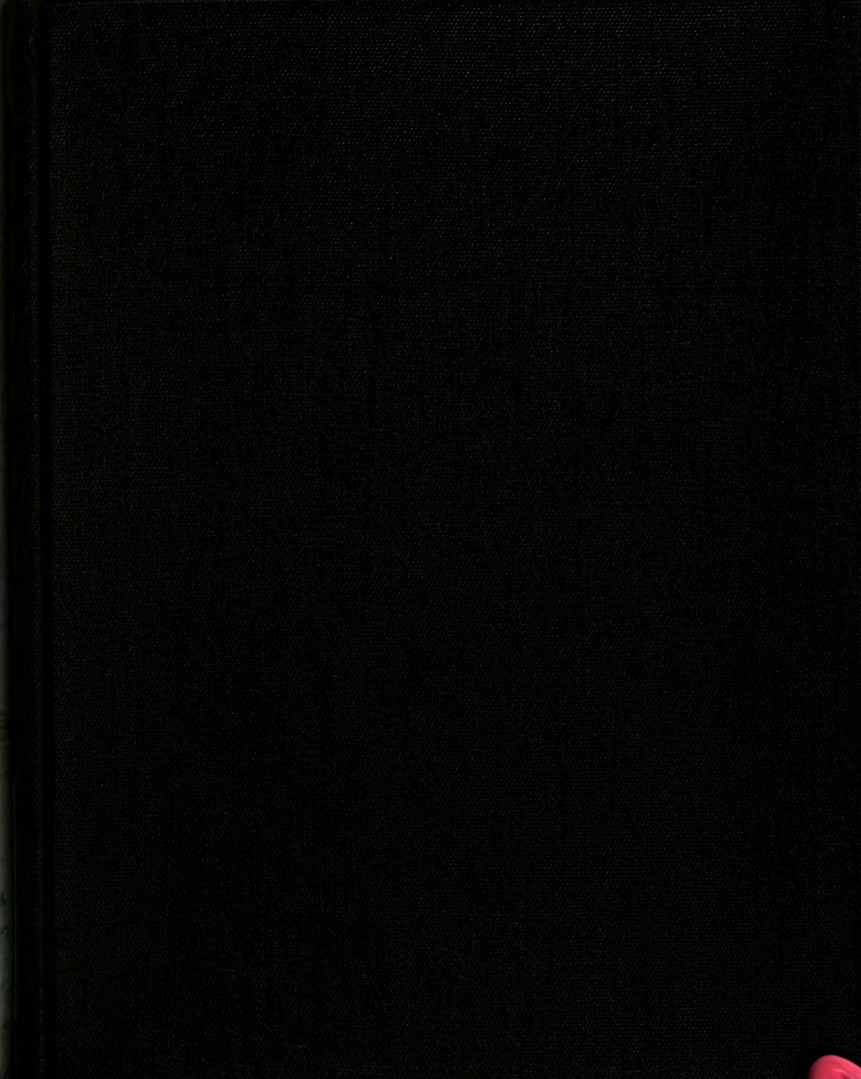






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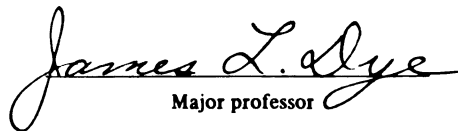
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**ELECTRON EMISSION AND SINGLE CRYSTAL X-RAY DIFFRACTION
STUDIES OF ALKALIDES AND ELECTRIDES**

By

Rui He Huang

A DISSERTATION

Submitted to

Michigan State University

**in partial fulfillment of the requirements
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ABSTRACT

ELECTRON EMISSION AND SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES OF ALKALIDES AND ELECTRIDES

By

Rui He Huang

The crystal structures of an electride, $K^+(C222).e^-$, and five alkalides, $Cs^+(18C6)_2.Cs^-$, $Cs^+(C222).Cs^-$, $Rb^+(C222).Rb^-$, $K^+(C222).Na^-$ and $Cs^+(15C5)_2.K^-$, were determined. The structure of $K^+(C222).e^-$ provides evidence of electron pairing, consistent with other properties of this electride. The long (in $Cs^+(18C6)_2.Cs^-$) and short (in $Cs^+(C222).Cs^-$) uniform chain packing of ceside anions in both cesides explains the presence of a Cs^- solid state NMR peak in $Cs^+(18C6)_2.Cs^-$ and its absence in $Cs^+(C222).Cs^-$. A dimer-type species, Rb_2^{2-} , was found for the first time in $Rb^+(C222).Rb^-$. The minimum and the effective radii obtained from these structures are: 2.55 and 2.73 Å for Na^- , 2.80 and 3.15 Å for K^- , 3.0 and 3.2 Å for Rb^- and 3.1 and 3.5 Å for Cs^- .

Photoemission studies of alkalides and electrides were made by quantum yield spectra. The photoemission peaks for the alkali metal anions are: 300 and 330 nm for Na^- , 370 nm for K^- and 380 nm for Rb^- . Quantum yields are strongly temperature dependent. Trace amount of Na contamination from Pyrex glassware has a great effect on the photoemission quantum yield spectra of electrides and alkalides other than sodides.

Thermionic emission was observed from crystals and films of alkalides and electrides at temperatures as low as -60°C . The temperature dependence of emission currents follows the Richardson-Dushman equation and the Richardson plots of the thermionic emission from crystals or films yield work functions of only a few tenths of an eV.

TO MY PARENTS

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CHAPTER 1

INTRODUCTION

Alkalides and electriles are two new classes of compounds discovered and studied in Dr. Dye's laboratory at Michigan State University during the last decade [1-4]. Twenty five alkalides and five electriles have been synthesized and characterized to date [5]. These unique ionic compounds consist of alkali metal cations shielded by large cyclic or bicyclic polyether or polyamine ligands and either large alkali metal anions, in which electrons are in filled s^2 orbitals, or electrons trapped at anionic sites. Because of the weak electron binding, it is not surprising that these crystalline compounds have some unusual chemical and physical properties.

Much work has been focussed on studies of these compounds by optical spectra, chemical analysis, NMR, EPR, magnetic susceptibility, DC conductivity and other techniques [3]. However, the research in two key fields, crystal structure and band structure, had been hindered by the difficulty of handling these compounds. The first alkalide, $\text{Na}^+(\text{C222})\cdot\text{Na}^-$ (C222=cryptand [222]), was synthesized and characterized

in 1974 [1] and the crystal structure was determined soon after the synthesis [2]. Since then many new alkalides and electrides have been discovered [3,5]. However, over a ten year period, many attempts to determine the crystal structures of other alkalides and of electrides failed because of the high reactivity of these compounds with air and/or moisture and the tendency towards irreversible decomposition at temperatures above about -40°C . Meanwhile, an EXAFS study of alkalides and electrides that contained rubidium was carried out to obtain some structural information [8,27]. However, only qualitative information about the structures could be obtained from the EXAFS experiments. In 1985, a new technique for growing and handling suitable single crystals was established in our laboratory by S. Dawes and O. Fussa, following the suggestions of Professors H. Hope and D. Powers of the University of California at Davis [6,7,8]. Since then, more than 10 crystal structures of alkalides and electrides have been determined, and this achievement has greatly advanced our understanding of the properties of these novel compounds [11,12,13]. In the present work, the crystal structures of one electride and five alkalides were determined and are reported.

Despite the difficulty of handling these compounds, studies in our laboratory prior to the present work had given us some information about the electronic band

structures of alkalides and electrides. This information can be summarized as follows:

1. The optical spectra of thin films of alkalides and electrides showed optical absorption peaks for Na^- , K^- , Rb^- and Cs^- at about 650, 800, 860 and 950 nm respectively [3,4,5]. These optical bands may represent the transitions from the S^2 ground states to the S^1P^1 excited states of the anions. For a localized electride, such as $\text{Cs}^+(18\text{C}6)_2 \cdot e^-$ (18C6=18crown6), a peak appeared at about 1.6 micrometers [14]. Some electrides, such as $\text{K}^+(\text{C}222) \cdot e^-$ and $\text{Li}^+(\text{C}211) \cdot e^-$, showed plasma-type spectra indicating different types of electron trapping [15,16]. Little was known about the band structures of electrides.

2. Powder DC conductivity measurements showed that most of the alkalides and electrides behave as semiconductors with band gaps ranging from 2.5 eV to a few tenths of an eV [3,4]. Since most of the alkalides contain some trapped electrons, which are believed to lie closer to the conduction band than do the alkali anions, the conductivities are dominated by the electride impurities and the apparent band gaps are about 0.5 to 1.0 eV. $\text{Na}^+(\text{C}222) \cdot \text{Na}^-$ is an exception. It can crystallize in rather pure form with very low concentration of trapped (or defect) electrons. Recent measurements of powder and single crystal

DC conductivity of $\text{Na}^+(\text{C}_{222})\cdot\text{Na}^-$ showed that the band gap in this compound is 2.4 ± 0.2 eV [9].

3. Preliminary studies of photoemission of sodides showed that sodide films had two major quantum yield peaks at 650 and 370 nm. They were assigned to the photoemissions from trapped electrons and the sodide ion, Na^- , respectively [10]. The quantum yield was a strongly temperature-dependent function and the mechanism was unknown.

Photoemission is known as the most powerful tool for studying band structure in solids. A part of the present work was to continue the work on photoemission of alkalides and electrides.

CHAPTER 2

CRYSTAL STRUCTURE DETERMINATION

Single crystal X-ray diffraction is one of the most powerful methods for understanding the properties of alkalides and electrides. Crystal structure determinations enable us to understand, and sometimes to predict, the electronic, magnetic, optical and other properties of these compounds. Sometimes it is the best way to determine the chemical stoichiometry. For example, it was thought that there was only an electride $\text{Cs}^+(\text{C}_{222})\cdot\text{e}^-$ in the Cs-C₂₂₂ system because no Cs^- NMR signal has been found in the system [14]. But the x-ray diffraction experiment in this work showed that there was a ceside, $\text{Cs}^+(\text{C}_{222})\cdot\text{Cs}^-$.

1. Experimental.

Although there are many ways of growing single crystals, all single crystals used in this work were grown by the temperature scanning technique. Polycrystalline samples used

for crystal growing were synthesized by the methods mentioned elsewhere [3,5]. A two-chamber apparatus for recrystallization was used. After the polycrystalline sample had been loaded into the apparatus at low temperature under a nitrogen atmosphere, the apparatus was pumped on a vacuum line, while been kept cold in a Dry-Ice bath, and dimethyl ether (DME) was introduced to dissolve the crystals. Then a co-solvent (trimethyl amine (TMA) or diethyl ether (DEE)) was distilled into the apparatus to form a mixed solvent solution in order to reduce the solubility. A saturated solution with some seed crystals was made by distilling out some of the solvent at the temperature at which crystal growing was to start. Then the apparatus was transferred to a thermal bath through which cold alcohol was circulated by a programmable NESLAB LT-9 bath. The cooling rate could be varied from 2 degrees/hour to .25 degrees/hour. After the temperature had been scanned according to the program and reached the lowest value, the mother liquor was poured into the other side and all of the solvents were distilled out, and the dry crystals were kept at dry-ice temperature until used. Usually 3 sets of samples were made simultaneously with the hope that one set would yield some good single crystals.

The recrystallization conditions are summarized in Table 2-1.

TABLE 2-1. RECRYSTALLIZATION CONDITIONS

Compound	Solvent System	Temperature Scan Range	Scan Time (hours)	Procedure
$\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$	DME/TMA	-42 - -56 °C	10	down-up- down
$\text{Cs}^+(\text{C222}).\text{Cs}^-$	DME/TMA	-42 - -63 °C	10	down-up- down
$\text{Cs}^+(\text{15C5})_2.\text{K}^-$	DME/TMA	-35 - -67 °C	50	down
$\text{Rb}^+(\text{C222}).\text{Rb}^-$	DME/DEE	-42 - -67 °C	50	down
$\text{K}^+(\text{C222}).\text{Na}^-$	DME/TMA	-39 - -67 °C	50	down
$\text{K}^+(\text{C222}).\text{e}^-$	DME/DEE	-50 - -67 °C	50	down

The techniques for examining and mounting single crystals have been described in detail by S. Dawes [7] and O. Fussa [8].

A Nicolet P3F diffractometer with an LT-1 low temperature device was used for data collection. The temperature of the crystals could be varied between -60 and -80°C.

The detailed crystal structure data (single molecule diagram, packing diagram, positional and thermal parameters, bond distances, etc.) of each structure can be found in the Appendices. Complete crystal data for each structure are published in the separate papers [26].

2. Crystal structure of $K^+(C_{222}).e^-$.

It was of great interest to determine the crystal structure of $K^+(C_{222}).e^-$ because evidence showed that it might be a delocalized electride or a spin-paired electride. The optical absorption spectrum of thin films of the compound showed a plasma-type spectrum similar to that in alkali metal-ammonia solutions and the magnetic susceptibility data showed that it had a weak paramagnetic Curie tail at low temperature (< 5 K) corresponding to less than 1% free electrons and then the susceptibility increased slowly with temperature up to 200 K [5,12,15]. Figure 2-1 shows the molar electronic susceptibility of $K^+(C_{222}).e^-$ obtained by M. Faber [15] and in this work. Although the paramagnetic Curie tails in the two runs are

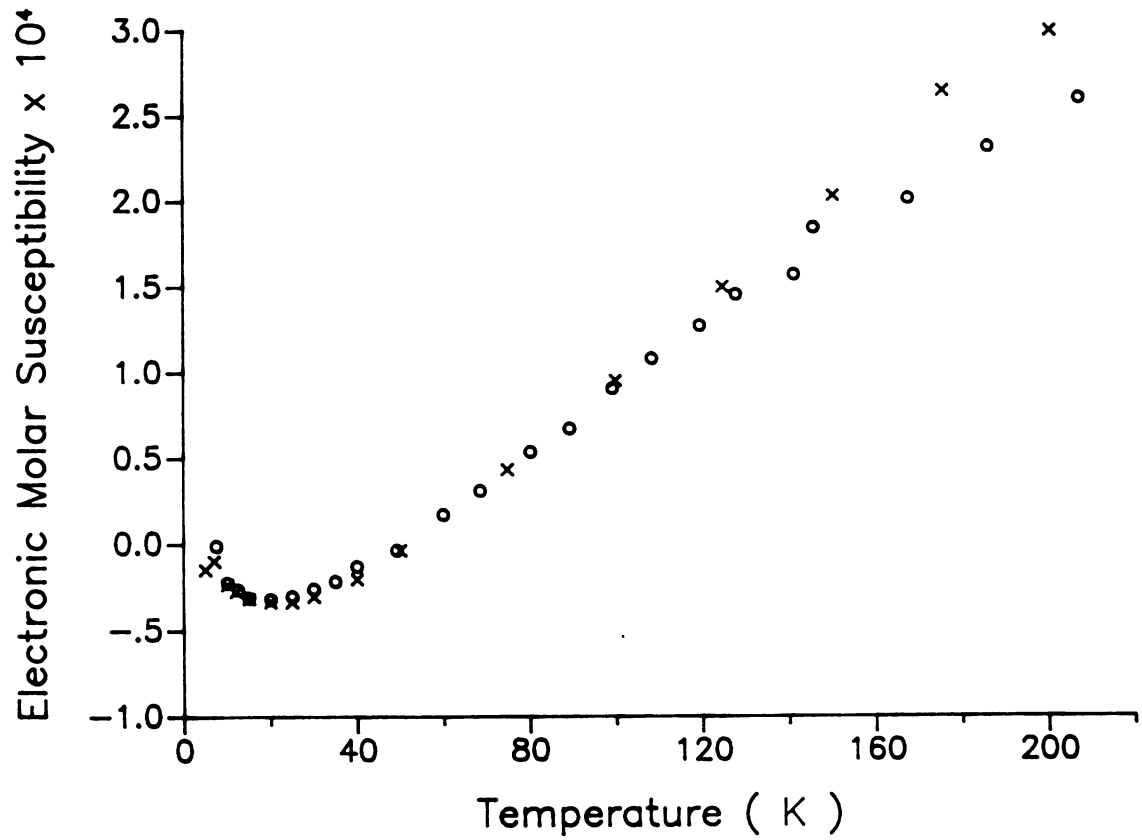


Figure 2-1. Molar electronic susceptibility of $\text{K}(\text{C}_{222})\cdot\text{e}^-$. Obtained from the overall susceptibility by subtracting the susceptibility of the decomposed sample and the low temperature Curie-law paramagnetism. Symbols are as follows: x from reference [15]. o from this work.

rather different (1% and .5% unpaired spins), the molar electronic susceptibilities in both measurements are remarkably close after the susceptibility of the decomposed sample (diamagnetic contribution) and the Curie paramagnetism were subtracted from the total susceptibility. The microwave conductivity measurement showed that this compound had a microwave conductivity similar to a powdered metal Zn (Table 2-2). Powder D.C. conductivity measurement of this electride have been unsuccessful for years. However, some successful experiments have been recently carried out which show that the electride $K^+(C222).e^-$ behaves as a semiconductor with a positive temperature coefficient of conductivity [12]. However, the activation energy is less than one tenth of an eV. All of these properties are so different from that of the electride $Cs^+(18C6)_2.e^-$ whose structure has been previously determined [6] that one should expect the electron trapping sites in these two electrides to be very different. The electride $K^+(C222).e^-$ behaves as an electride with electron pairs trapped in very shallow sites.

The parameters of recrystallization are shown in Table 2-1. Because of its tendency towards decomposition at rather low temperature ($-40^\circ C$), recrystallization had to be done at temperatures lower than $-50^\circ C$. The single crystals were black in color and flat with the dimensions of a few mm in two directions (the a and c axes). The crystal data are

Table 2-2. Microwave Absorption Measurements

Microwave Frequency : X-band, 9.0 GHz
 Temperature : -85 °C
 Tubing : 3mm OD quartz

Sample	Transmission Signal (arbitrary scale, mV on detector)
Empty tube	80
Cu (powder)	3.5
Zn (powder)	7
$\text{Na}^+(\text{C222})\cdot\text{Na}^-$	78
$\text{Cs}^+(\text{18C6})_2\cdot\text{e}^-$	78
$\text{K}^+(\text{15C5})_2\cdot\text{e}^-$	74
$\text{Rb}^+(\text{C222})\cdot\text{e}^-$	42
$\text{K}^+(\text{C222})\cdot\text{e}^-$	10

summarized in Table 2-3. The structure confirmed that the electrider consists of complexed cations and "empty" spaces containing only noise level electron density. The structure of the cryptated cation $K^+(C222)$, which has K^+-O distances ranging from 2.795 to 2.858 Å and K^+-N distances of 2.958 and 2.981 Å, is similar to that in the salt $K^+(C222).I^-$ [23]. In order to study the correlation of the electrider structure with its properties we need to investigate the shape and the distribution of the "empty" spaces where the trapped electrons probably "reside". This was done by using an Evans and Sutherland PS-300 display system in which the a-axis of the crystal is taken to be the x-axis of the display in a right-handed x-y-z orthogonal system, and the b-axis of the crystal is located in the x-y plane. Therefore, the b-axis of a monoclinic crystal is taken as the y-axis. The van der Waal's surfaces of atoms and ions are used to display the packing, and channels in structures are bounded by the van der Waal's surfaces of the complexed cations and anions. Roughly speaking, the "empty" spaces form a two-dimensional network of channels along the z and x axes in this electrider. There are no continuous channels along the y-axis.

On the x-y plane the cryptated cations form hexagonal patterns with the cryptands interlocking into each other to form very efficient packing (Figure 2-2). The vertical displacement of alternate cations of a hexagonal-type ring

Table 2-3. Crystal Data of $\text{K}^+(\text{C222})\cdot\text{e}^{-**}$

Crystal dimensions	:	0.2 x 0.6 x 0.8 mm
Temperature	:	202 K
Space group	:	monoclinic, C2/c
Cell paramaters	:	a=12.129(8), b=20.692(13), c=21.519(16) Å, beta=95.23(6)°, V=5378(6) Å ³ , Z=8
Peak width at half-height	:	0.30 degree
Scan type	:	theta - 2theta
Scan rate	:	4 degrees/min. (in 2theta)
Maximum 2 theta	:	45 degrees
No. of refl.measured	:	6692
No. of unique refl.	:	6394
No. of refl. used in refinement	:	3614 with $F_o^2 > 3.0 \text{ sigma}(F_o^2)$
Corrections	:	Lorentz-polarization Linear decay (1.001 to 1.061 on I) Reflection averaging ($R_{\text{int}}=1.7\%$) Empirical absorption (0.92 to 1.00 on I)
Solution	:	Direct methods

Table 2-3. (cont'd)

Hydrogen atoms : Located and refined isotropically

R : 0.041

R_w : 0.040

High peak in final
diff. map : 0.10 (1) e/Å³

Low peak in final
diff. map : -0.11(1) e/Å³

Esd of obs. of
unit weight : 0.96

Convergence,
largest shift : 0.03 sigma

** For the explanation of the entries in the table, see
Appendix 2.

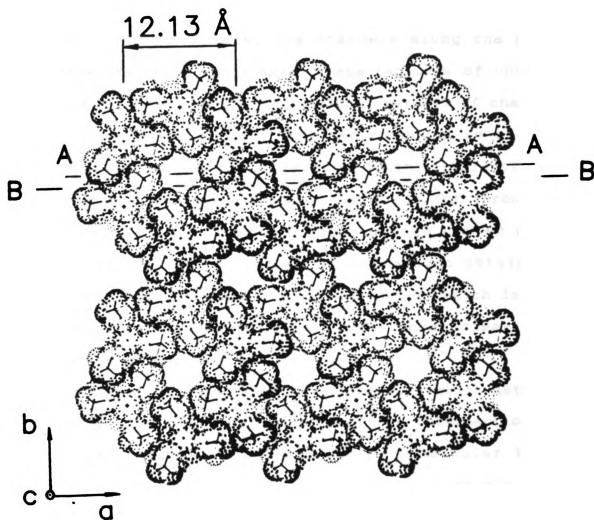


Figure 2-2. Complexed cation hexagonal packing patterns on an a - b plane in $K^+(C_{222}).e^-$ obtained by the Evans and Sutherland PS-300 display system.

is 1.7 Å (along the z-axis). At the center of each hexagonal ring there is a hexagonal-type channel going along the z-axis with a diameter of about 4 Å.

