreement with the current view that the trapped electrons occupy vacant Na<sup>-</sup> sites. The weak-contact coupling and long dipole-dipole distance of 8.1 Å found for these four ions are also in agreement with this model. The electron-nuclear coupling for the odd Cs<sup>+</sup> ion, which



Figure 6-4. The time domain data shown in (A) were obtained by backtransformation of the Cs ESEEM frequency components from the spectrum of Fig. 6-3A along with the component at 0 MHz (a 0.4 MHz width was used in the windowing of this peak). (B) shows the result of an ESEEM simulation where 4 Cs nuclei with  $A_{iso} = 0.07$  MHz and r = 8.1, and 1 Cs nucleus with  $A_{iso} = 0.34$  MHz and r = 5.8 were considered

is most likely the "axial" cation opposite the "contact pair," is described by a higher contact coupling, 0.34 MHz, and a dipole-dipole distance of 5.8 Å. This distance is much shorter than the 7.2 Å distance obtained using x-ray crystallographic techniques and most likely indicates that appreciable unpaired electron spin density is delocalized onto the complexant molecule of this cation.

Alternative models for simulating the Cs ESEEM were considered, but the calculated distances obtained using these models were less plausible than those described above. For example, models where only the four complexed Cs<sup>+</sup> ions coplanar with the vacant Na<sup>-</sup> site contributed to the observed couplings were considered. If one adopts a model for which two cesium cations are strongly coupled and two are more weakly coupled, all Cs<sup>+</sup> ion dipole-dipole distances must be < 6.5 Å to predict modulation depths in agreement with those found experimentally. If one considers one of the four in-plane Cs<sup>+</sup> ions to be more tightly coupled than the other three, a dipole-dipole distance of < 6 Å must be used for it. Although the x-ray crystal structure of this material shows that all of the distances between the central Na<sup>-</sup> site and the four in-plane Cs<sup>+</sup> ions are slightly different, their structural relationship to the central Na<sup>-</sup> site is so similar that both of these models seem less plausible than the one presented above.

The results of our ESEEM analysis for the "stronger" coupled cesium ion differ from those reported for recent ENDOR studies of  $Cs+(HMHCY)Na^{-10}$ . In this ENDOR work, a pair of lines split by 0.31 MHz about the <sup>133</sup>Cs larmor frequency was observed. The analysis of these data considered the source of line broadening for the Cs ENDOR peaks to be due to nuclear quadrupole interactions and reported a value of 5.3 MHz for  $e^2qQ$ . This value is high, if one compares it to literature values reported for cesium halide molecules studied in the gas phase $^{25}$ . However, there is little or no precedence for the measurement of <sup>133</sup>Cs<sup>+</sup> quadrupole coupling parameters in the solid state. The choice to ignore the effects of dipole-dipole coupling in the analysis of the <sup>133</sup>Cs<sup>+</sup> ENDOR was based on the long, 7.2 Å, distance reported for the nearest cation. As stated above, if nuclear quadrupole coupling is ignored in the ESEEM analysis, a dipole-dipole distance of 5.8 Å is required to account for the modulation depths, or amplitudes, observed experimentally. If weak nuclear quadrupole interactions are included in our ESEEM simulations, only the damping of the predicted functions is affected, and the 5.8 Å dipole-dipole distance is still required to predict signal amplitudes in agreement with experiment. The inclusion of larger nuclear quadrupole interactions in the simulations would affect both observed modulation frequencies and amplitudes and may allow for longer dipole-dipole distances. To study these effects, the calculations must be done numerically, as outlined by Mims. <sup>26,27</sup> Although it is clear that electron-nuclear dipole-dipole coupling is important in this system, the effects of larger nuclear quadrupole couplings remain to be seen. Data from ongoing solid-state NMR studies and further development of our ESEEM analysis methods will allow the relative contributions of these interactions to be sorted out.