The channels along the z-axis zigzag towards the x (mainly) and the y axes. The channels along the x-axis zigzag towards the y and z axes. These two sets of channels intersect to form the two-dimensional network of channels. It is the intersections that make the compound so special. Figure 2-3 shows the cross section of the intersection of the channels in the x-z plane (101) which is cut through the plane A-A on the Figure 2-2 (through the center of the channel). Figure 2-4 is another cross section obtained by cutting through the plane B-B in Figure 2-2, which is about 1.5 Å from the plane A-A. This figure shows clearly the intersection of two sets of channels.

To investigate the shape of the intersections in detail we took two series of cross sections of one intersection. One set consists of the cross sections perpendicular to its "long axis" (The "long axis" is perpendicular to the y-axis and at an angle of 40 degrees with the x-axis in the x-z plane.)(Figure 2-5). Another set consists of the cross sections parallel to the "long axis" and perpendicular to the x-z plane (Figure 2-6). These figures show that each intersection has a dumbbell shape with a long dimension of about 12 Å and 6x4 Å cross sections at both ends and 4x4 Å cross sections at the middle. The 6x4x4 Å site at each end of the dumbbell cavity is surprisingly close in volume to

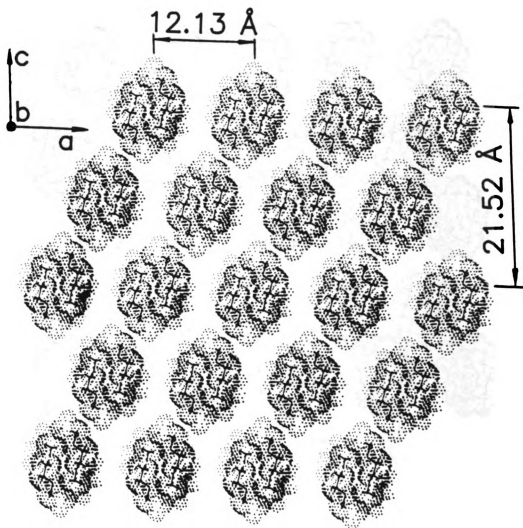


Figure 2-3. Cross section of the A-A plane in Figure 2-2 showing the channels along the z- and x-axis in $\text{K}^+(\text{C222})\cdot\text{e}^-$. The channels along the x-axis appear rather small in this view.

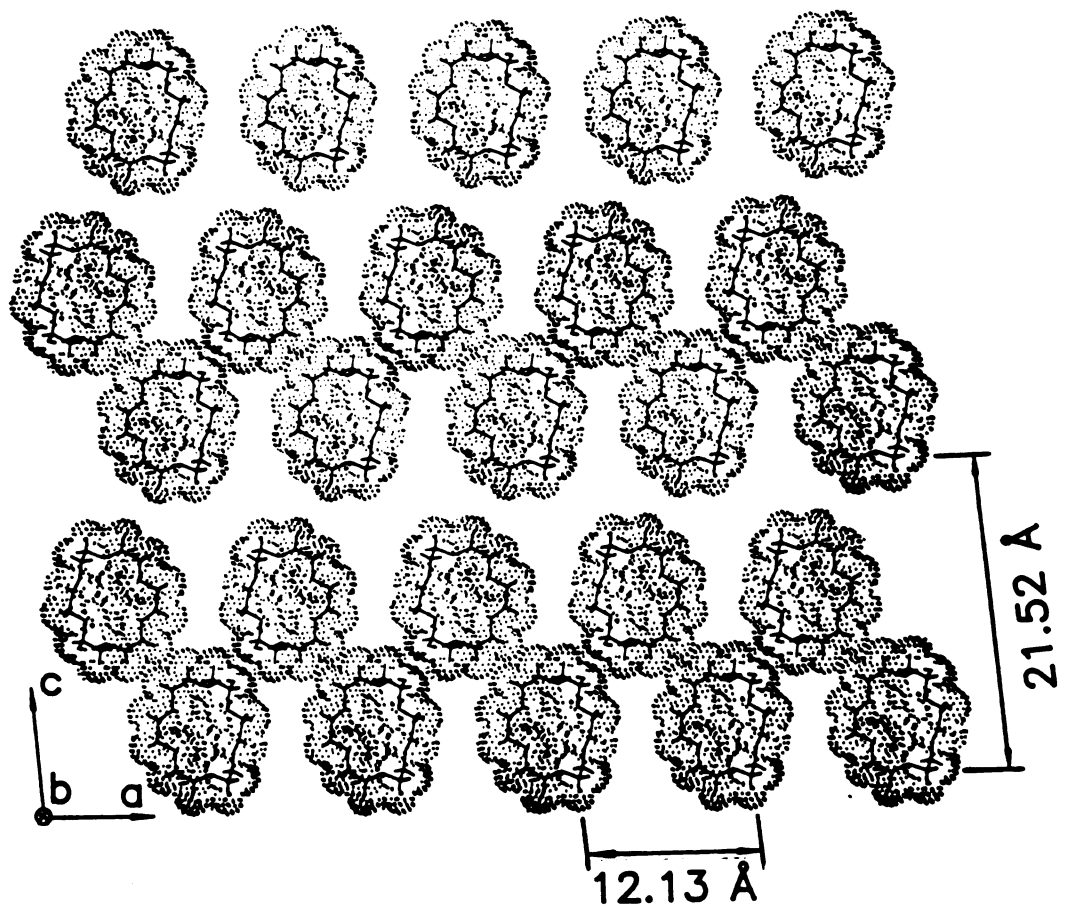


Figure 2-4. A cross section of the B-B plane in Figure 2-2 showing the channels along the z- and x-axis. The intersection is clearly shown and the channels along the x-axis are large in this view. The alternate x-channels appear closed in this view but would appear open if the view displaced by about 3 Å along the y-axis.

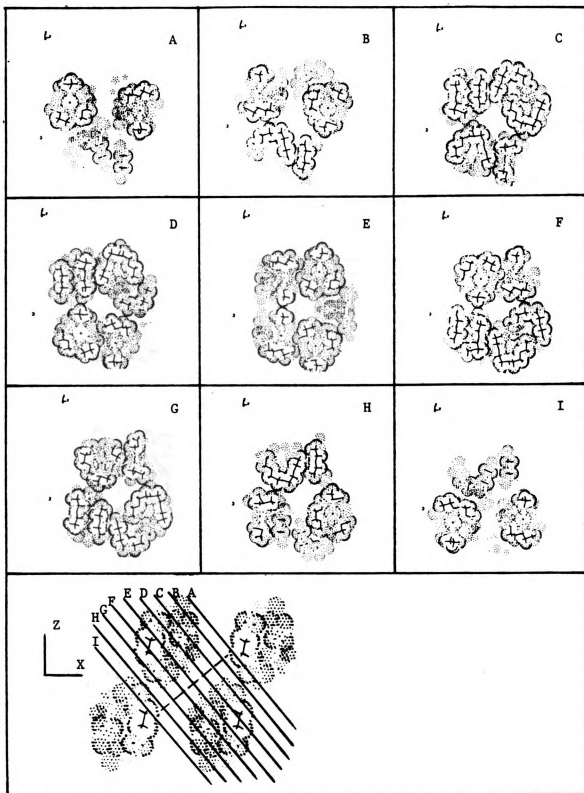


Figure 2-5. Cross sections of an intersection of channels in $K^+(C222).e^-$. These cross sections are perpendicular to the "long axis" of the intersection.

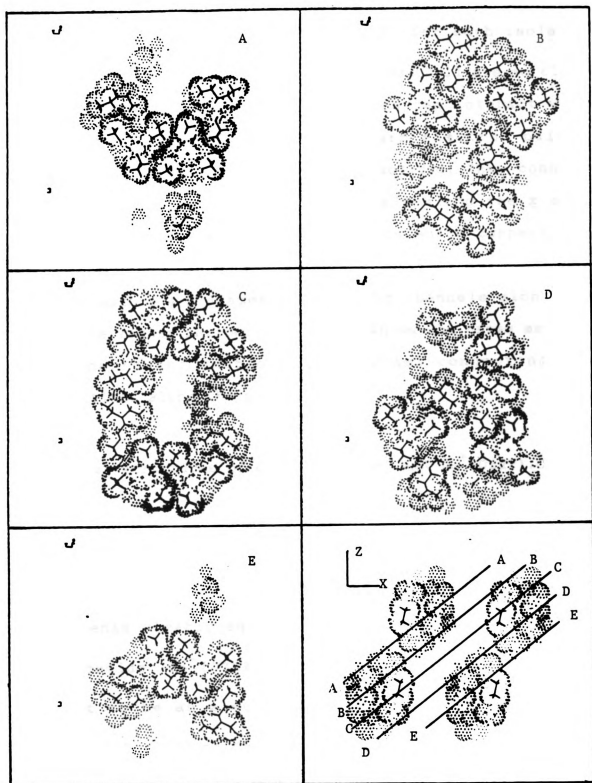


Figure 2-6. Cross sections of an intersection of channels in $K^+(C222).e^-$. These cross sections are parallel to the "long axis" of the intersection and perpendicular to the $x-z$ plane.

the trapping sites in $\text{Cs}^+(18\text{C6})_2 \cdot \text{e}^-$ [7] for each isolated trapped electron. The two sites in a dumbbell are so close to each other that the trapped electrons can interact with each other strongly enough to form electron pairs. Furthermore, these dumbbells are not isolated. They connect with each other through the channels along the z-axis (mainly) and the x-axis. The channels which connect the dumbbells along the z-axis are rather uniform and hexagonal in shape with a 4 Å diameter. But, the channels along the x-axis are rather narrow. Figure 2-7 shows the cross section at the narrowest section of a channel connecting two intersections along the x-axis.

3. Crystal structures of $\text{Cs}^+(18\text{C6})_2 \cdot \text{Cs}^-$ and $\text{Cs}^+(\text{C222}) \cdot \text{Cs}^-$.

$\text{Cs}^+(18\text{C6})_2 \cdot \text{Cs}^-$ was the first ceside compound synthesized and characterized [17,18]. Optical and solid state NMR experiments clearly showed the existence of Cs^- . But the second ceside, $\text{Cs}^+(\text{C222}) \cdot \text{Cs}^-$, was not identified and was thought to be an electride $\text{Cs}^+(\text{C222}) \cdot \text{e}^-$ or mixture of electrides because no Cs^- NMR signal was found in the Cs-C222 system [14]. Therefore it came as a surprise that the x-ray crystal structure data showed that the compound was a ceside $\text{Cs}^+(\text{C222}) \cdot \text{Cs}^-$.

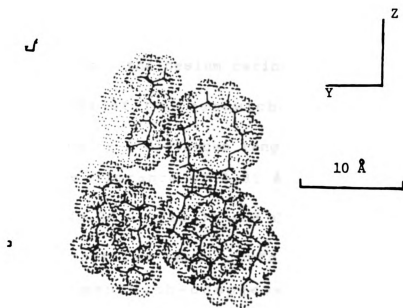


Figure 2-7. Cross section of the narrowest section of a channel along the x-axis connecting two intersections in $\text{K}^+(\text{C222})\cdot\text{e}^-$.

The recrystallization conditions for the preparation of these crystals are shown in Table 2-1.

Summaries of the crystal data are presented in Tables 2-4 and 2-5 for $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$ and $\text{Cs}^+(\text{C222}).\text{Cs}^-$, respectively.

In $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$, the cesium cation is coordinated to the 12 oxygen atoms of two sandwich-forming crown ether molecules with $\text{Cs}^+ - \text{O}$ distances ranging from 3.113 to 3.516 Å. The average distance of 3.31 Å is close to those in $\text{Cs}^+(\text{18C6})_2.\text{Na}^-$ (3.36 Å) [19,7] and $\text{Cs}^+(\text{18C6})_2.\text{e}^-$ (3.35 Å) [6]. Thus, except for small conformational effects, the nature of the sandwich-complexed cesium cation is independent of the anion. The inclusive cesium cation in $\text{Cs}^+(\text{C222}).\text{Cs}^-$ has six $\text{Cs}^+ - \text{O}$ distances ranging from 2.89 to 2.99 Å, with two nitrogen atoms at 3.07 Å. Its structure is very similar to that in $\text{Cs}^+(\text{C222}).\text{SCN}^-. \text{H}_2\text{O}$ [20]. In both ceside structures, the cesium anions are in pockets lined with H atoms from the crown ethers or cryptands. The closest $\text{Cs}^- - \text{H}$ distances are 4.29 Å [$\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$] and 4.37 Å [$\text{Cs}^+(\text{C222}).\text{Cs}^-$]. A hydrogen van der Waals radius of 1.2 Å yields a minimum radius of 3.1 Å. We expect Cs^- to be rather polarizable so that H atoms might penetrate somewhat into the outer electron density. The average distances of Cs^- to the 15 closest atoms (all are H atoms) are 4.66 Å

Table 2-4. Crystal Data of $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$

Crystal dimensions	:	0.3 x 0.4 x 0.7 mm
Temperature	:	204 K
Space group	:	orthorhombic, Pbca
Cell parameters	:	a=16.212(8), b=16.374(6), c=31.315(14) Å, V=8312(6) Å ³ , Z=8
Peak width at half-height	:	0.34 degree
Scan type	:	omega
Scan rate	:	4 degrees/min (in omega)
Maximum 2 theta	:	45 degrees
No. of refl.measured	:	6585
No. of unique refl.	:	5413
No. of refl. used in refinement	:	2221 with $F_o^2 > 3.0 \text{ sigma}(F_o^2)$
Corrections	:	Lorentz-polarization Linear decay (1.022 to 1.146 on F)
Solution	:	Patterson method
Hydrogen atoms	:	ride on carbon atoms

Table 2-4. (cont'd.)

R	:	0.041
R_w	:	0.041
High peak in final diff. map	:	$0.48(7) \text{ e}/\text{\AA}^3$
Low peak in final diff. map	:	$-0.37(7) \text{ e}/\text{\AA}^3$
Esd of obs. of unit weight	:	1.27
Convergence, largest shift	:	0.08 sigma

Table 2-5. Crystal Data of $\text{Cs}^+(\text{C222})\cdot\text{Cs}^-$

Crystal dimensions	:	0.2 x 0.2 x 0.2 mm
Temperature	:	206 K
Space group	:	monoclinic, $P2_1/n$
Cell paramaters	:	$a=13.371(2)$, $b=11.252(2)$, $c=21.529(3)$ Å, $\beta=94.80(1)^\circ$, $V=3227.7(9)$ Å ³ , $Z=4$
Peak width at half-height	:	0.27 degree
Scan type	:	Wyckoff w
Scan rate	:	8 degrees/min. (in omega)
Maximum 2 theta	:	45 degrees
No. of refl.measured	:	4702
No. of unique refl.	:	4211
No. of refl. used in refinement	:	1418 with $F_o^2 > 2.0 \text{ sigma}(F_o^2)$
Corrections	:	Lorentz-polarization Linear decay (1.011 to 1.076 on I) Reflection averaging ($R_{\text{int}}=0.036$)
Solution	:	direct method

Table 2-5. (cont'd)

Hydrogen atoms	:	ride on carbon atoms
R	:	0.071
R_w	:	0.057
High peak in final diff. map	:	$0.88(17) \text{ e}/\text{\AA}^3$
Low peak in final diff. map	:	$-0.93(17) \text{ e}/\text{\AA}^3$
Esd of obs. of unit weight	:	1.29
Convergence, largest shift	:	0.05 sigma

$[\text{Cs}^+(\text{18C6})_2.\text{Cs}^-]$ and $4.70 \text{ \AA}$ $[\text{Cs}^+(\text{C222}).\text{Cs}^-]$. These yield an effective radius of $3.5 \text{ \AA}$ for Cs^- , the biggest monatomic ion in nature!

The large size of Cs^- in both crystals makes the packing rather complicated. In $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$, both the cations and the anions form zig-zag chains along the b-axis with uniform interionic distances of $8.78 \text{ \AA}$ and $8.86 \text{ \AA}$ respectively and each Cs^- is also $8.12 \text{ \AA}$ from another Cs^- in an adjacent chain. Figure 2-8 shows the ionic chain packing in $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$. The "coordination shell" of each Cs^- is completed by seven complexed cations at distances of 8.09 , 8.30 , 8.31 , 8.45 , 9.28 , 9.52 and $9.65 \text{ \AA}$. In $\text{Cs}^+(\text{C222}).\text{Cs}^-$, the most striking feature of the ion-packing is the very short, uniform Cs^- - Cs^- distances of $6.38 \text{ \AA}$ in zig-zag chains parallel to the b-axis showing that the anions are in contact. This feature can be seen in Figure 2-9. The resulting distortion of the outer $6s$ wavefunction may broaden the Cs^- NMR signal beyond detection limits. This may be the reason for the absence of a Cs^- signal in the solid state NMR spectrum of the compound. In addition to the two adjacent anions in the chain, each Cs^- has nine neighboring cryptated Cs^+ ions at 7.13 , 8.10 , 8.60 , 8.83 , 8.89 , 8.97 ,

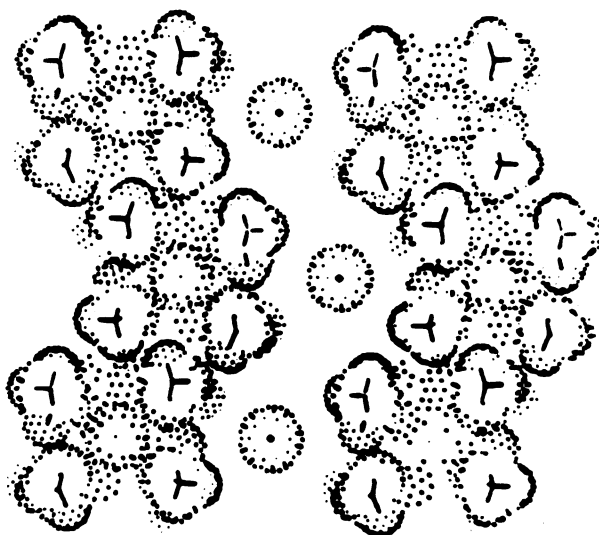


Figure 2-8. A thin section on the b-c plane of the $\text{Cs(18C6)}_2.\text{Cs}^-$ structure showing the ionic chain packing.

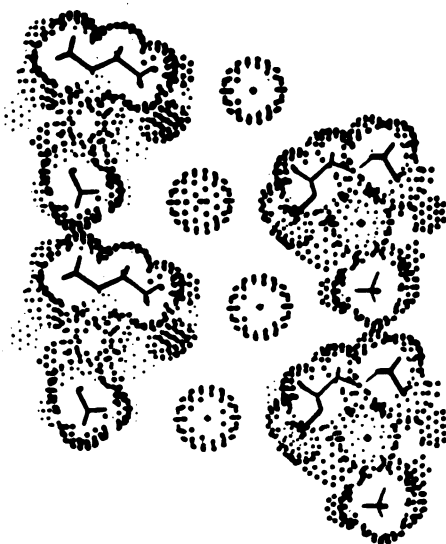


Figure 2-9. A thin section on the b-c plane of the $\text{Cs}^+(\text{C222}).\text{Cs}^-$ structure showing the ionic chain packing.

8.97, 9.11 and 9.11 Å. The nearest Cs^- in an adjacent chain is at 10.03 Å.

4. Crystal structure of $\text{Rb}^+(\text{C222})\cdot\text{Rb}^-$.

The Rb-C222 system has been studied for some time[15]. It was believed that there were two compounds : $\text{Rb}^+(\text{C222})\cdot\text{e}^-$ and $\text{Rb}^+(\text{C222})\cdot\text{Rb}^-$. The existence of two compounds was implied by the EXAFS study [8,15], but there has not been reliable chemical analysis data to verify this. Solid state NMR experiments have failed to give any Rb^- signal in the system. A preliminary experiment showed that the sample of " $\text{Rb}^+(\text{C222})\cdot\text{e}^-$ " had a rather high powder conductivity but no quantitative DC conductivity data were obtained [15].

The original goal of this work was to determine the crystal structure of the proposed electride : $\text{Rb}^+(\text{C222})\cdot\text{e}^-$. Therefore the crystalline material from a Rb-C222 (1:1 ratio) synthesis was used along with some excess complexant C222 in the recrystallization to ensure the formation of the electride. The recrystallization methods are given in the Table 2-1. Only a few well-formed black single crystals were obtained.

The crystal data are summarized in the Table 2-6. One should notice that the a and c values of the cell parameters are identical within the standard deviations. Every effort

Table 2-6. Crystal Data of $\text{Rb}^+(\text{C222})\cdot\text{Rb}^-$

Crystal dimensions	:	0.25 x 0.30 x 0.40 mm
Temperature	:	218 K
Space group	:	triclinic, $\bar{P}1$
Cell paramaters	:	a=12.418(4), b=12.419(3), c=11.582(3) Å, alpha=106.36(2), beta=94.80(3), gamma=62.38(2)°, v=1506.8(7) Å ³ , Z=2
Peak width at half-height	:	0.50 degree
Scan type	:	theta- 2theta
Scan rate	:	4 degrees/min. (in 2theta)
Maximum 2 theta	:	45 degrees
No. of refl.measured	:	5210
No. of unique refl.	:	3970
No. of refl. used in refinement	:	1671 with $F_o^2 > 3.0 \text{ sigma}(F_o^2)$
Corrections	:	Lorentz-polarization Linear decay (1.000 to 1.461 on I) Reflection averaging ($R_{\text{int}}=0.066$) Empirical absorption (0.59 to 1.00 on I)
Solution	:	Patterson method

Table 2-6. (cont'd)

Hydrogen atoms : ride on carbon atoms

R : 0.061

R_w : 0.069

High peak in final
diff. map : 0.84(9) e/Å³

Esd of obs. of
unit weight : 2.86

Convergence,
largest shift : 0.13 sigma

has been made to describe the structure in a higher symmetry class unsuccessfully.

An unexpected result was that the crystal structure data showed that the compound was a rubidide rather than an electrider. In this compound, the distance between Rb^- and the closest H atom is 4.2 Å and the average distance of a Rb^- to the closest 14 atoms (all H atoms) is 4.4 Å. These give a minimum radius of 3.0 Å and an effective radius of 3.2 Å for the Rb^- anion. A striking feature of the structure is that the rubidium anions form pairs in the crystal. The distance between two paired rubidium anions is only 5.1 Å which is 1.3 Å shorter than the diameter of Rb^- (6.4 Å). The distance of an Rb^- ion in a pair to the nearest Rb^- in an adjacent pair is 7.9 Å. These results suggested a dimer-type structure. Figure 2-10 clearly shows the nature of the "dimer" in this rubidide.

Alkali dimers in the gas phase have been known for a long time [21,22]. They are stable because the two s-electrons are in the bonding orbital. The dissociation energies are in the range of 0.5 to 1.0 eV for Cs_2 to Li_2 . The observation of anionic dimers (with two negative charges) of alkali metals, however , has not been reported. No theoretical calculation data are available, but a zeroth order picture would predict no bonding. There are two electrons in the antibonding orbital in the dimer Rb_2^{2-} ; it

may not be stable and it is possible that it loses an electron from this antibonding orbital to become more stable. This may explain the rather high conductivity of the compound. The diamagnetic nature of the compound would require rather strong interactions between the electrons, however.

Although the overall structure of $\text{Rb}^+(\text{C222}).\text{Rb}^-$ is quite different from that of $\text{K}^+(\text{C222}).\text{e}^-$ (monoclinic, C2/c), the packings in both structures are similar. In $\text{Rb}^+(\text{C222}).\text{Rb}^-$, complexed cations form the same type of hexagonal patterns in the a-b plane as in $\text{K}^+(\text{C222}).\text{e}^-$. The cavities for the Rb_2^{2-} dimers are also similar to those for the electron pairs in $\text{K}^+(\text{C222}).\text{e}^-$ (Figure 2-10 and Figure 2-3). Figure 2-11 shows the hexagonal packing patterns in $\text{Rb}^+(\text{C222}).\text{Rb}^-$. Most of the properties of $\text{Rb}^+(\text{C222}).\text{Rb}^-$ are still unknown, mainly because there may be an electride $\text{Rb}^+(\text{C222}).\text{e}^-$ mixed with the rubidide, thus making the measurements more difficult to interpret. Low temperature powder x-ray crystallography should help us to understand this system.

5. Crystal structure of $\text{K}^+(\text{C222}).\text{Na}^-$.

As was mentioned before, the structure of $\text{K}^+(\text{C222}).\text{e}^-$ featured an electron pairing which was quite different from

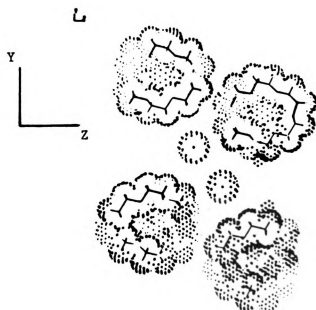


Figure 2-10. A thin section on the b - c plane of the $\text{Rb}^+(\text{C}_{222})\cdot\text{Rb}^-$ structure showing the formation of the dimer Rb_2^{2-} .

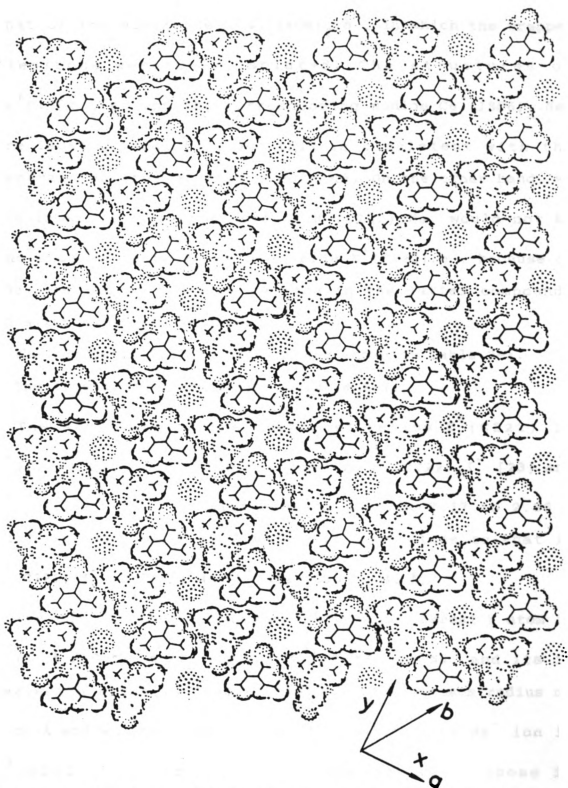


Figure 2-11. A thin section of the structure of $\text{Rb}^+(\text{C222}).\text{Rb}^-$ in the *a-b* plane showing the hexagonal-type packing patterns similar to those in $\text{K}^+(\text{C222}).\text{e}^-$.

that of the electride, $\text{Cs}^+(18\text{C6})_2.\text{e}^-$, in which the trapped electrons were well isolated. The structures of $\text{Cs}^+(18\text{C6})_2.\text{e}^-$ and the corresponding sodide $\text{Cs}^+(18\text{C6})_2.\text{Na}^-$ are isostructural [6] and this is consistent with the general features of this electride. On the other hand, we predicted that the structure of $\text{K}^+(\text{C222}).\text{Na}^-$ would not be the same as that of the electride $\text{K}^+(\text{C222}).\text{e}^-$, because of the presence of electron pairing in the latter compound. This turned out to be true.

The recrystallization methods are shown in Table 2-1.

The crystal data are shown in Table 2-7.

The structure of the cryptated cation $\text{K}^+(\text{C222})$ in $\text{K}^+(\text{C222}).\text{Na}^-$ is similar to those in $\text{K}^+(\text{C222}).\text{I}^-$ [23] and $\text{K}^+(\text{C222}).\text{e}^-$. The K^+-O distances range from 2.77 to 2.86 Å with an average 2.82 Å which is very close to that in $\text{K}^+(\text{C222}).\text{I}^-$ (2.79 Å) and $\text{K}^+(\text{C222}).\text{e}^-$ (2.83 Å).

The distance between an Na^- ion and its nearest H atom is 3.75 Å and the average distance between the Na^- and its 14 nearest H atoms is 3.93 Å. These give a minimum radius of 2.55 Å and an effective radius of 2.73 Å for the Na^- ion in $\text{K}^+(\text{C222}).\text{Na}^-$. These figures are close to those in $\text{Cs}^+(18\text{C6})_2.\text{Na}^-$ (2.47 and 2.65 Å)[7] and $\text{Rb}^+(15\text{C5})_2.\text{Na}^-$ (2.60 and 2.99 Å)[8].

Table 2-7. Crystal Data of $K^+(C222).Na^-$

Crystal dimensions	:	0.4 x 0.5 x 0.8 mm
Temperature	:	206 K
Space group	:	orthorhombic, Fdd2
Cell parameters	:	a=15.769(7), b=25.245(7), c=13.818(13) Å, V=5501(3) Å ³ , Z=8
Peak width at half-height	:	0.90 degree
Scan type	:	theta - 2theta
Scan rate	:	2 degrees/min. (in 2theta)
Maximum 2 theta	:	50 degrees
No. of refl.measured	:	2764
No. of unique refl.	:	1275
No. of refl. used in refinement	:	1198 with $F_o^2 > 3.0$ (F_o^2)
Corrections	:	Lorentz-polarization Linear decay (0.972 to 1.526 on I) Reflection averaging ($R_{int}=1.2\%$) Numerical absorption (0.889 to 0.928 on I) Extinction (coefficient = 1.28×10^{-7})
Solution	:	Patterson method

Table 2-7. (cont'd)

Hydrogen atoms	:	Located and refined isotropically
R	:	0.021
R _w	:	0.021
High peak in final diff. map	:	0.03(1) e/Å ³
Low peak in final diff. map	:	-0.02(1) e/Å ³
Esd of obs. of unit weight	:	0.38
Convergence, largest shift	:	0.10 sigma

The packing of the cations and anions is rather simple: all cations are in special positions and the cations and anions pack alternately along the c -axis. Each anion Na^- is coordinated by six cations at the distances of 5.736, 7.783, 7.783, 7.971, 7.971 and 8.082 Å, and vice versa for each cation. The shortest Na^- - Na^- and K^+ - K^+ distances are 8.204 Å.

6. Crystal structure of $\text{Cs}^+(\text{15C5})_2.\text{K}^-$.

Several potasside compounds have been synthesized and studied [24]. The structure of $\text{Cs}^+(\text{15C5})_2.\text{K}^-$ is the first crystal structure of a potasside.

Potassides are known to be difficult to handle and easy to decompose. It took several attempts to get good quality single crystals. The recrystallization conditions are shown in Table 2-1. The crystal data are given in Table 2-8. Its structure is very similar to that of $\text{Rb}^+(\text{15C5})_2.\text{Na}^-$ ($C2/m$, $a=11.555$, $b=13.587$, $c=9.958$ Å, $\beta=92.03$ degree, $V=1562.4$ Å³, $z=2$) [8,19].

Only one half of the crown ether (15C5) is crystallographically unique. Both cations and anions are in special positions. The crown atom C8 (see the molecular diagram) was found to be disordered and was refined as two half-occupancy atoms C8a and C8b.

Table 2-8. Crystal Data of $\text{Cs}^+(15\text{C5})_2.\text{K}^-$

Crystal dimensions	:	0.2 x 0.4 x 0.9 mm
Temperature	:	213 K
Space group	:	monoclinic, C2/m
Cell paramaters	:	a=11.537(4), b=13.679(3), c=10.624(3) Å, beta=90.12(2)°, V=1676.6(8) Å ³ , Z=2
Peak width at half-height	:	0.40 degree
Scan type	:	theta-2theta
Scan rate	:	2 degrees/min (in 2theta)
Maximum 2 theta	:	60 degrees
No. of refl.measured	:	4345
No. of unique refl.	:	1570
No. of refl. used in refinement	:	1453 with $F_o^2 > 3.0 \text{ sigma}(F_o^2)$
Corrections	:	Lorentz-polarization Linear decay (0.996 to 1.317 on I) Reflection averaging ($R_{\text{int}}=2.3\%$) Numerical absorption (0.404 to 0.812 on I)
Solution	:	direct methods

Table 2-8. (cont'd.)

Hydrogen atoms	:	located and refined isotropically
R	:	0.067
R_w	:	0.075
High peak in final diff. map	:	0.72(6) e/Å ³
Low peak in final diff. map	:	-0.57(6) e/Å ³
Esd of obs. of unit weight	:	1.459
Convergence, largest shift	:	0.13 sigma

The cations and anions each form planes parallel to the a-b plane respectively and the two types of planes alternate along the c-axis with intervals of 5.32 Å (1/2 of c). Each cation is coordinated by 8 anions at distances of 7.859, 7.859, 7.885, 7.885, 8.686, 8.686, 8.686 and 8.686 Å and vice versa for anions. The shortest $K^- - K^-$ and $Cs^+ - Cs^+$ distances are 8.985 Å. Therefore the anions are well isolated from each other. The ^{39}K solid state NMR spectrum of this compound showed a K^- peak at -105 ppm from $K^+(aq.)$ [24].

The distance between a K^- and its nearest H atom is 3.97 Å and the average of the 16 shortest $K^- - H$ distances is 4.34 Å. These values yield a minimum radius of 2.8 Å and an effective radius of 3.15 Å for K^- .

CHAPTER 3

PHOTOEMISSION OF ALKALIDES AND ELECTRIDES

3.1 Background.

In the last two decades photoelectron spectroscopy (PES) has been developed into a powerful technique for studying electronic structures in gases [28,29], liquids [30] and solids [31,32] and has been widely used in solid state physics [31,32] (especially semiconductor physics), surface science [32], chemical analysis [33,34] and other related fields.

Photoelectron emission (photoemission) was discovered in 1887 by Hertz [36] when he was studying the nature of sparking phenomena. The puzzling facts that photoemission happened only under certain color lights for certain materials and that the photoemission intensity depended on the intensity of light was resolved by Einstein in 1905 [37] in terms of the simple relationship:

$$E_{\text{kin.max}} = h\nu - \phi \quad (3.1)$$

i.e. the maximum kinetic energy E_{kin} of a photoelectron is equal to a quantized package of light energy $h\nu$ minus the "work function" ϕ which is related to the emitter. This equation remains to date the most fundamental relationship in photoemission and forms the basis of the single-(independent)electron approximation. Figure 3-1 shows the Einstein relation.

Photoemission is actually a complicated, many-body process. This problem can not be solved without making approximations. The single-electron approximation assumes that the incident photon interacts with a single electron and the total energy of the photon is absorbed by the electron. Then the Einstein equation can be rewritten in more complete form as:

$$E_{kin} = h\nu - \phi - E_i \quad (3.2)$$

where E_i is the energy of the electron, i.e. the ionization energy. We see the photoemission process as one in which a photon excites an electron from an occupied state (initial state) to an empty state (final state). The number of possible transitions is proportional to the number of available states in both energy levels. That is, the photoemission spectra reflect the product of the densities of the initial and final states.

$$n(E) = N_c(E) \times N_v(E-h\nu) \quad (3.3)$$

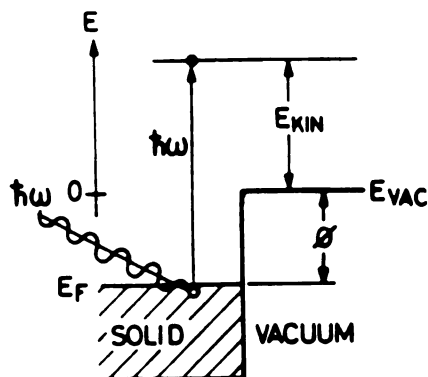


Figure 3-1. Photoexcitation of electrons from a solid by photons of energy $\hbar\omega$. ϕ is the workfunction, E_{vac} is the energy of the vacuum level, E_{kin} is the kinetic energy of emitted electrons, E_F is the Fermi energy.

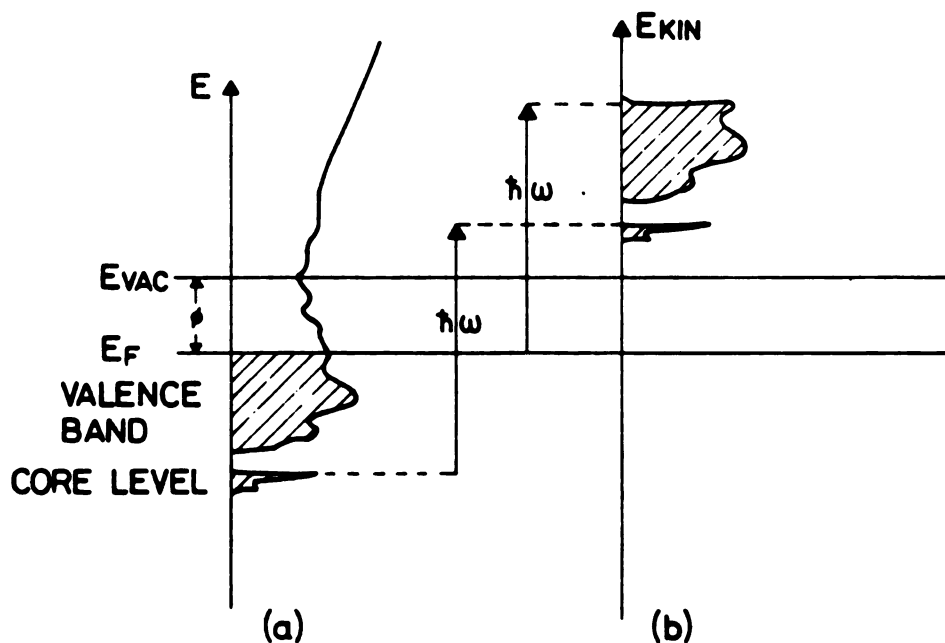


Figure 3-2. Illustration of the fact that the density of electronic states distribution of the emitter, part (a), is reflected in the photoemission spectral fine structure, part (b). [ref.32].

$n(E)$ is the number of electrons excited to the energy E , $N_c(E)$ and $N_v(E-h\nu)$ are the densities of states at the final state energy E and the initial state energy $E-h\nu$ respectively.

We assume further that the final state is a free electron state in the vacuum for which the density of states is rather flat. We may then take the density of final states as a constant.

Under these assumptions we rewrite the equation (3.3)

$$n(E) = N_v(E-h\nu) \quad (3.4)$$

i.e. the photoemission spectra map out the density profile of the initial states which is the information about energy states that we want to know. This is illustrated in Figure 3-2.

Beyond the approximation mentioned above we have to consider a number of points. First, the final state may be a state of the excited electron in the bulk which is not equivalent to a state in the vacuum continuum. The excited electron may suffer from scattering (electron-electron or electron-phonon scattering, elastic or inelastic) before it reaches the surface. Scattering causes broadening of the photoemission peaks or the appearance of energy-loss peaks on the low kinetic energy side of the true photoemission peaks. Second, the final states and initial states can show strong spatial variation (particularly in the surface region) which forms the basis for the study of the angular

distribution spectrum of photoemission. Third, the optical excitation can be a many-body process and the initial states may include the states of some other electrons. These effects are manifested in the so-called shake-up and shake-off processes [34,35].

With all these effects to complicate the process, photoemission would seem to be uninterpretable in terms of the known electronic energy levels in solids. This, however, is not true. Not all of the above possible contributions occur at the same time or with the same weight. In fact, the simple density of states model works remarkably well for most experimental spectra.

Photoemission is a process that involves both surface and volume effects, and therefore can provide information on surface as well as bulk electronic structures. The surface sensitivity of photoemission is determined by the fact that, although the usual light beam can penetrate far into solids (on the order of several tens of atomic layers, hundreds of Å), photoelectrons that are excited by light suffer from electron-electron and/or electron-phonon collisions in solids and thus the mean free path is very limited. Figure 3-3 shows the relationship of the mean free path to the kinetic energy of photoelectrons. In the region of a few eV to 1000 eV the mean free path is only a few tens of angstroms. Therefore, the surface condition is extremely important in photoemission. This is why the development and application of quantitative photoemission methods had been

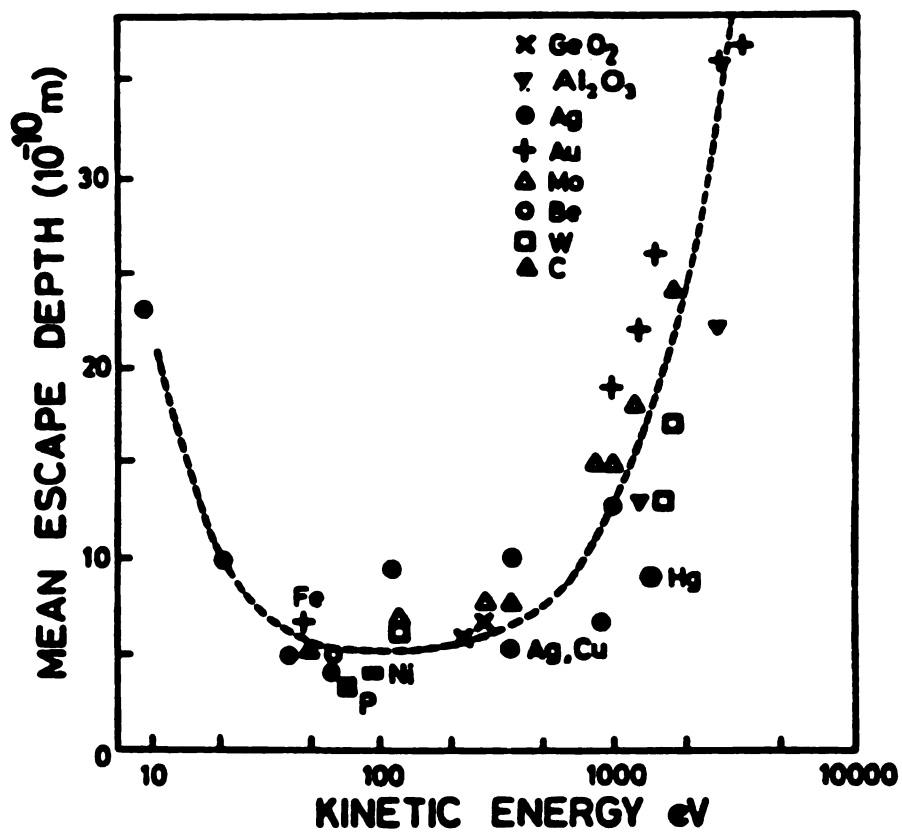


Figure 3-3. Energy dependence of the escape depth of excited electrons showing the mean free path as a function of kinetic energy. [Ref.34]

hampered by poor vacuum techniques until the 60's when ultra high vacuum (UHV) was available. It is known that under a vacuum of 10^{-5} to 10^{-6} torr, a monolayer of molecules of vapor gas will be deposited onto a clean surface in less than a second. But it will take hours if the vacuum is 10^{-10} torr. Only under UHV or the complete absence of reactive gases can accurate, reproducible PES data from solids be obtained.