In conclusion, the results of ESEEM studies on Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> presented in this work are consistent with the proposal that trapped electrons in this material occupy vacant Na<sup>-</sup> sites. <sup>6</sup> The most likely

model for the two distinct sets of weak <sup>133</sup>Cs magnetic couplings reported here is that the four Cs cations in the *ac* plane(Fig. 6-1B) are nearly equivalent and weakly coupled, while the "axial" Cs<sup>+</sup> found in the bc plane, and shielded from the trapped electron by the complexant molecule, is more strongly coupled. The small isotropic hyperfine couplings measured for these distinct cesium ions show that a significant amount of unpaired electron spin density is found at atoms > 8 Å away from the "contact pair." The proposed difference in couplings between trapped electrons and complexed Cs<sup>+</sup> ions in the ac plane and the more distant  $Cs^+$  ion perpendicular to the ac plane may lead to the onset of interesting electrical properties, as doping levels are varied and further characterization of these materials is done. Because the EPR spectrum of the polycrystalline sodide is mostly isotropic, confirmation of our assignment of the larger cesium hyperfine coupling will require single crystal ESEEM studies. The detailed information regarding electron locales obtained in these studies will be important for reaching a full understanding of their chemical and physical properties.

#### VI.D Acknowledgements

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### CHAPTER VII

### CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

## **VII.A General Conclusions**

Crystalline alkalide and electride salts can be prepared as stable compounds *in vacuo* at low temperature and always contain the trapped electrons to different extents due to the presence in solution of solvated electrons as a result of the dissociation equilibrium. The value of X-band and G-band EPR and pulsed EPR spectroscopy to study the trapped electrons in alkalides and electrides has been demonstrated. A new crystalline sodide, Na<sup>+</sup>HMHCYNa<sup>-</sup> was synthesized and characterized by EPR spectroscopy.

The hyperfine splittings of X-band EPR spectra for K+HMHCYNa<sup>-</sup>, Rb+HMHCYNa<sup>-</sup>, and Cs+HMHCYNa<sup>-</sup> confirm the formation of a *contact-ion pair* between a trapped electron and a cation and these EPR spectra are in agreement with the single crystal structures. The hyperfine splittings of three sodides of unknown-structure, K+18C6Na<sup>-</sup>, Rb+18C6Na<sup>-</sup> and Na+HMHCYNa<sup>-</sup> indicate the presence of substantial contact between the trapped electron and the cation. The central single peak of K+18C6Na<sup>-</sup> and Rb+18C6Na<sup>-</sup> probably arises from the trapped electron at an interstitial site. The g-values of hyperfine peaks for the above sodides are smaller than the free electron value, 2.0023 and show a small spin-orbit interaction.

The trapped electron in the sandwich complexed sodide,  $Cs^{+}(18C6)_2Na^{-}$  is isolated from the cations and shows no resolved

hyperfine splitting because of shielding of the cations by the pair of complexant molecules. Two additional trapping sites exist for the sandwich complexed alkalides,  $Cs+(18C6)_2Na^-$  and  $Cs+(18C6)_2Cs^-$ . An additional narrow central peak of  $Cs+(18C6)_2Na^-$  and  $Cs+(18C6)_2Cs^-$  probably corresponds to electron trapping at an interstitial site, whereas the broad peak corresponds to the trapped electron at the vacant anionic site. Electrons in alkalides and electrides are trapped at anionic vacant sites as F-centers. The g-values of sandwich complexed sodides are close to the free electron value, which shows a negligible spin-orbit interaction.

The X-band and G-band EPR studies of pure crystalline  $Cs^+(18C6)_2e^-$  have confirmed that the electron is trapped at the anionic site. The electronic charge distribution of the trapped electron for  $Cs^+(18C6)_2e^-$  is non-spherical and is in agreement with the shape of the cavity. The contamination of  $Cs^+(18C6)_2e^-$  by small amounts of  $Cs^-$  is apparently responsible for the previously observed line narrowing presumably due to rapid spin-spin exchange.

In present work, most sodides except  $Rb+18C6Na^{-}$  and  $Cs+(18C6)_2Na^{-}$  show nearly Lorenztian lineshapes. The lineshapes of  $Rb+18C6Na^{-}$  and  $Cs+(18C6)_2Na^{-}$  correspond to a combination of Lorenztian and Gaussian shapes.