The power of PES over other methods of studying the electronic structures in solids, such as optical absorption or reflection spectroscopy is the following: First, an optical spectrum integrates over all possible excitations for which energy conservation holds, while in PES the final states are known (the states in vacuum continuum with energy E_{kin}). Only the initial states which fit the Einstein equation are responsible for the spectrum. Second, PES resolves the final state energy of the excited electron directly and thus permits the determination of absolute energies, while an optical spectrum determines the difference of levels only.

There are two major measurements in PES: energy distribution curves (EDC), and quantum yield spectra.

EDC is most often used. It is obtained by measuring the intensities of photoelectrons with different kinetic energies while the energy of the photon is fixed. Figure 3-2 shows the principle behind EDC.

A quantum yield spectrum is made by measuring the total photoemission current under a potential which is high enough to collect all photoelectrons while the wavelength of the light is scanned. It is an integral measurement over all photoemission electrons. Usually a quantum yield spectrum is used to determine the work function of a solid by extrapolating the quantum yield curve to zero yield. Figure 3-4 shows a quantum yield spectrum of copper.

Some previous work had been done on the relative quantum yield spectra of some sodides in our laboratory [10]. The photoemission cell shown in Figure 3-5 was used. A small ion pump was used to maintain a vacuum of better than 10^{-4} Torr. The sodide films were made on a platinum electrode by dissolving sodide crystals in methylamine and then evaporating the solvent. The photoemission quantum yields from the films of four sodides were similar with one peak at 370 nm and another at about 600 nm. The yields were strongly temperature-dependent and the reason was not known. The two peaks were assigned to trapped electrons (600 nm) and sodide anions (370 nm).

The present studies continued the work on photoemission. A new apparatus was built and experiments on other alkalides and electrides as well as on sodides were carried out.

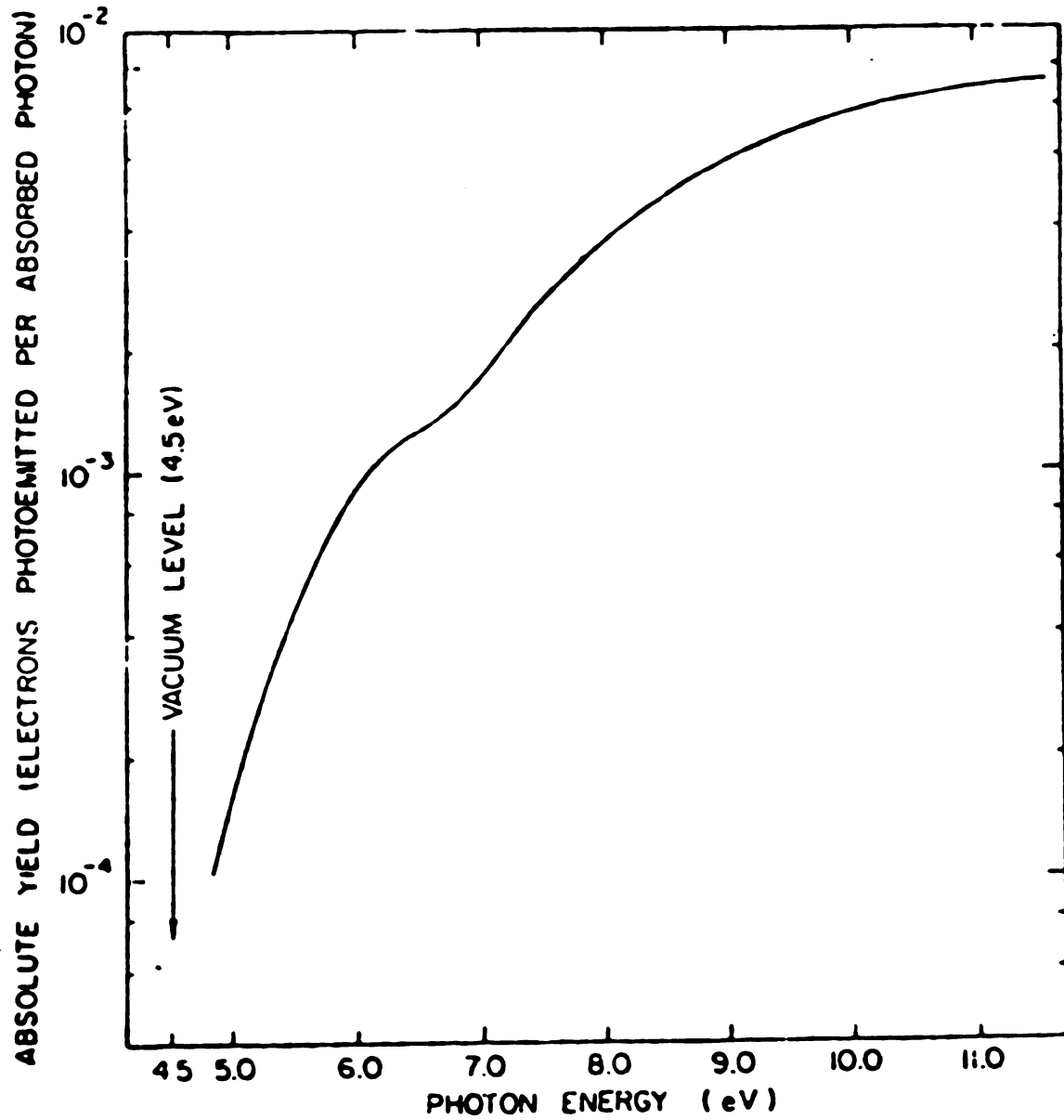


Figure 3-4. Quantum yield spectrum of a clean copper surface. [Ref.42]

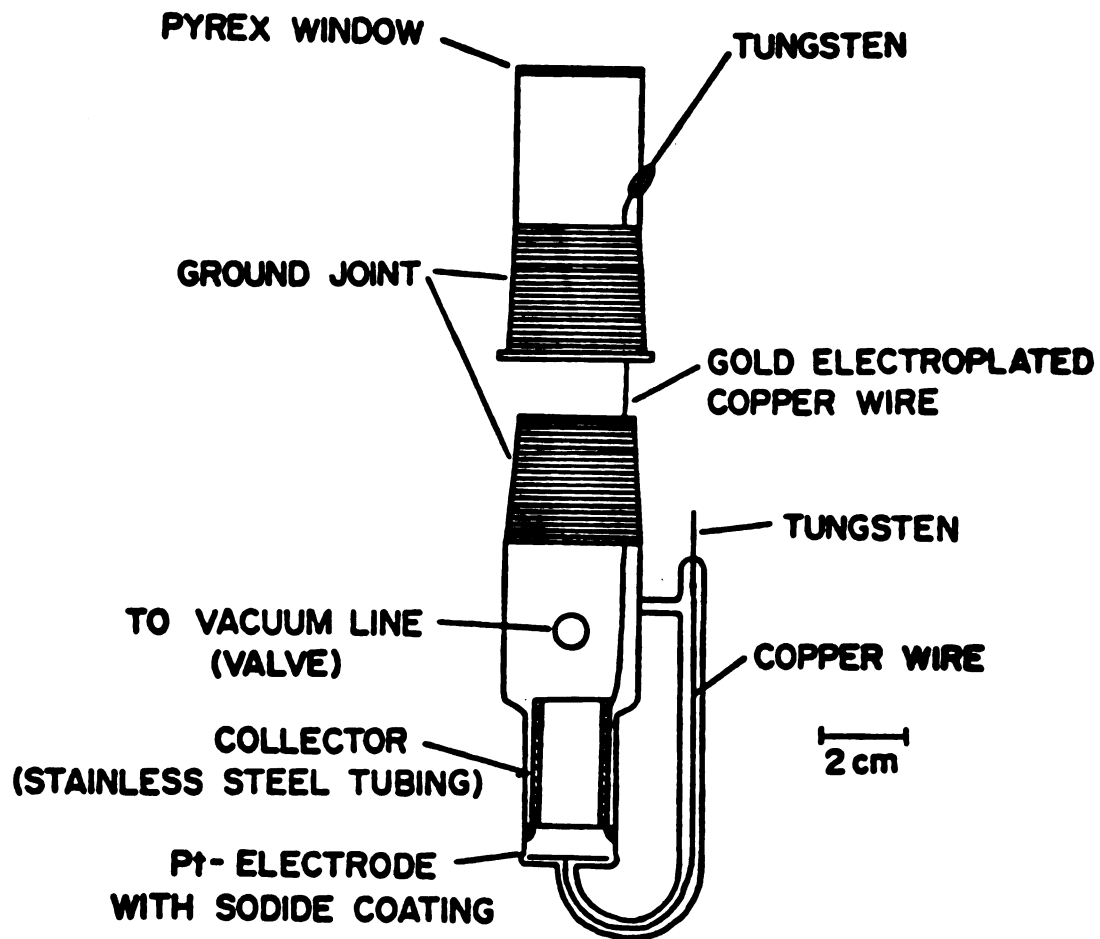


Figure 3-5. Photoemission cell for studying the photoemission of sodides. [Ref.10]

3.2 Experimental.

3.2.1 Experimental system.

The experimental set-up is shown diagrammatically in Figure 3-6. The system consists of the following parts:

A. Photoemission chamber.

The spherical retarding potential analyzer consists of an emitter, grid and collector (anode). The emitter is cooled with cold nitrogen gas. The whole cathode unit except the sample holder on its top is enclosed in a vacuum jacket to keep its outside surface warm while the sample holder is cold. This avoids solvent condensation on the probe during the film making process. The grid is made from stainless steel and has a diameter of 2 inches. The potential on the grid can be controlled for different purposes. Usually the grid is at the cathode potential during EDC measurements in order to form a field-free region for photoemission. In quantum yield experiments, however, the grid is connected to the collector in order to sweep all emitted electrons from the region of the cathode. The spherical collector is made of brass and has a 4" diameter. It is isolated from the ground by Teflon.

The vacuum chamber is made from stainless steel with a quartz window on its top to allow the light beam to come in. The chamber is also the housing for the preamplifier.

B. Optical system.

Photoemission Apparatus

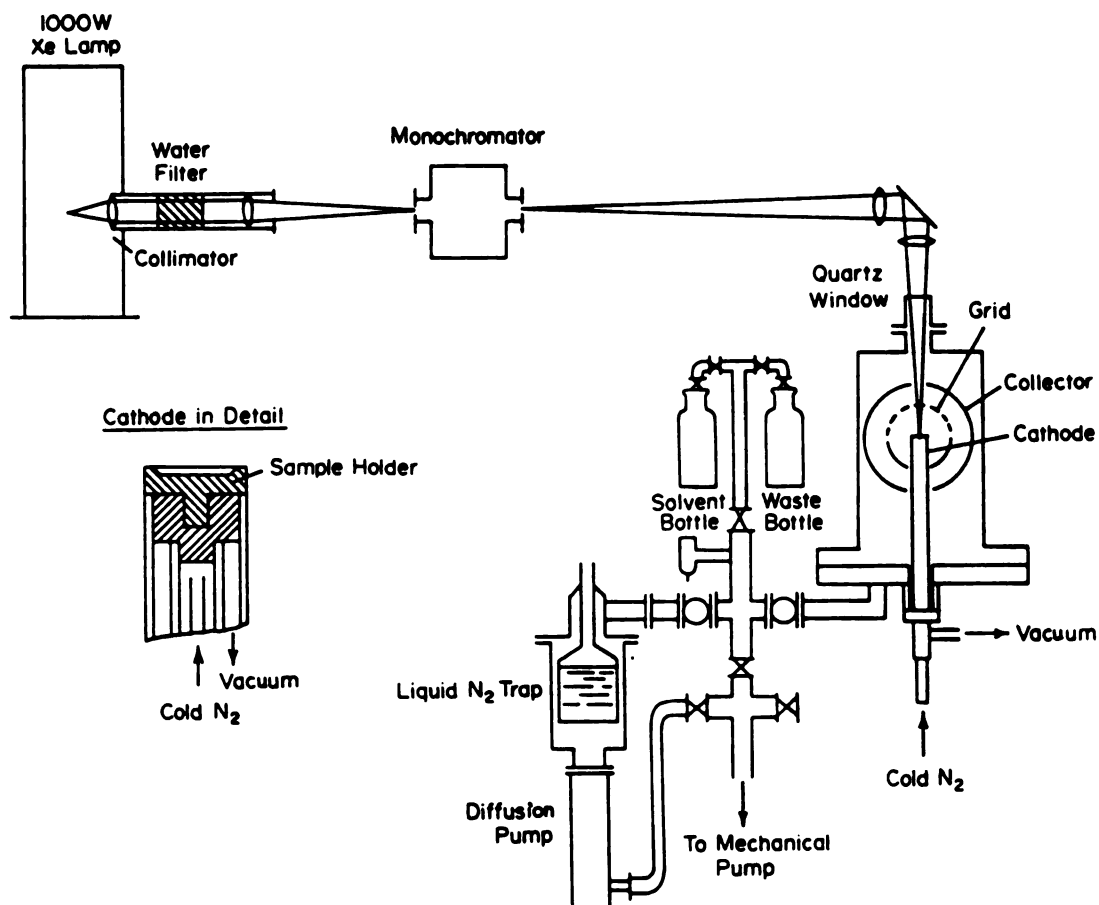


Figure 3-6. Photoemission experimental system used in this work.

A 1000 watt Xe-lamp serves as the light source. After passing through a water filter (not used when IR light is needed.) and an Oriel 77250 monochromator, the light beam is collimated and focussed on the sample holder.

C. Vacuum system.

The vacuum system consists of a liquid nitrogen trap, a diffusion pump and a mechanical pump. Usually the vacuum is between 5×10^{-6} and 1×10^{-5} torr.

D. Solvent system.

In order to make films on the holder, some solvent is used. Usually MeNH_2 or Me_2O is used. A solvent bottle and a waste bottle are connected to the vacuum chamber.

E. Electronic system.

The electronic system consists of a preamplifier, a main amplifier and an x-y recorder. The sensitivity of the electronic system is about one picoampere.

3.2.2 Experimental procedure.

A. Film making.

After the mechanical and then the diffusion pump are turned on, liquid nitrogen is poured into the trap. The vacuum should then be at about $1-2 \times 10^{-5}$ torr. The valve between the trap and the manifold is closed and house nitrogen is introduced into the chamber to bring the pressure to atmospheric. The emitter probe is lowered from the chamber onto a support. Nitrogen gas, cooled by liquid

nitrogen in a dewar, passes through the probe, and the temperature of the holder (-100 to -50°C) is controlled by regulating the flow . The crystalline sample is then put on the holder. When strong static electricity tends to make the crystals fly off the holder, one or two drops of cold pentane are added to the crystals to keep them in the cathode cup. The probe is inserted back into the chamber and the chamber is evacuated. During the whole experiment, cold nitrogen gas is used to keep the sample holder at the desired temperature. When the vacuum in the chamber reaches 1×10^{-5} torr or lower, the valve between the trap and the manifold is closed and solvent vapor is introduced into the chamber and condenses on the holder. The crystals dissolve and a blue solution can be seen through the quartz window. Then the solvent is evaporated by opening the valve to the waste bottle which is kept in liquid nitrogen. In this way, a fresh solvent-free film is deposited on the holder.

B. Quantum yield measurement.

A potential high enough to collect all photoelectrons (usually $5-10\text{ V}$) is applied to the collector and the grid. The photocurrent is converted into a voltage signal by the preamplifier and the main amplifier and is recorded by an x-y recorder where the time base mode is used for the wavelength scan. While the wavelength is being scanned, the photocurrent is recorded. The photon flux was measured by a UV detector (1 cm^2 area, model UV-444 BQ from EG & G, calibrated by EG & G.). The quantum yield was calculated

without making a reflection correction. Therefore the calculated quantum yields are lower than the actual values.

C. EDC measurement. The potential on the grid is set to the ground. The wavelength is fixed at a certain value. The retarding potential is scanned and is input into the x mode of the recorder. The photocurrent is recorded by the y mode.

3.3 Results and discussion.

Attempts to measure energy distribution curves were unsuccessful. Whenever the retarding potential was set to zero, the photocurrent was zero. The reason is obvious, however : a space charge built up on the film which prevented the electron from escaping from the surface. This problem is common when semiconductor films are used. It could also be seen that as soon as a fresh film was made the color changed from golden or red to gray in seconds. This might indicate that surface contamination is a serious problem that could be the major source of the space charge. Alternatively, the color change could result from the formation of a finely divided polycrystalline film as the last traces of solvent were removed. Because of these problems only photoemission quantum yields are reported in this work. The reproducibility obtained suggests that such measurements may not be as sensitive to surface contamination as are EDC studies.

The following sodides, potassides and electrides were tested first by the quantum yield experiment: $\text{Na}^+(\text{C222}).\text{Na}^-$,

$K^+(15C5)_2.Na^-$, $K^+(15C5)_2.K^-$, $K^+(15C5)_2.e^-$, $Cs^+(18C6)_2.Na^-$, $Cs^+(18C6)_2.e^-$. While $Na^+(C222).Na^-$, $Cs^+(18C6)_2.Na^-$ and $Cs^+(18C6)_2.e^-$ gave very low quantum yields. $K^+(15C5)_2.Na^-$, $K^+(15C5)_2.K^-$ and $K^+(15C5)_2.e^-$ showed high yields. Surprisingly, the spectra of these compounds with different anions Na^- , K^- and e^- were initially very similar. The quantum yield spectra showed a few peaks in the UV and visible region and the photoemission extended into the IR region up to about 1 micron but did not show any peaks in the region of 600 nm and longer wavelengths.

In addition to the previously observed peak at about 370 nm there were two other peaks in these compounds: 300 nm and 330 nm independent of the anions (Na^- , K^- or e^-). This was unexpected and caused us to abandon the method for a long time. We expected that different anions would give different peaks.

The origin of these uniform results was finally found. The key was Na contamination, apparently from Pyrex glass. All of the compounds used earlier in this work had been synthesized in Pyrex glass apparatus. It has been known for a long time that when Pyrex glassware comes in contact with a solution of alkali anions other than sodide, a rapid exchange process occurs:



The exchange process reaches an equilibrium with a small amount of Na^- in the solution. This Na contamination was too small to affect most optical, NMR or other measurements. However it affects the photoemission spectrum very seriously because photoemission is very sensitive to the surface. When a film is made the major compound (containing K^- or e^-) may have crystallized first and the Na^- last so that the concentration of Na^- in the surface layer may be much higher than the average value. Figure 3-7 shows the marked effect of Na contamination.

The photoemission quantum yield spectrum of $\text{K}^+(15\text{C5})_2\text{K}^-$ which was synthesized in a quartz cell is shown in Figure 3-8. It is clear that the peak at 370 nm is from K^- . There are two small shoulders at 300 and 330 nm which could be from a small amount of Na contamination. This is strongly suggested by the photoemission spectrum of $\text{Na}^+(\text{C222}).\text{Na}^-$ shown in Figure 3-9. The Na contamination may be from a trace of Na in the K metal or from the glassware used in the K metal distribution or distillation.

Figure 3-10 shows the spectrum of $\text{Rb}^+(15\text{C5})_2.\text{Rb}^-$ in which there is a new peak at 380 nm in addition to the peaks at the same location as those of K^- and Na^- (370, 330, 300 nm). The new peak is assigned to Rb^- . The major peaks of K^-

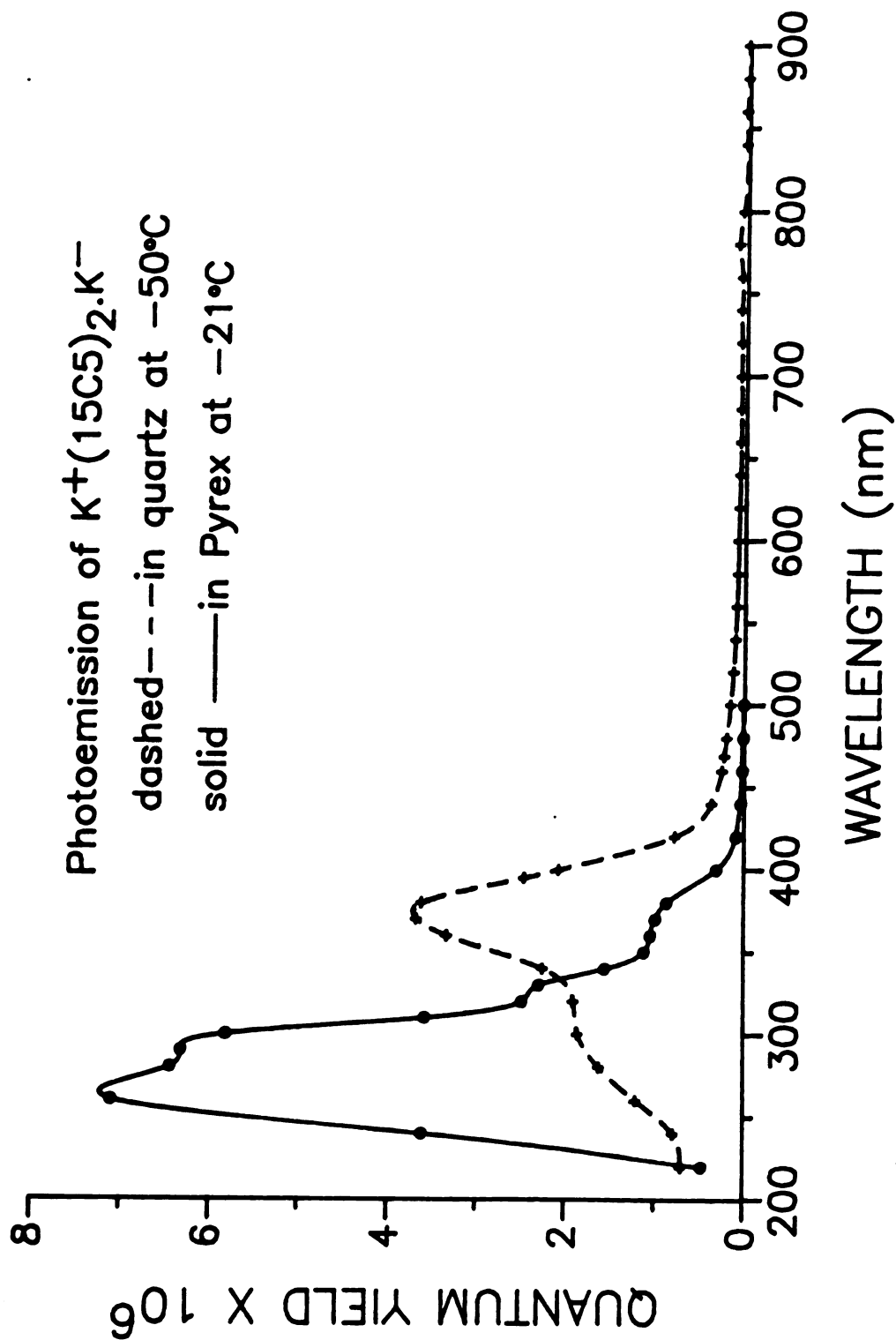


Figure 3-7. Quantum yield spectra of $K^+(15C5)_2.K^-$ showing the effect of Na contamination. Solid curve, synthesized in a Pyrex cell. Dashed curve, synthesized in a quartz cell.

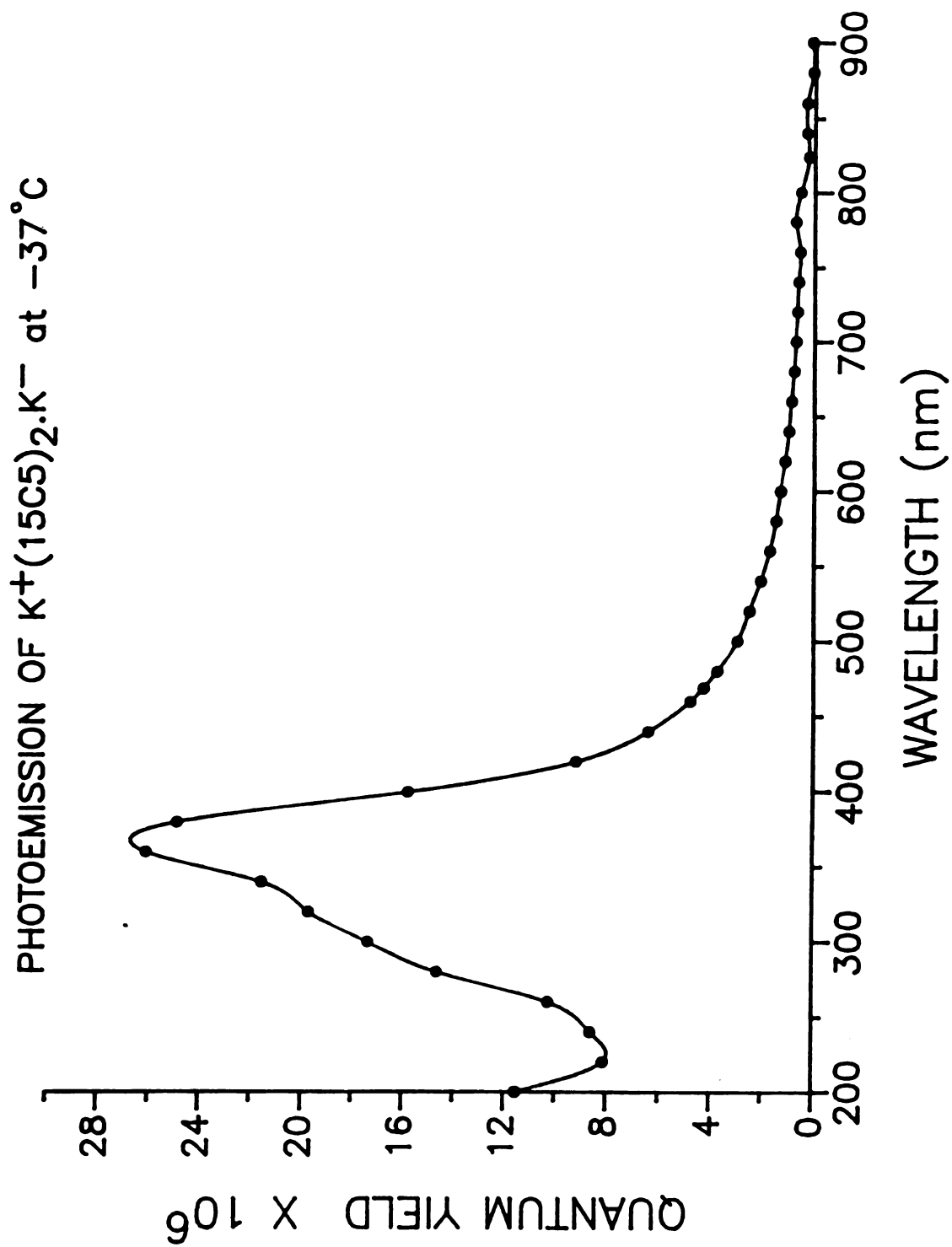


Figure 3-8. Quantum yield spectrum of $K^+(15C5)_2.K^-$ at $-37^\circ C$.

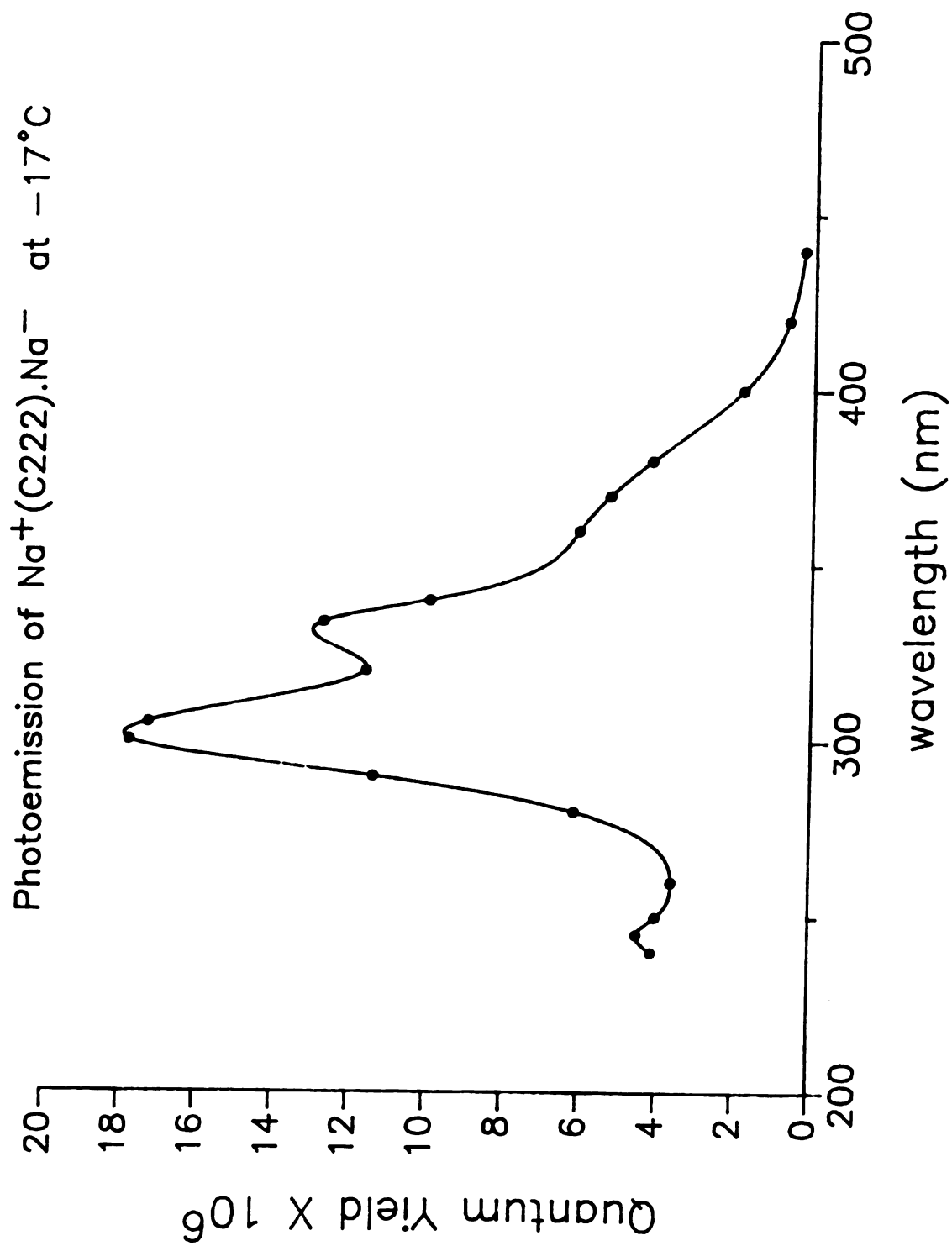


Figure 3-9. Quantum yield spectrum of $\text{Na}^+(\text{C222}).\text{Na}^-$ at -17°C .

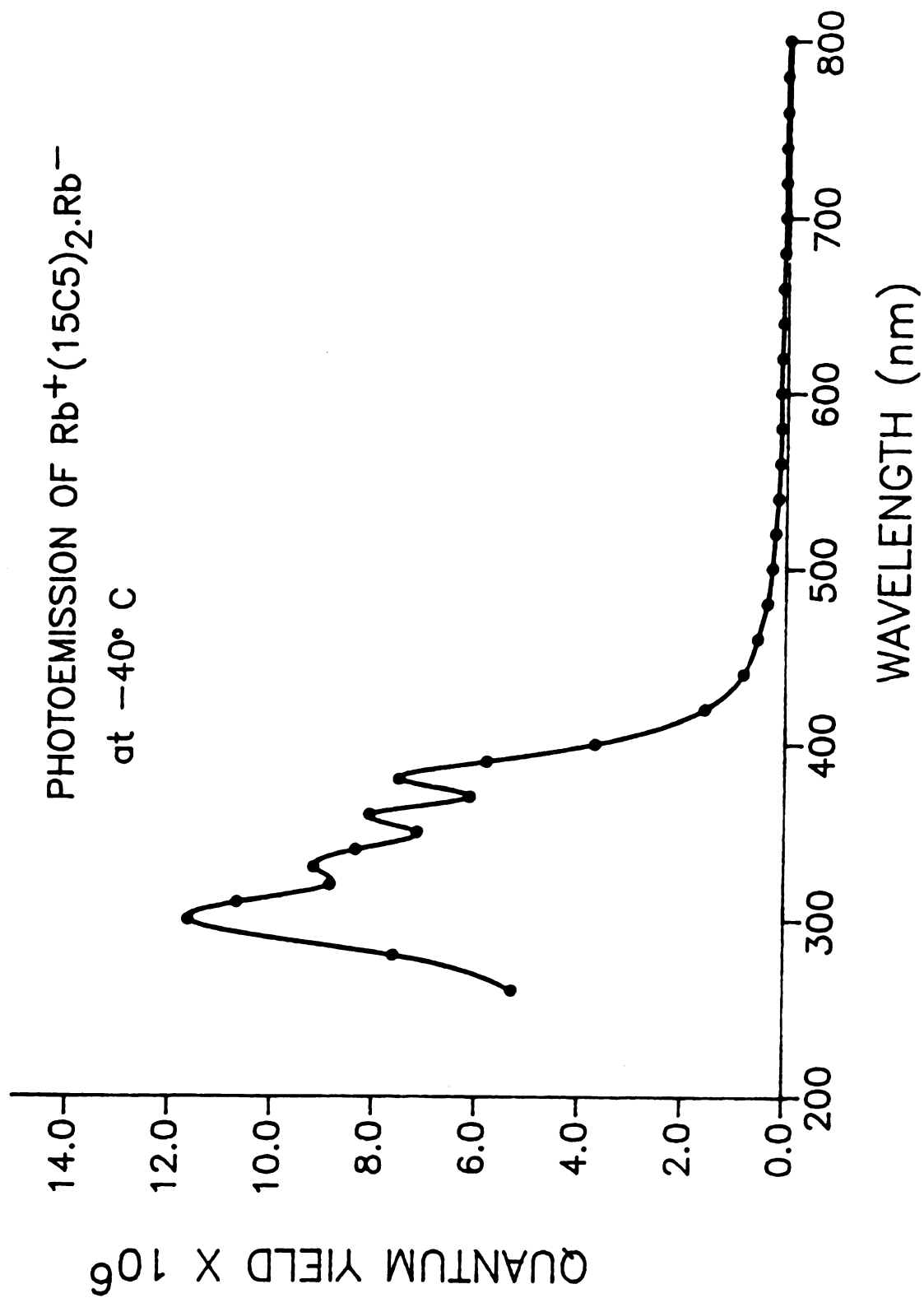


Figure 3-10. Quantum yield spectrum of $\text{Rb}^+(15\text{C5})_2\cdot\text{Rb}^-$ at -40°C .

and Rb^- are very close, consistent with the optical absorption results.

What is/are responsible for the photoemission in the low energy region is still not clear. It is believed to be from trapped electrons. However the emission from an electride film did not give a substantially higher yield at low energies. Figure 3-11 shows the quantum yield spectrum of a film of $\text{K}^+(\text{15C5})_2 \cdot \text{e}^-$. The signal does not seem to be much higher than that from $\text{K}^+(\text{15C5})_2 \cdot \text{K}^-$. However, we should remember that there is always some electride $\text{K}^+(\text{15C5})_2 \cdot \text{e}^-$ mixed with the potasside and some K^- in the electride. The photoemission spectrum of $\text{K}^+(\text{15C5})_2 \cdot \text{K}^-$ may have some contribution from the electride, and vice versa. We must consider the complication that different phases are formed from different compounds (electride and alkalide) in a thin film. The phase with the higher quantum yield will then dominate the spectrum.

All photoemission spectra showed a strong temperature dependence. Figure 3-12 shows the temperature dependence of the quantum yield of $\text{K}^+(\text{15C5})_2 \cdot \text{K}^-$. The mechanism behind it is still not clear. Surface contamination resulting in an insulating layer on the surface may be responsible. Alternatively, the photoemission mechanism may involve a thermal activation step. In order to eliminate the effects

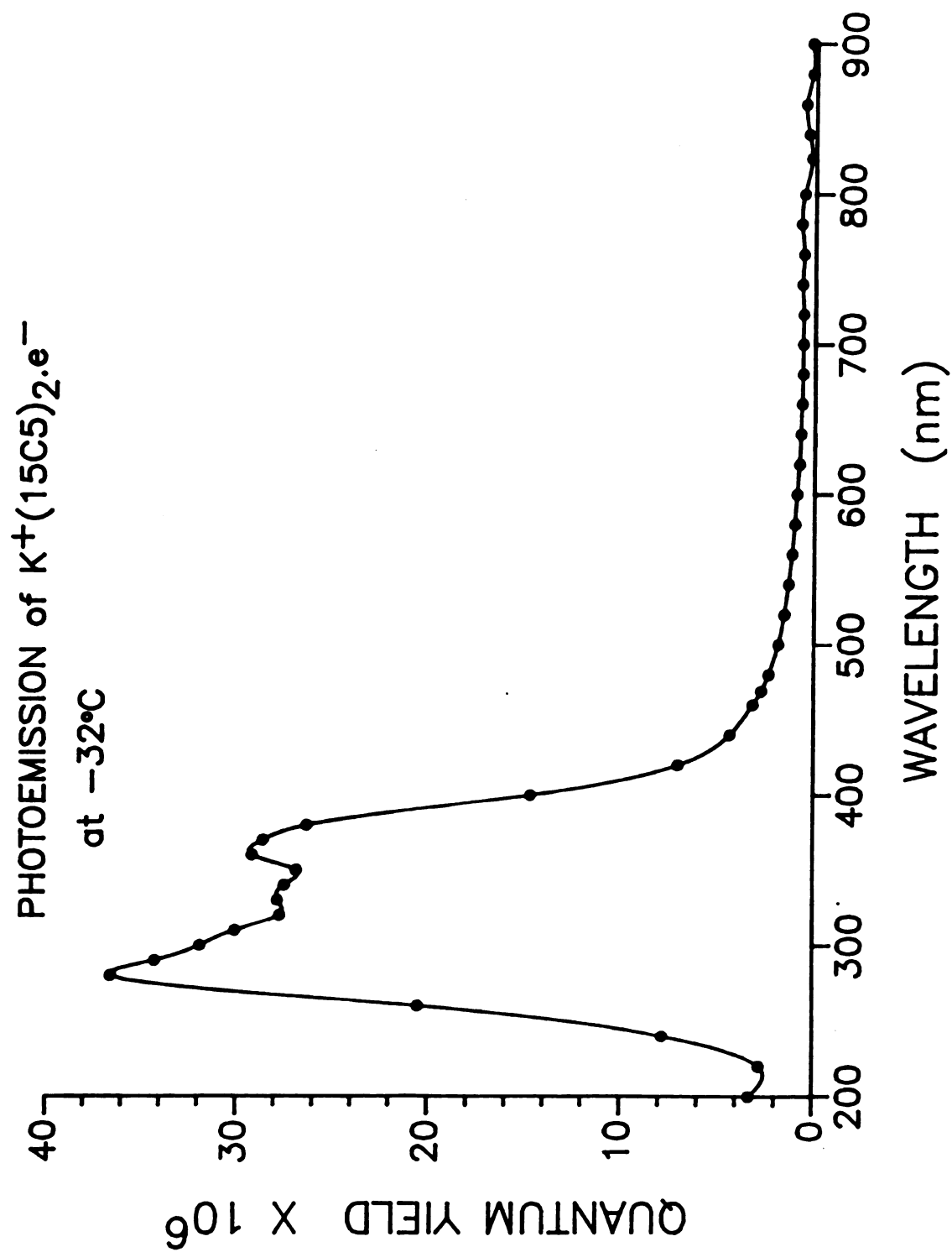


Figure 3-11. Quantum yield spectrum of $K^+(15C5)_2 \cdot e^-$ at -32°C .