The temperature dependences of the EPR intensities of most sodides follow the Curie-law and these results confirm that the trapped electrons do not strongly interact with one another. The temperature dependences of  $K+18C6Na^{-}$ ,  $Rb+18C6Na^{-}$ , and  $Cs+(18C6)_2Cs^{-}$ , on the other hand, show spin-paring between trapped electrons of two different site. The spin-pairing energies of K+18C6Na<sup>-</sup> and Rb+18C6Na<sup>-</sup>, and Cs+(18C6)<sub>2</sub>Cs<sup>-</sup> are 1.19  $\times 10^{-2}$ , 2.11  $\times 10^{-2}$ , and 1.24  $\times 10^{-2}$  eV, respectively.

The strong hyperfine coupling due to contact-ion pair between a trapped electron and a Cs<sup>+</sup> cation was observed with EPR spectroscopy for Cs<sup>+</sup>HMHCYNa<sup>-</sup>. The weak hyperfine coupling between a trapped electron and five surrounding Cs<sup>+</sup> cations in Cs<sup>+</sup>HMHCYNa<sup>-</sup> was observed by ESEEM studies and is in agreement with the ENDOR results. Two distinct sets of weak <sup>133</sup>Cs hyperfine couplings are observed. The four Cs cations in the *ac* plane are nearly equivalent and weakly coupled. The "axial" Cs<sup>+</sup> cation in the *bc* plane is shielded from the trapped electron by the complexant molecule, but is more strongly coupled than are the other four "distant" Cs<sup>+</sup> ions. The results of ESEEM suggest that the electronic charge distribution of the trapped electron in Cs<sup>+</sup>HMHCYNa<sup>-</sup> is elliptical.

# VII.B. Suggestions for Future Work

Much progress has been made in the last several years in the study of alkalides and electrides. Crystal structure determinations, the synthesis of more stable compounds, and the application of these compounds by using their strong reducing power are important steps which have been taken. Several suggestions for further study can be made based on the results of the present work.

1. ESEEM, and pulsed EPR spectroscopy in general, have proven useful to study the local structure of the trapped electron in Cs<sup>+</sup>HMHCYNa<sup>-</sup>, whose crystal structure is known. Further investigations of ESEEM for the sodides of Rb<sup>+</sup>18C6Rb<sup>-</sup>, K<sup>+</sup>18C6Na<sup>-</sup>, and Rb+18CNa<sup>-</sup>, which show strong hyperfine coupling between a trapped electron and a cation, should be made. It may possible to determine the local structure and electron charge distribution of the trapped electron for sodides of unknown-structure.

2. One of the advantages of the pulsed-ENDOR method compared with cw-ENDOR is that the entire sequence can usually be made short enough to exclude unwanted relaxation. At X-band magnetic fields, the proton ENDOR spectra often overlap with and obscure the spectra of the important heteronuclei such as  $^{14}$ N,  $^{13}$ C. This technique leads to enhancement of the intensities of heteronulcear signals and the suppression of proton signals. Cs<sup>+</sup>HMHCYNa<sup>-</sup>, whose methyl groups have been substituted by  $^{13}$ C should be investigated by the pulsed-ENDOR. The results of ESEEM and cw-ENDOR for Cs<sup>+</sup>HMHCYNa<sup>-</sup> could then be compared with the results of the pulsed-ENDOR studies.

3. A primitive experiment of photoinduced EPR for Rb+18C6Nahas given promising results. The combination of a cw-EPR or pulsed EPR and a portable YAG laser makes it attractive to study the electron distribution in excited states by using photoinduced EPR spectroscopy.

4. Single crystal EPR is powerful way to investigate the local structure around an unpaired electron. The single crystal EPR should be studied to investigate the local structure near trapped electrons in electrides. A two dimensional goniometer should be developed which can operate below -40 °C in order to study the single crystal EPR spectra of alkalides and electrides as a function of orientation.

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