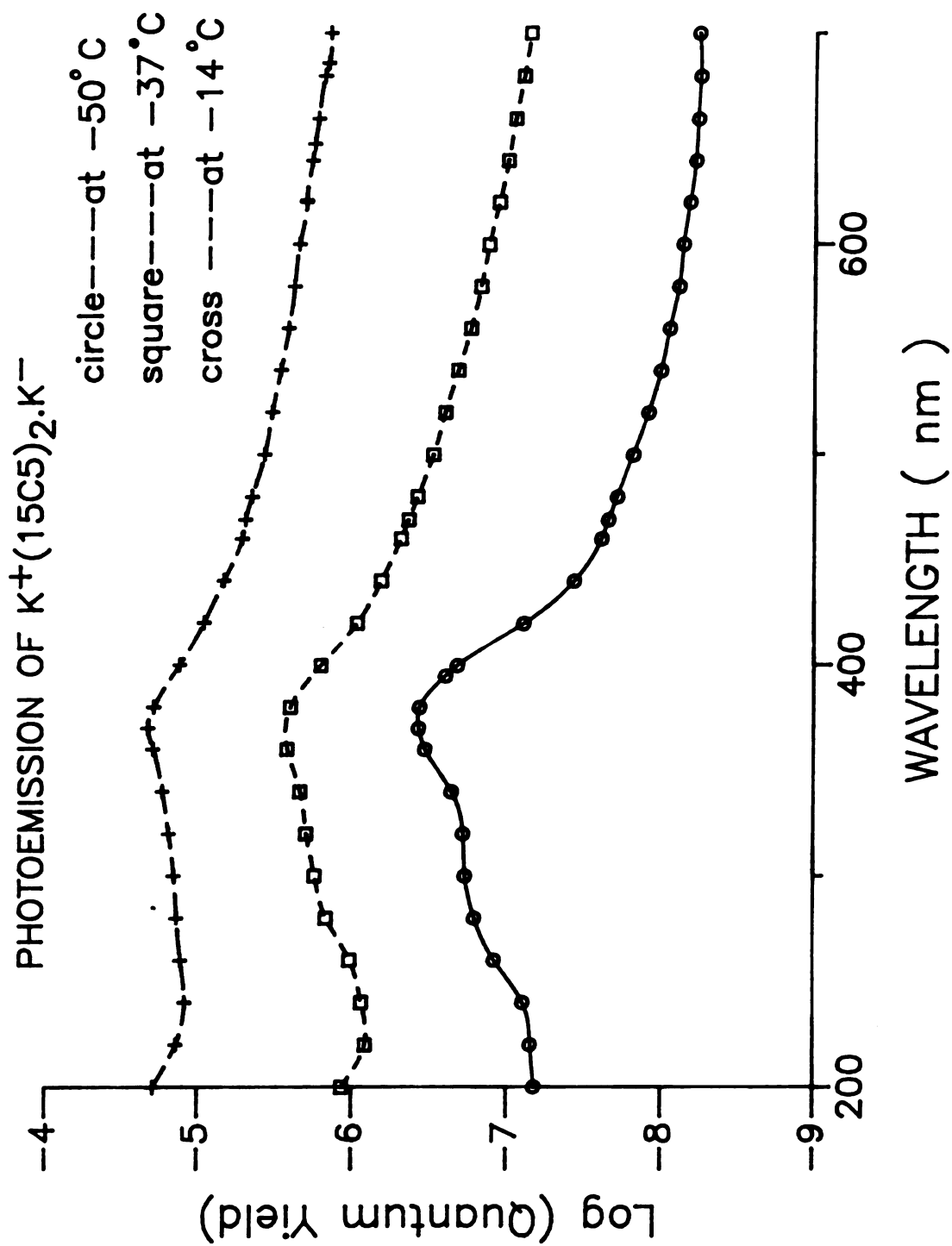


Figure 3-12. Temperature dependence of the quantum yield of $K^+(15C5)_2 \cdot K^-$.

of surface contamination it will be necessary to construct a system that will allow us to obtain better vacuum conditions.

Alkalides and electrides are, we believe, some of the most difficult materials to handle in photoemission studies due to their high reactivities with air and/or moisture and the sensitivities to heat. Although the surface contamination was a serious problem and EDC measurements were unsuccessful, the quantum yield measurements were surprisingly reproducible. The shifts of peaks for Na^- , K^- or Rb^- in different runs with the same or different cations were within the experimental errors (a few nm), therefore these peaks are real. The in situ film making technique used in this work ensures that the films are fresh. It is certainly much better than the preformed film technique which we have tried before. The use of ultra high vacuum technique and/or modern photoemission apparatus should help us to overcome the surface contamination problems.

CHAPTER 4

Thermionic Emission from Alkalides and Electrides

When a metal is heated to a high temperature, the electrons in the conduction band may gain enough energy to overcome the work function barrier and escape from the metal surface into a vacuum. This is the well-known thermionic emission phenomena. From the Boltzmann distribution, the number of electrons with energy E is

$$N = N_0 \exp (-E/kT) \quad (4.1)$$

N_0 being the total number of electrons in the ground states.

It is clear that only when kT is comparable to E will there be a significant number of electrons which are able to escape. At room temperature, kT is about 0.025 eV. The work functions of normal metals are higher than 2 eV, so there is no thermionic emission from normal metals at room temperature. The work functions of common semiconductors (defined as the energy difference between the Fermi energy and the vacuum continuum) are usually at least a few eV.

In alkalides and electrides, however, the valence electrons are either weakly bound (in alkalides) or trapped in the lattice (electrides). The cations are well shielded by the big cryptand or crown ether molecules. Therefore we should expect the work functions to be lower than those of normal semiconductors.

Thermionic emission was reported from solvated electrons in Na-hexamethylphosphoric triamide solution by Delahay [30] and by Gremmo and Randles [41]. This thermionic emission was seen at room temperature and the temperature dependence of the thermoemission current yielded an activation energy of about 1 eV.

Thermionic emission from alkalides and electrides was first seen with a sample of $K^+(15C5)_2.K^-$ during a photoemission experiment. After a fresh film had been made by $MeNH_2$ evaporation, the potential between the anode and the cathode yielded a high current signal without any light illumination at low temperatures (about $-60^\circ C$). Figure 4-1 shows the current signal during $MeNH_2$ evaporation. It can be seen that either when the film was still wet or the film was fresh, the thermionic emission signal was high (a few nA) and then decreased with time and stabilized at a few pA.

Thermionic emission has now been observed from crystals of alkalides and electrides as well as from films formed by solvent evaporation. After the crystalline alkalides or electrides were loaded onto the sample holder and covered

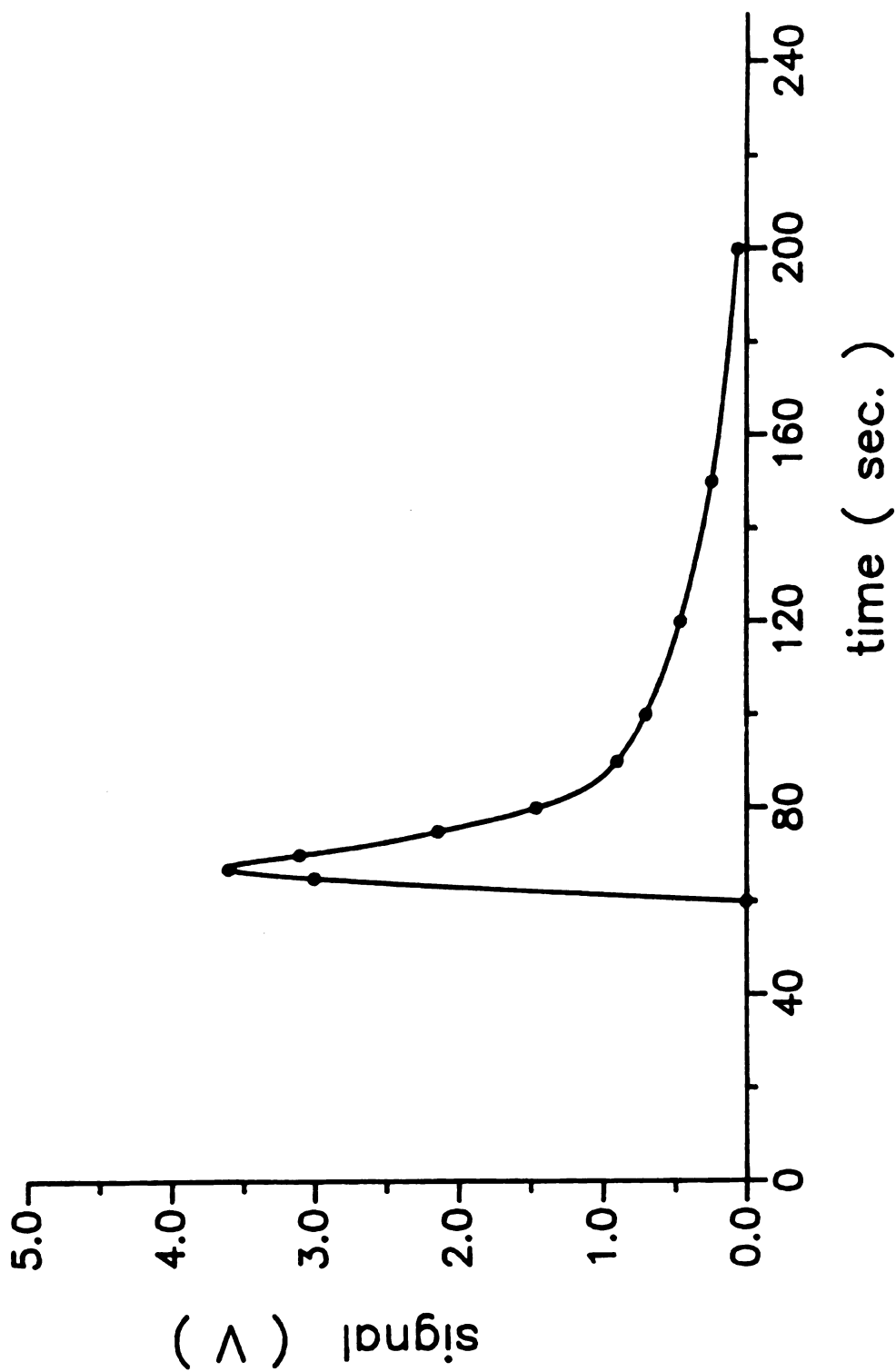


Figure 4-1. Thermionic emission current signal during film making of $K^+(15C5)_2 \cdot K^- \cdot MeNH_2$ was used as solvent. The temperature was about $-60^\circ C$.

with pentane (to avoid static electricity) and then inserted into the vacuum chamber, the pentane was pumped out and a current signal appeared (a few nA). The signal stayed at a few pA for a long time (a few hours) at temperatures around -60°C .

The thermionic emission current depended on the temperature and the potential between the emitter and the collector. The current- potential curve reached saturation at relatively low potentials. In our case, the saturation potential was only a few volts. Figure 4-2 shows the saturation curve for a film of $\text{Rb}^+(15\text{C5})_2.\text{Rb}^-$. The saturation potential was about 5 V.

The temperature dependence follows the Richardson-Dushman equation:

$$j = A (1-r)T^2 \exp(-e\phi/kT) \quad (4.2)$$

j is the current density, T is the temperature, A is a constant related to elementary physical constants, r is the reflection coefficient for electrons. This equation was derived from a thermodynamic method that involved the use of Clapeyron's equation under the assumption that the electron gas in gas phase is in equilibrium with the hot conductor and obeys the laws for an ideal gas[39,40]. Assuming that A , r and ϕ are independent of temperature, one can find the work function ϕ by plotting $\ln (j/T^2)$ versus $1/T$ (Richardson plot). Preliminary results showed work

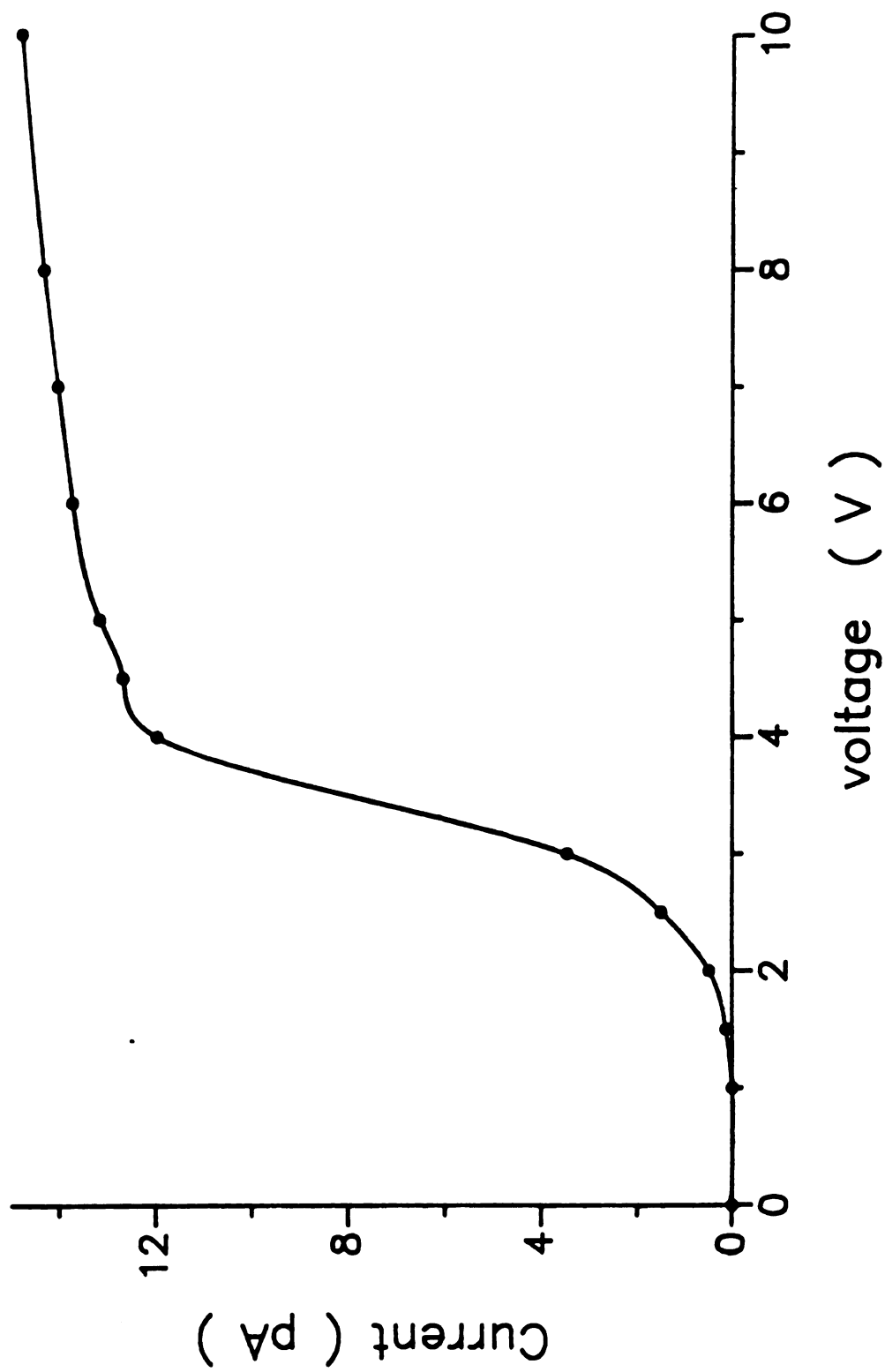


Figure 4-2. Saturation curve of the thermionic emission current for a film of $\text{Rb}^+(15\text{C5})_2\cdot\text{Rb}^-$ at -30°C .

functions that ranged from 0.2 eV to 0.6 eV as shown in Figure 4-3.

The work function is a many-body phenomena. This problem can not be solved exactly. However the problem is conceptually simple: a finite piece of the solid is considered and its ground state energy E_N is calculated in the neutral state with N electrons. A calculation is performed for the state of charge $+1$, with only $N-1$ electrons, and the corresponding ground state energy E_{N-1} is obtained. The difference $E_N - E_{N-1}$ is taken as the work function. Surface, of course, plays the major role in the work function. Sometimes one assumes that the surface is made of whole cells with the same shape and same charge distribution as in the bulk. But a real surface actually does not have the same charge distribution as the bulk. Sometimes electrons tend to "spill out" of the surface plane so as to decrease their kinetic energy. And sometimes a smoothing out of the rough charge distribution due to crevices between Wigner-Seitz cells at the surface takes place[31]. Figure 4-4 shows the "spill out" and "smooth out" processes. In the case of "spill out", a surface charge layer is introduced and tends to increase the work function. On the other hand, smoothing processes tend to decrease the work function.

Therefore we have

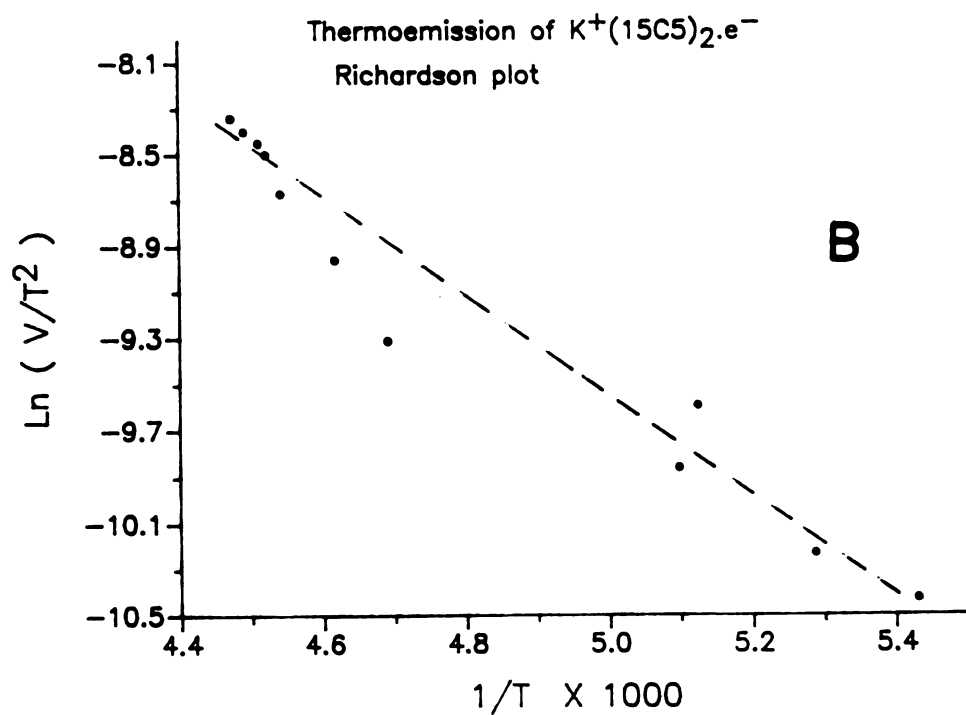
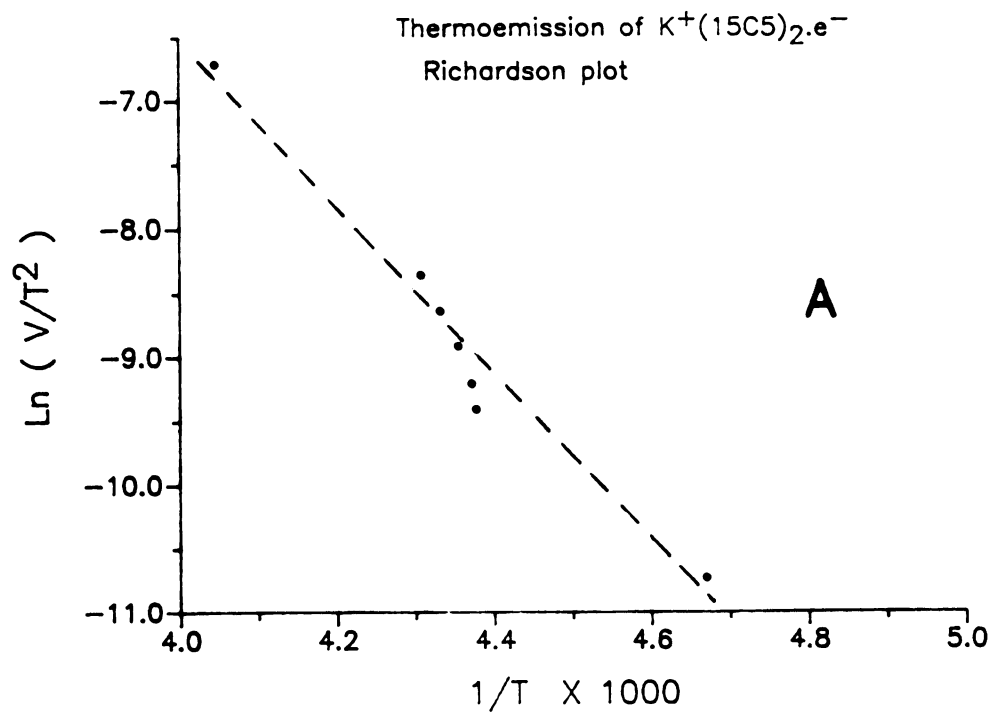


Figure 4-3. Richardson plot of the thermionic emission of $K^+(15C5)_2.e^-$ from film (A) and crystals (B).

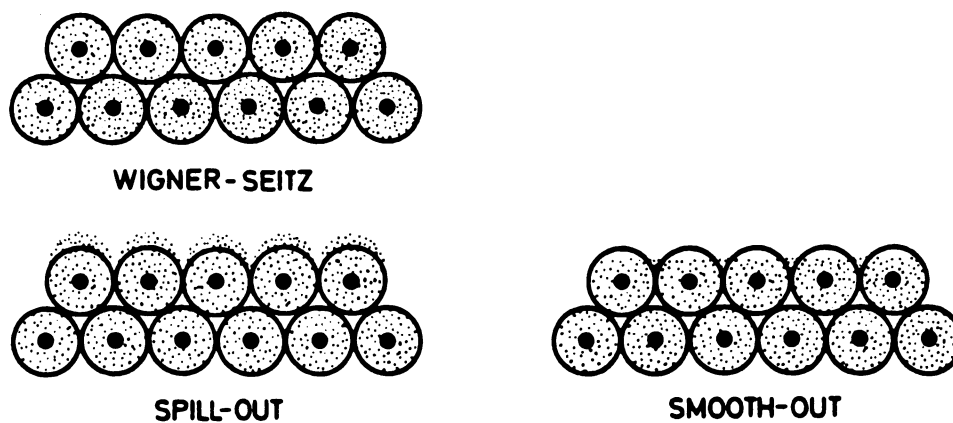


Figure 4-4. Diagram showing the electron distribution in the Wigner-Seitz spheres and the effects of electron spill-out and smooth-out near a surface. [Ref.31]

$$\phi = -\mu + D \quad (4.3)$$

where $E_N - E_{N-1} = -\mu$, the so-called internal work function, μ is the electrochemical potential and D is the total double layer dipole from the "spill out" and/or smoothing.

For alkalides and electrides, valence electrons are either weakly bound (in alkalides) or trapped (electrides). The contribution from the electrochemical potential is expected to be small. The contribution of D depends on the electron density near the surface and the tightness of packing. Since the complexed cations and alkalide anions are all large species and the cations are well-shielded by the cryptand or crown ether molecules, the electron density is low and the packing is loose near the surface. This makes the contribution of D to the work function small. Overall we should expect low work functions for these compounds.

Unfortunately the vacuum in our system was not good enough to keep the films clean and surface contamination was a serious problem.

Nevertheless, thermionic emission at temperatures as low as 200 K has not been previously reported and this is certainly the lowest thermionic emission temperature observed from any solid. Work functions as low as 0.5 eV are the lowest for any solid and suggest numerous applications for electrides.

CHAPTER 5

SUMMARY AND CONCLUSIONS

1. The crystal structures of one electride and five alkalides have been determined. The crystal structure of $K^+(C222).e^-$ provides the structural evidence for electron pairing, consistent with other properties of this electride. A minimum radius of 3.1 Å and an effective radius of 3.5 Å have been obtained from the structures of $Cs^+(18C6)_2.Cs^-$ and $Cs^+(C222).Cs^-$. The cesium anions form chains in both structures. The cesium anions in $Cs^+(18C6)_2.Cs^-$ are well-isolated from each other, while the anions in $Cs^+(C222).Cs^-$ are in contact with each other. The structures provide the explanation for the presence of a Cs^- solid state NMR peak in $Cs^+(18C6)_2.Cs^-$ and the absence in $Cs^+(C222).Cs^-$. The anions in $Rb^+(C222).Rb^-$ form dimer-type species Rb_2^{2-} . The minimum and effective radii obtained from these structures

are: 3.0 and 3.2 Å for Rb^- , 2.8 and 3.15 Å for K^- and 2.55 and 2.73 Å for Na^- .

2. Photoemission from some sodides, potassides, rubidides and electriles has been studied. Sodium contamination from Pyrex glassware has a great effect on the photoemission quantum yield spectra of the electriles and alkalides other than sodides.. The photoemission peaks for the alkali metal anions are: 300 and 330 nm for Na^- , 370 nm for K^- and 380 nm for Rb^- . In most of the cases the photoemission extends into the IR region (about 1 micron). The quantum yields are strongly temperature dependent.

3. Thermionic emission has been observed from the crystals and films of alkalides and electriles at temperatures as low as -60°C . Fresh or wet films (or crystals) show high emission currents. The temperature dependence of the thermionic emission current follows the Richardson-Dushman equation and the Richardson plots of the films and crystals of alkalides and electriles yield work functions of a few tenths of an eV.

APPENDICES

APPENDIX 1.

Crystal structure data of $K^+(C_{222}).Na^-$, $Cs^+(18C6)_2.Cs^-$,
 $Cs^+(C_{222}).Cs^-$, $Rb^+(C_{222}).Rb^-$, $K^+(C_{222}).Na^-$
and $Cs^+(15C5)_2.K^-$.

This appendix collects some major structural data for each of these compounds. These data are the following:

1. drawing of single molecule.
2. stereoview of unit cell.
3. table of positional parameters and their estimated standard deviations.
4. table of bond distances.

For those structures in which the H-atoms ride on the carbon atoms to which they belong, the parameters related to H-atoms are not included.

Table A-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
Potassium Cryptand [2.2.2] Electride

Atom	x	y	z	B($\text{\AA}^2$)
----	-	-	-	-----
K1	0.75630(4)	0.08333(3)	0.04166(3)	3.227(9)
O4	0.8032(2)	-0.03005(9)	-0.0224(1)	4.42(4)
O7	0.8697(2)	-0.0209(1)	0.1070(1)	4.99(5)
O13	0.5596(1)	0.0827(1)	0.10540(8)	4.09(4)
O16	0.5516(1)	0.11103(9)	-0.02329(8)	3.34(4)
O21	0.8879(1)	0.16757(8)	-0.02146(9)	3.61(4)
O24	0.8695(2)	0.1868(1)	0.10733(9)	4.57(5)
N1	0.7364(2)	0.0833(1)	-0.0974(1)	3.56(4)
N10	0.7759(2)	0.0831(2)	0.1797(1)	5.26(6)
C2	0.7343(2)	0.0165(2)	-0.1199(1)	4.53(7)
C3	0.8205(2)	-0.0266(1)	-0.0863(2)	5.07(7)
C5	0.8767(2)	-0.0752(2)	0.0101(2)	5.71(8)
C6	0.8512(2)	-0.0805(2)	0.0757(2)	6.02(8)
C8	0.8543(3)	-0.0265(2)	0.1722(2)	6.89(9)
C9	0.8624(3)	0.0376(2)	0.2025(2)	6.31(9)
C11	0.6691(3)	0.0626(2)	0.2019(2)	6.9(1)
C12	0.5712(3)	0.0980(2)	0.1699(2)	6.36(9)
C14	0.4735(2)	0.1199(1)	0.0736(1)	3.77(6)
C15	0.4546(2)	0.0989(1)	0.0079(1)	3.71(6)
C17	0.5338(2)	0.0960(1)	-0.0880(1)	3.90(6)
C18	0.6332(2)	0.1168(2)	-0.1203(1)	4.04(6)
C19	0.8318(2)	0.1180(2)	-0.1197(1)	4.13(6)
C20	0.8600(2)	0.1800(1)	-0.0858(1)	4.15(6)
C22	0.9254(2)	0.2245(1)	0.0109(2)	4.42(7)
C23	0.9610(2)	0.2094(1)	0.0771(2)	4.61(7)
C25	0.8990(3)	0.1795(2)	0.1724(2)	6.42(9)
C26	0.8048(3)	0.1487(2)	0.2025(2)	6.6(1)
H2a	0.745(2)	0.014(1)	-0.164(1)	2.1(6)*
H2b	0.665(2)	-0.003(1)	-0.114(1)	1.8(6)*
H3a	0.812(2)	-0.068(1)	-0.103(1)	2.2(6)*
H3b	0.894(2)	-0.012(1)	-0.090(1)	2.7(7)*
H5a	0.951(2)	-0.060(1)	0.005(1)	2.5(7)*
H5b	0.864(2)	-0.118(1)	-0.010(1)	3.0(7)*
H6a	0.778(2)	-0.095(1)	0.081(1)	3.2(7)*
H6b	0.893(2)	-0.111(1)	0.100(1)	2.8(7)*
H8a	0.905(3)	-0.056(2)	0.192(2)	5.1(9)*
H8b	0.785(3)	-0.049(2)	0.173(2)	5(1)*

Table A-1 (continued)

Table of Positional Parameters and
Their Estimated Standard Deviations for
Potassium Cryptand [2.2.2] Electride

Atom	x	y	z	B(Å ²)
-----	---	---	---	-----
H9a	0.861(3)	0.031(2)	0.251(1)	3.6(8)*
H9b	0.936(2)	0.057(1)	0.195(1)	2.6(7)*
H11a	0.667(2)	0.071(2)	0.248(1)	3.9(8)*
H11b	0.658(3)	0.013(2)	0.197(2)	7(1)*
H12a	0.501(3)	0.084(2)	0.191(1)	4.3(8)*
H12b	0.573(3)	0.143(2)	0.176(1)	4.1(8)*
H14a	0.493(2)	0.167(1)	0.076(1)	1.5(6)*
H14b	0.406(2)	0.116(1)	0.096(1)	1.3(5)*
H15a	0.436(2)	0.053(1)	0.003(1)	1.0(5)*
H15b	0.394(2)	0.127(1)	-0.014(1)	1.3(5)*
H17a	0.472(2)	0.119(1)	-0.105(1)	0.7(5)*
H17b	0.514(2)	0.049(1)	-0.092(1)	1.0(5)*
H18a	0.617(2)	0.109(1)	-0.167(1)	2.7(7)*
H18b	0.644(2)	0.165(1)	-0.114(1)	1.6(6)*
H19a	0.819(2)	0.127(1)	-0.166(1)	1.4(6)*
H19b	0.894(2)	0.089(1)	-0.114(1)	1.7(6)*
H20a	0.921(2)	0.202(1)	-0.104(1)	1.7(6)*
H20b	0.801(2)	0.212(1)	-0.092(1)	1.2(5)*
H22a	0.867(2)	0.255(1)	0.007(1)	2.1(6)*
H22b	0.984(2)	0.242(1)	-0.009(1)	2.4(6)*
H23a	1.017(2)	0.175(1)	0.080(1)	2.1(6)*
H23b	0.990(2)	0.249(1)	0.099(1)	2.4(6)*
H25a	0.923(3)	0.223(2)	0.192(2)	5.0(9)*
H25b	0.961(2)	0.151(2)	0.177(1)	3.5(8)*
H26a	0.824(3)	0.149(2)	0.251(2)	4.7(9)*
H26b	0.738(3)	0.179(2)	0.193(2)	4.4(8)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$\begin{aligned}
 (4/3) * [& a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\
 & + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\
 & + bc(\cos \alpha) * B(2,3)]
 \end{aligned}$$

Table A-2

Table of Bond Distances (in Angstroms) for
Potassium Cryptand [2.2.2] Electride

Atom1	Atom2	Distance
-----	-----	-----
K1	O4	2.805(2)
K1	O7	2.857(2)
K1	O13	2.858(2)
K1	O16	2.795(2)
K1	O21	2.798(2)
K1	O24	2.847(2)
K1	N1	2.981(2)
K1	N10	2.958(2)
O4	C3	1.412(4)
O4	C5	1.429(4)
O7	C6	1.414(4)
O7	C8	1.437(4)
O13	C12	1.418(4)
O13	C14	1.422(3)
O16	C15	1.428(3)
O16	C17	1.424(3)
O21	C20	1.418(3)
O21	C22	1.421(3)
O24	C23	1.417(4)
O24	C25	1.421(4)
N1	C2	1.464(4)
N1	C18	1.476(3)
N1	C19	1.479(4)
N10	C9	1.462(5)
N10	C11	1.483(4)
N10	C26	1.474(5)
C2	C3	1.508(4)
C5	C6	1.477(6)
C8	C9	1.478(6)
C11	C12	1.507(5)
C14	C15	1.478(4)
C17	C18	1.508(4)
C19	C20	1.499(4)
C22	C23	1.483(5)
C25	C26	1.506(5)

Table A-2 (continued)

Table of Bond Distances (Continued) for
Potassium Cryptand [2.2.2] Electride

Atom1	Atom2	Distance
C2	H2a	0.98(3)
C2	H2b	0.95(3)
C3	H3a	0.94(3)
C3	H3b	0.95(3)
C5	H5a	0.97(3)
C5	H5b	0.99(3)
C6	H6a	0.95(3)
C6	H6b	0.94(3)
C8	H8a	0.94(3)
C8	H8b	0.96(4)
C9	H9a	1.06(3)
C9	H9b	1.01(3)
C11	H11a	1.01(3)
C11	H11b	1.04(4)
C12	H12a	1.03(3)
C12	H12b	0.93(3)
C14	H14a	1.00(3)
C14	H14b	0.99(3)
C15	H15a	0.97(2)
C15	H15b	1.01(2)
C17	H17a	0.94(2)
C17	H17b	1.01(2)
C18	H18a	1.02(3)
C18	H18b	1.01(3)
C19	H19a	1.01(3)
C19	H19b	0.96(3)
C20	H20a	0.99(3)
C20	H20b	0.98(2)
C22	H22a	0.95(3)
C22	H22b	0.93(3)
C23	H23a	0.97(3)
C23	H23b	0.99(3)
C25	H25a	1.03(4)
C25	H25b	0.96(3)
C26	H26a	1.04(3)
C26	H26b	1.02(3)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

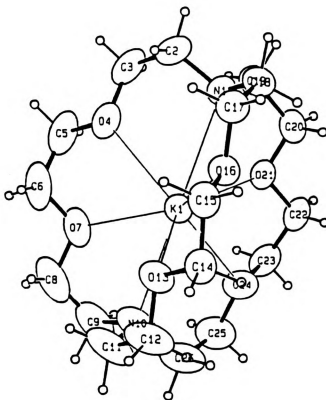


Figure A-1. Drawing of single molecule of $K^+(C_{222}) \cdot e^-$.

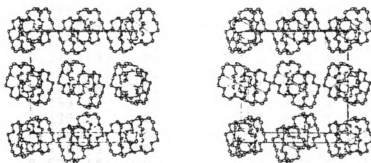


Figure A-2. Stereoview of the unit cell of $K^+(C_{222}) \cdot e^-$.

Table B-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
Cesium (18-Crown-6)₂ Cesium

Atom	x	y	z	B(Å ²)
----	-	-	-	-----
Cs1	0.34763(4)	0.42001(3)	0.36264(2)	4.33(1)
Cs2	0.35442(8)	0.42456(9)	0.09779(3)	13.94(4)
O1	0.4636(5)	0.5064(4)	0.4312(2)	7.9(2)
O4	0.5077(5)	0.5372(4)	0.3433(3)	7.2(2)
O7	0.3824(5)	0.5604(4)	0.2809(2)	6.2(2)
O10	0.2260(5)	0.4780(4)	0.2890(2)	6.4(2)
O13	0.1829(4)	0.5353(3)	0.3710(2)	6.4(2)
O16	0.3044(5)	0.5816(4)	0.4324(2)	6.6(2)
O21	0.2389(5)	0.3601(4)	0.4383(2)	7.5(2)
O24	0.1887(5)	0.2994(4)	0.3561(3)	7.3(2)
O27	0.3060(5)	0.2581(4)	0.2921(2)	7.5(2)
O30	0.4609(6)	0.3390(4)	0.2906(3)	9.1(2)
O33	0.5152(5)	0.3048(4)	0.3755(3)	8.4(2)
O36	0.3970(5)	0.2826(4)	0.4419(2)	7.2(2)
C2	0.5458(9)	0.5090(8)	0.4142(5)	11.2(5)
C3	0.5552(8)	0.5658(7)	0.3771(4)	10.5(4)
C5	0.5151(7)	0.5891(6)	0.3072(4)	8.0(3)
C6	0.4660(8)	0.5557(6)	0.2720(4)	9.0(4)
C8	0.3314(8)	0.5337(6)	0.2461(3)	8.1(4)
C9	0.2441(9)	0.5365(7)	0.2582(3)	8.4(4)
C11	0.1442(7)	0.4824(6)	0.3051(4)	8.6(4)
C12	0.1317(7)	0.5500(6)	0.3357(4)	7.3(3)
C14	0.1711(7)	0.5952(5)	0.4043(4)	8.0(4)
C15	0.2213(8)	0.5729(7)	0.4434(3)	8.3(3)
C17	0.3562(8)	0.5664(6)	0.4688(3)	8.7(4)
C18	0.4430(9)	0.5756(7)	0.4555(4)	10.6(4)
C22	0.1575(7)	0.3491(6)	0.4252(4)	9.5(4)
C23	0.1424(8)	0.2817(6)	0.3936(4)	9.8(4)
C25	0.1755(7)	0.2393(6)	0.3240(4)	9.1(4)
C26	0.2221(8)	0.2639(6)	0.2852(3)	9.0(4)
C28	0.353(1)	0.2775(7)	0.2546(4)	12.2(6)
C29	0.439(1)	0.2727(7)	0.2649(4)	11.8(5)
C31	0.5440(9)	0.3389(7)	0.3043(5)	11.9(5)
C32	0.5597(9)	0.2791(8)	0.3383(5)	12.8(5)
C34	0.5255(8)	0.2539(7)	0.4097(4)	10.5(4)
C35	0.4847(8)	0.2837(7)	0.4484(4)	10.1(4)
C37	0.3549(9)	0.3105(7)	0.4777(3)	10.4(5)
C38	0.265(1)	0.3028(7)	0.4706(3)	10.2(5)

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$\begin{aligned}
 (4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\
 + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\
 + bc(\cos \alpha) * B(2,3)]
 \end{aligned}$$

Table B-2

Table of Bond Distances (in Angstroms) for
Cesium (18-Crown-6)₂ Cesium

Atom1	Atom2	Distance
-----	-----	-----
Cs1	O1	3.185(8)
Cs1	O4	3.283(7)
Cs1	O7	3.486(6)
Cs1	O10	3.178(7)
Cs1	O13	3.281(7)
Cs1	O16	3.503(6)
Cs1	O21	3.113(7)
Cs1	O24	3.252(7)
Cs1	O27	3.516(7)
Cs1	O30	3.197(8)
Cs1	O33	3.332(7)
Cs1	O36	3.444(7)
O1	C2	1.44(2)
O1	C18	1.405(13)
O4	C3	1.391(15)
O4	C5	1.420(13)
O7	C6	1.387(15)
O7	C8	1.436(13)
O10	C9	1.392(12)
O10	C11	1.420(14)
O13	C12	1.404(13)
O13	C14	1.444(12)
O16	C15	1.397(14)
O16	C17	1.437(13)
O21	C22	1.394(15)
O21	C38	1.443(13)
O24	C23	1.422(15)

Table B-2 (continued)

Table of Bond Distances (Continued) for
Cesium (18-Crown-6)₂ Ceside

O24	C25	1.424(13)
O27	C26	1.382(15)
O27	C28	1.431(15)
O30	C29	1.398(14)
O30	C31	1.41(2)
O33	C32	1.43(2)
O33	C34	1.368(14)
O36	C35	1.436(15)
O36	C37	1.389(14)
C2	C3	1.49(2)
C5	C6	1.46(2)
C8	C9	1.47(2)
C11	C12	1.477(15)
C14	C15	1.51(2)
C17	C18	1.48(2)
C22	C23	1.50(2)
C25	C26	1.49(2)
C28	C29	1.44(2)
C31	C32	1.47(2)
C34	C35	1.47(2)
C37	C38	1.48(2)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

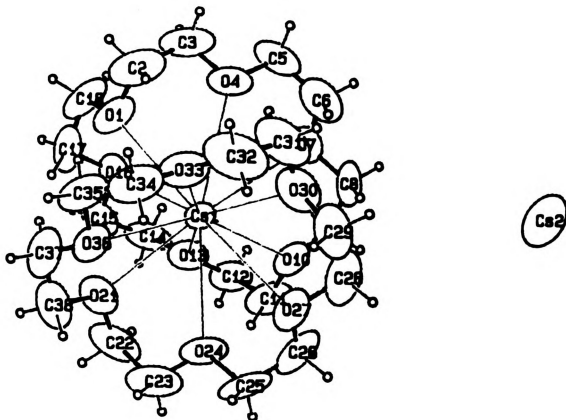


Figure B-1. Drawing of single molecule of $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$.

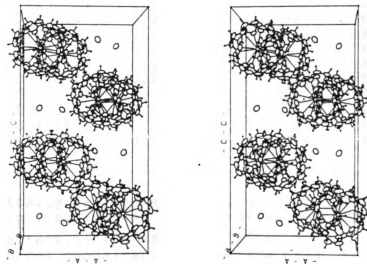


Figure B-2. Stereoview of the unit cell of $\text{Cs}^+(\text{18C6})_2.\text{Cs}^-$.

TABLE C-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
Cesium Cryptand [2.2.2] Ceside

Atom	x	y	z	B(Å ²)
----	-	-	-	-----
Cs1	0.2363(1)	0.0587(2)	0.58667(7)	3.97(3)
Cs2	0.7442(2)	0.0689(3)	0.8196(1)	9.60(7)
O4	0.345(1)	0.276(1)	0.6304(7)	4.9(4)
O7	0.459(1)	0.063(2)	0.5946(7)	5.6(4)
O13	0.220(1)	-0.136(1)	0.6801(7)	5.1(4)
O16	0.082(1)	0.066(2)	0.6780(6)	6.1(4)
O21	0.114(1)	0.155(2)	0.4818(7)	6.4(5)
O24	0.194(1)	-0.081(1)	0.4703(6)	5.3(4)
N1	0.117(1)	0.290(2)	0.6012(8)	4.7(5)
N10	0.345(2)	-0.178(2)	0.5732(9)	6.1(6)
C2	0.187(1)	0.379(2)	0.629(1)	4.6(6)
C3	0.293(2)	0.376(2)	0.608(1)	6.3(8)
C5	0.444(2)	0.270(2)	0.615(1)	7.4(9)
C6	0.490(2)	0.158(2)	0.635(1)	6.1(7)
C8	0.496(2)	-0.048(2)	0.612(1)	7.4(8)
C9	0.453(2)	-0.146(2)	0.571(1)	6.7(8)
C11	0.332(2)	-0.254(2)	0.625(1)	7.5(8)
C12	0.232(2)	-0.248(2)	0.649(1)	6.8(8)
C14	0.130(2)	-0.132(2)	0.708(1)	5.5(7)
C15	0.107(2)	-0.006(2)	0.7288(9)	6.9(9)
C17	0.068(2)	0.190(3)	0.696(1)	8.2(9)
C18	0.040(2)	0.263(2)	0.641(1)	6.8(8)
C19	0.082(2)	0.336(2)	0.538(1)	5.9(8)
C20	0.038(2)	0.239(2)	0.495(1)	5.9(8)
C22	0.082(2)	0.077(3)	0.432(1)	8.8(9)
C23	0.172(2)	-0.002(2)	0.4214(9)	6.4(8)
C25	0.279(2)	-0.149(2)	0.461(1)	5.8(7)
C26	0.304(2)	-0.231(2)	0.513(1)	8.0(9)

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$\begin{aligned}
 (4/3) * [& a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\
 & + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\
 & + bc(\cos \alpha) * B(2,3)]
 \end{aligned}$$

TABLE C-2

Table of Bond Distances (in Angstroms) for
Cesium Cryptand [2.2.2] Ceside

Atom1	Atom2	Distance
Cs1	O4	2.959(15)
Cs1	O7	2.972(14)
Cs1	O13	2.99(2)
Cs1	O16	2.967(14)
Cs1	O21	2.888(15)
Cs1	O24	2.974(14)
Cs1	N1	3.08(2)
Cs1	N10	3.06(2)
O4	C3	1.39(3)
O4	C5	1.39(3)
O7	C6	1.41(3)
O7	C8	1.39(3)
O13	C12	1.44(3)
O13	C14	1.39(3)
O16	C15	1.38(3)
O16	C17	1.46(4)
O21	C20	1.43(3)
O21	C22	1.42(3)
O24	C23	1.39(3)
O24	C25	1.40(3)
N1	C2	1.46(3)
N1	C18	1.43(3)
N1	C19	1.49(3)
N10	C9	1.49(3)
N10	C11	1.42(3)
N10	C26	1.48(3)
C2	C3	1.52(3)
C5	C6	1.46(4)
C8	C9	1.49(4)
C11	C12	1.47(4)
C14	C15	1.53(3)
C17	C18	1.46(3)
C19	C20	1.51(3)
C22	C23	1.52(4)
C25	C26	1.47(3)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

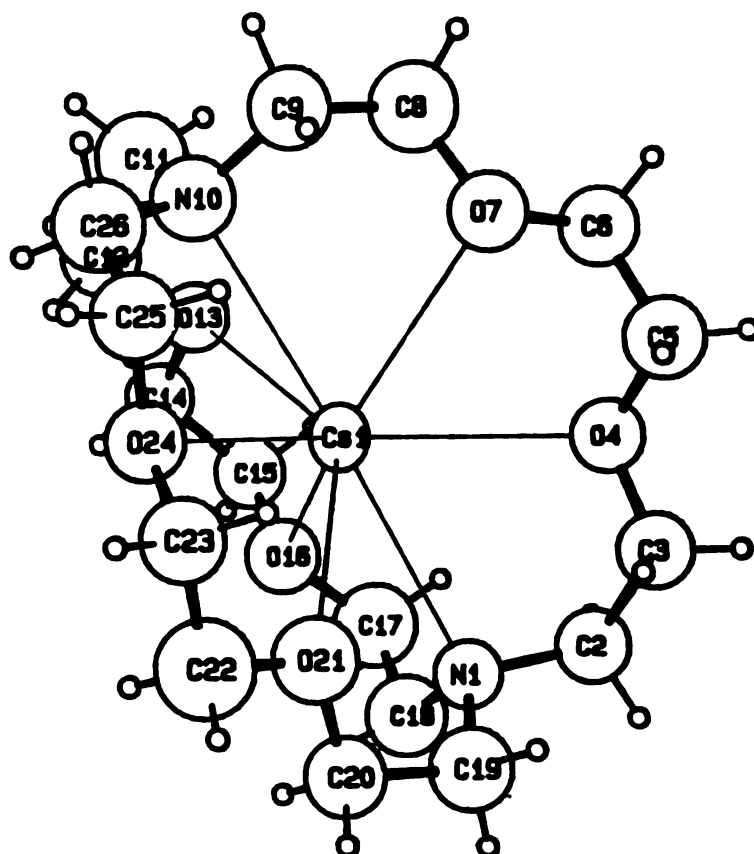


Figure C-2. Stereoview of the unit cell of $\text{Cs}^+(\text{C222})\cdot\text{Cs}^-$.

TABLE D-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
Rubidium Cryptand[2.2.2] Rubidide

Atom	x	y	z	B(Å ²)
-----	-	-	-	-----
Rb1(+)	-0.1561(1)	-0.1890(1)	-0.0467(1)	4.02(3)
Rb2(-)	0.5357(2)	0.3664(2)	0.6427(2)	10.01(8)
O4	-0.3598(8)	-0.0203(8)	-0.1442(9)	5.4(3)
O7	-0.3200(8)	0.0660(8)	0.0994(9)	5.3(3)
O13	0.0653(8)	-0.2053(8)	0.0430(9)	5.8(3)
O16	0.0427(8)	-0.2229(8)	-0.2076(9)	5.2(3)
O21	-0.1622(8)	-0.4271(8)	-0.165(1)	6.5(3)
O24	-0.2030(9)	-0.3240(8)	0.093(1)	6.7(3)
N1	-0.165(1)	-0.264(1)	-0.315(1)	6.5(4)
N10	-0.148(1)	-0.116(1)	0.220(1)	6.3(4)
C2	-0.287(1)	-0.180(2)	-0.341(2)	7.4(6)
C3	-0.339(1)	-0.040(1)	-0.271(1)	6.8(5)
C5	-0.415(1)	0.111(1)	-0.076(2)	6.0(5)
C6	-0.430(1)	0.126(1)	0.054(1)	5.8(5)
C8	-0.337(1)	0.081(1)	0.224(1)	6.8(5)
C9	-0.219(2)	0.023(1)	0.270(2)	7.4(6)
C11	-0.023(2)	-0.162(1)	0.246(1)	7.9(6)
C12	0.058(1)	-0.140(1)	0.166(1)	7.1(6)
C14	0.145(1)	-0.195(1)	-0.032(1)	6.2(4)
C15	0.153(1)	-0.269(1)	-0.158(1)	5.7(4)
C17	0.049(1)	-0.295(1)	-0.327(1)	6.4(5)
C18	-0.073(1)	-0.245(2)	-0.375(1)	7.7(6)
C19	-0.136(2)	-0.399(1)	-0.358(2)	8.4(7)
C20	-0.205(1)	-0.431(1)	-0.279(2)	8.5(7)
C22	-0.228(1)	-0.452(1)	-0.088(2)	7.4(5)
C23	-0.178(1)	-0.451(1)	0.031(2)	7.4(5)
C25	-0.162(1)	-0.314(1)	0.210(1)	7.3(5)
C26	-0.203(2)	-0.178(1)	0.277(1)	8.6(6)

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$\begin{aligned}
 (4/3) * [& a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\
 & + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\
 & + bc(\cos \alpha) * B(2,3)]
 \end{aligned}$$

TABLE D-2

Table of Bond Distances (in Angstroms) for
Rubidium Cryptand[2.2.2] Rubidide

Atom1	Atom2	Distance
Rb1	O4	2.888(9)
Rb1	O7	2.866(7)
Rb1	O13	2.853(11)
Rb1	O16	2.929(11)
Rb1	O21	2.922(10)
Rb1	O24	2.869(13)
Rb1	N1	3.002(14)
Rb1	N10	2.976(13)
O4	C3	1.43(2)
O4	C5	1.420(14)
O7	C6	1.39(2)
O7	C8	1.41(2)
O13	C12	1.41(2)
O13	C14	1.40(2)
O16	C15	1.40(2)
O16	C17	1.40(2)
O21	C20	1.41(2)
O21	C22	1.41(2)
O24	C23	1.42(2)
O24	C25	1.44(2)
N1	C2	1.47(2)
N1	C18	1.49(3)
N1	C19	1.47(2)
N10	C9	1.47(2)
N10	C11	1.45(2)
N10	C26	1.50(3)
C2	C3	1.51(2)
C5	C6	1.48(2)
C8	C9	1.47(2)
C11	C12	1.54(3)
C14	C15	1.46(2)
C17	C18	1.51(2)
C19	C20	1.52(3)
C22	C23	1.49(3)
C25	C26	1.49(2)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

RB2

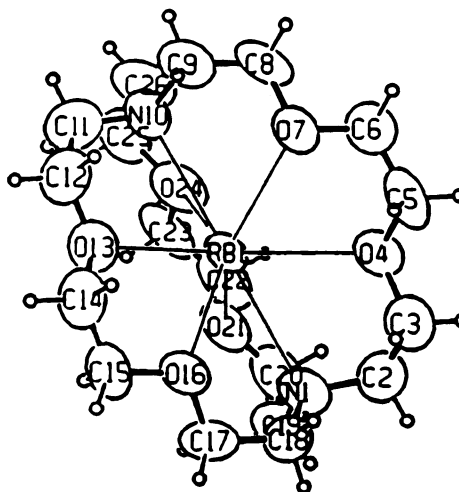


Figure D-1. Drawing of single molecule of $\text{Rb}^+(\text{C}_{222})\cdot\text{Rb}^-$.



Figure D-2. Stereoview of the unit cell of $\text{Rb}^+(\text{C}_{222})\cdot\text{Rb}^-$.

TABLE E-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
 $K^+(\text{Cryptand}[2.2.2]).Na^-$

Atom	x	y	z	B($\text{\AA}^2$)
-----	-	-	-	-----
K1	0.000	0.000	0.000	2.447(9)
Na1	0.000	0.000	0.4151(1)	6.41(4)
O4	-0.0007(1)	0.09556(6)	0.0989(1)	4.00(3)
O7	-0.1552(1)	0.04284(6)	0.0677(1)	3.85(3)
O13	0.06218(9)	0.04014(6)	-0.1801(1)	2.97(3)
N1	0.1544(1)	0.06749(7)	-0.0041(2)	3.33(4)
C2	0.1485(2)	0.10556(9)	0.0771(2)	4.44(5)
C3	0.0643(2)	0.13368(9)	0.0834(2)	4.33(5)
C5	-0.0800(2)	0.1207(1)	0.1173(2)	4.68(6)
C6	-0.1438(2)	0.0792(1)	0.1457(2)	4.80(6)
C8	-0.2226(2)	0.0064(1)	0.0884(2)	4.59(6)
C9	-0.2300(1)	-0.03334(9)	0.0088(2)	4.31(5)
C11	0.1605(1)	0.09597(9)	-0.0963(2)	3.95(5)
C12	0.1457(1)	0.06197(9)	-0.1840(2)	3.84(5)
C14	0.0458(1)	0.00877(9)	-0.2633(2)	3.49(5)
H2a	0.196(2)	0.133(1)	0.074(2)	2.7(6)*
H2b	0.157(1)	0.0848(9)	0.134(2)	1.3(5)*
H3a	0.066(2)	0.1558(9)	0.144(2)	2.5(6)*
H3b	0.051(1)	0.1562(8)	0.023(2)	1.0(5)*
H5a	-0.101(1)	0.1427(8)	0.057(2)	1.6(5)*
H5b	-0.073(1)	0.1455(8)	0.168(2)	1.6(5)*
H6a	-0.126(1)	0.0602(9)	0.205(2)	1.8(5)*
H6b	-0.197(2)	0.095(1)	0.155(2)	3.7(7)*
H8a	-0.277(1)	0.0258(9)	0.095(2)	1.7(5)*
H8b	-0.211(1)	-0.0102(8)	0.151(2)	1.1(5)*
H9a	-0.236(1)	-0.0137(8)	-0.053(2)	1.0(5)*
H9b	-0.283(1)	-0.0561(9)	0.021(2)	1.6(5)*
H11a	0.215(1)	0.1138(9)	-0.107(2)	1.7(5)*
H11b	0.117(1)	0.1218(8)	-0.093(2)	0.8(4)*
H12a	0.151(1)	0.0837(8)	-0.241(2)	1.1(5)*
H12b	0.189(1)	0.0341(9)	-0.190(2)	1.7(5)*
H14a	0.085(1)	-0.0222(8)	-0.263(2)	1.0(4)*
H14b	0.053(1)	0.0303(8)	-0.327(2)	0.9(5)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:
(4/3) * [a²*B(1,1) + b²*B(2,2) + c²*B(3,3)
+ ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3)
+ bc(cos alpha)*B(2,3)]

TABLE E-2

Table of Bond Distances (in Angstroms) for
 $K^+(\text{Cryptand}[2.2.2]).Na^-$

Atom1	Atom2	Distance
K1	O4	2.773(2)
K1	O7	2.835(2)
K1	O13	2.860(2)
K1	O4'	2.773(2)
K1	O7'	2.834(2)
K1	O13'	2.860(2)
K1	N1	2.973(2)
K1	N1'	2.972(2)
O4	C3	1.422(3)
O4	C5	1.426(3)
O7	C6	1.427(3)
O7	C8	1.434(3)
O13	C12	1.429(3)
O13	C14	1.420(3)
N1	C2	1.480(3)
N1	C11	1.466(3)
N1	C9'	1.482(2)
C2	C3	1.509(4)
C5	C6	1.506(4)
C8	C9	1.493(4)
C11	C12	1.504(4)
C14	C14'	1.511(2)
C2	H2a	1.01(2)
C2	H2b	0.96(2)
C3	H3a	1.01(3)
C3	H3b	1.04(2)
C5	H5a	1.05(2)
C5	H5b	0.95(2)
C6	H6a	0.99(2)
C6	H6b	0.95(3)
C8	H8a	1.00(2)
C8	H8b	0.98(2)
C9	H9a	0.99(2)
C9	H9b	1.03(2)
C11	H11a	0.98(2)
C11	H11b	0.95(2)
C12	H12a	0.96(2)
C12	H12b	0.99(2)
C14	H14a	1.00(2)
C14	H14b	1.04(2)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

' indicates an atom at - X, - Y, Z

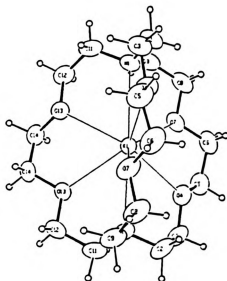


Figure E-1. Drawing of single molecule of $K^+(C_{222}).Na^-$.

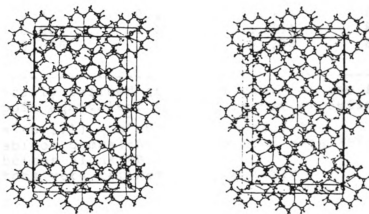


Figure E-2. Stereoview of the unit cell of $K^+(C_{222}).Na^-$.

Table F-1

Table of Positional Parameters and
Their Estimated Standard Deviations for
Cesium (15-Crown-5)₂ Potasside

Atom	x	y	z	B(Å ²)
-----	-	-	-	-----
Cs1	0.500	0.000	0.500	5.43(2)
K1	0.500	0.500	0.000	5.87(9)
O1	0.4754(7)	0.000	0.2033(8)	5.8(2)
O4	0.5141(5)	-0.1790(4)	0.3301(5)	5.7(1)
O7	0.7271(5)	-0.1056(4)	0.4388(6)	6.7(1)
C2	0.4117(8)	-0.0877(7)	0.1790(8)	6.4(2)
C3	0.4872(9)	-0.1710(7)	0.204(1)	7.5(3)
C5	0.614(1)	-0.2347(6)	0.3558(9)	7.8(3)
C6	0.7228(8)	-0.1789(8)	0.347(1)	8.8(3)
C8a	0.828(1)	-0.031(1)	0.470(2)	5.8(4)
C8b	0.819(1)	0.055(1)	0.384(2)	6.4(4)
H2a	0.391(6)	-0.073(5)	0.110(7)	3(2)*
H2b	0.369(6)	-0.075(5)	0.237(7)	4(2)*
H3a	0.461(6)	-0.218(6)	0.179(7)	4(2)*
H3b	0.543(4)	-0.154(4)	0.167(4)	-0(1)*
H5a	0.600(6)	-0.288(5)	0.314(6)	3(2)*
H5b	0.605(5)	-0.239(4)	0.420(5)	1(1)*
H6a	0.778(6)	-0.209(5)	0.345(6)	3(2)*
H6b	0.734(6)	-0.153(6)	0.284(7)	4(2)*
H8aa	0.902	-0.061	0.465	8.7*
H8ab	0.816	-0.008	0.554	8.7*
H8ba	0.802	0.033	0.301	8.7*
H8bb	0.888	0.091	0.384	8.7*

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\ + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\ + bc(\cos \alpha) * B(2,3)]$$

Starred atoms were refined isotropically.

Table F-2

Table of Bond Distances (in Angstroms) for
Cesium (15-Crown-5)₂ Potasside

Atom1	Atom2	Distance
Cs1	O1	3.171(8)
Cs1	O4	3.056(5)
Cs1	O7	3.078(5)
O1	C2	1.436(10)
O4	C3	1.383(12)
O4	C5	1.418(12)
O7	C6	1.400(12)
O7 ⁱ	C8a	1.593(14)
O7 ⁱ	C8b	1.403
C2	C3	1.463(13)
C5	C6	1.476(14)
C8a	C8b	1.50(2)
C2	H2a	0.79(7)
C2	H2b	0.82(7)
C3	H3a	0.76(8)
C3	H3b	0.79(5)
C5	H5a	0.87(7)
C5	H5b	0.69(6)
C6	H6a	0.76(7)
C6	H6b	0.77(8)
C8a	H8aa	0.95
C8a	H8ab	0.95
C8b	H8ba	0.95
C8b	H8bb	0.95

Numbers in parentheses are estimated standard deviations
in the least significant digits.

ⁱ indicates an atom at x, - y, z

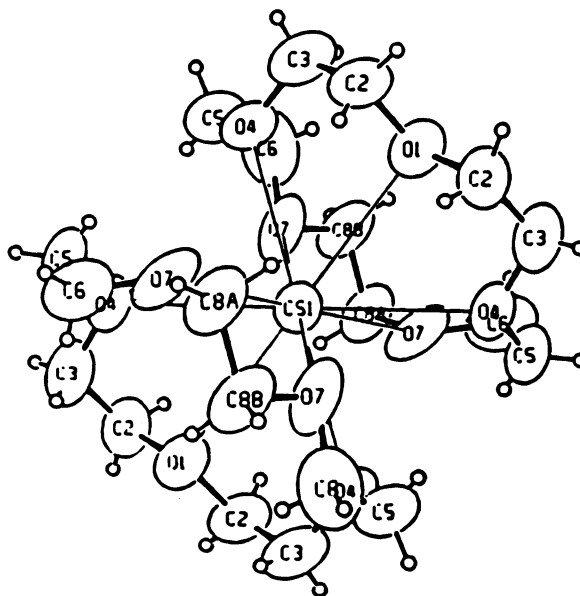


Figure F-1. Drawing of single molecule of $\text{Cs}^+(\text{15C5})_2.\text{K}^-$.

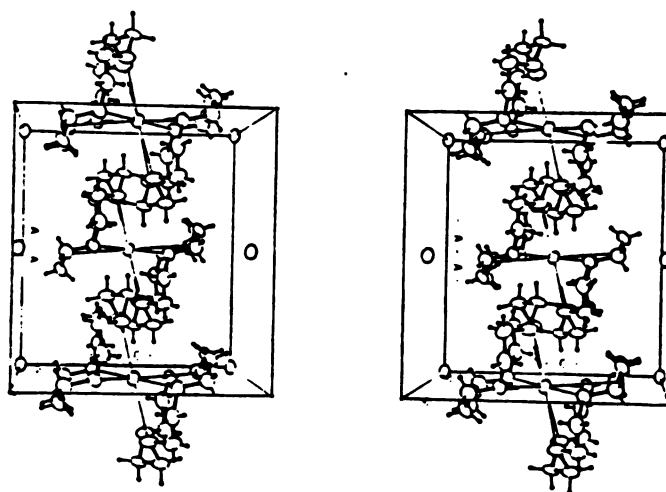


Figure F-2. Stereoview of the unit cell of $\text{Cs}^+(\text{15C5})_2.\text{K}^-$.

Appendix 2.

Explanation of the entries in the tables of crystal data.

1. Temperature - the temperature of the single crystal on the x-ray diffractometer.
2. Peak width at half-height - the width of the peak of a standard reflection at the half-height of the peak.
3. Scan type - the mode of scan during the data collection. The angle between the x-ray beam and the detector is 2θ .
4. Scan rate - the rate with which the angle (2θ or ω) is scanned during the data collection.
5. Unique reflections - the reflections which are not related by the symmetry of the reciprocal lattice.
6. Corrections - the corrections made to the intensities of reflections.
7. Solution - the method for solving the structure.
8. Hydrogen atoms - the way the hydrogen atoms were treated during the refinement.
9. R - the residual index. $R = \sum |F_o - F_c| / \sum F_o$, where F_o is the structure factor related to the intensity observed, F_c is the structure factor calculated. The sum is over all the reflections used in the refinement.
10. R_w - the weighted residual index.

$$R_w = \text{SQRT}[\sum w (F_o - F_c)^2 / \sum w F_o^2] \quad \text{and}$$

$$w = 4F_o^2 / [\sigma(F_o^2)]^2$$

11. High peak in final difference map - the highest peak in the final difference electron density map.
12. Standard deviation of observation of unit weight - it is calculated by the formula

$$\text{SQRT}[(\sum w(F_o - F_c)^2) / (N_1 - N_2)]$$

where N_1 is the number of the observed reflections used in the refinement and N_2 is the number of parameters in the refinement.

13. Convergence, largest shift - the largest of shifts of parameters during the final refinement cycle.

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