

SPECTROSCOPIC STUDIES OF SELECTED RADICAL ANION
DERIVATIVES OF TETRACYANOETHYLENE

By

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CHAPTER I

INTRODUCTION

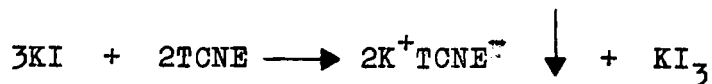
The first percyanoolefin, tetracyanoethylene, was successfully prepared in 1957 by a research group at the duPont Laboratories (1). Tetracyanoethylene (ethenetetracarbonitrile) was found to be an unusually reactive compound which also exhibits a strong tendency to form charge-transfer complexes (2). Tetracyanoethylene (TCNE) is one of the strongest π acids to be studied with respect to charge-transfer characteristics, with many interesting results. One type of complex, formed with aromatic donors, has been used in a sensitive spot test procedure for the analysis of chromatographic separations (3).

Phillips, Rowell, and Weissman (4) are credited with the discovery of the radical anion derivatives of TCNE in 1960. This first preparation was accomplished by mixing TCNE and potassium in the vapor phase with the derivative obtained as a red-purple crystal. The electron paramagnetic resonance (EPR) studies performed by these investigators showed conclusively that the species observed was the radical anion of TCNE ($\text{TCNE}^{\cdot-}$). The EPR studies of solutions containing TCNE and $\text{TCNE}^{\cdot-}$ also indicated that rapid electron exchange occurred between these two species. The exchange reaction between $\text{TCNE}^{\cdot-}$ salts and 7,7,8,8-tetracyanoquinodimethan (TCNQ) resulting in

free TCNE and the insoluble salts of the $\text{TCNQ}^{\cdot-}$ further proves that the radical anion is formed non-destructively, without severe structural modification.

The TCNE molecule belongs to the $D_{2h}(\equiv V_h)$ symmetry group (5). Geometrically (6), this implies that TCNE is a planar molecule similar to ethylene. There is no indication that the anion has a different geometric form than the free molecule, although the interatomic dimensions are probably changed by the added radical electron. Since this molecule is centrosymmetric, the mutual exclusion principle should prevent any infrared fundamental from appearing in the Raman spectrum or vice-versa. This fact is significant in the context of the interpretation presented later in the discussion of results.

The preparation of these anion salts in polar solvents, such as acetonitrile and tetrahydrofuran, has been described by Webster, Mahler and Benson (7 - 8). They successfully observed the oxidation of copper, magnesium, and lead by TCNE (in acetonitrile) to produce the corresponding anion salts. The high electron affinity of TCNE makes it possible to prepare the anion salts in solution, by using alkali metal salts containing highly polarizable anions. These reactions require a non-aqueous solvent with sufficiently polar character to partially ionize the metal salt. Potassium iodides and cyanides readily undergo this reaction even at reduced temperatures.



Although the high electron affinity of the neutral TCNE indicates a high polarizing power, the TCNE^- can be attributed a high polarizability. It is therefore assumed that the anion salts are stabilized by the polarizing action of the essentially point charge cation upon the highly polarizable TCNE^- . This stabilization is in addition to the normal Coulombic attraction expected with two charged species.

The original qualitative anion infrared spectrum, in which only the absorption maxima are reported (8), is rather unusual. The major bands, only three in number, appear in the 1300 and 2200 cm^{-1} regions. This spectrum was run in a KBr medium for routine characterization during the preparations by Webster, Mahler, and Benson (8). The apparent lack of any absorption in the region where certain TCNE fundamentals (IR) appear was quite unexpected. Since the weak charge-transfer complexes of TCNE were known not to exhibit this anomaly, the anion salts (or dative TCNE complexes) seemed worthy of further investigation.

It was originally thought that the semiconducting properties (9) of the anion salts might be related to the odd spectral behavior. Other dative complexes (10) are known which show metallic characteristics and, in turn, have unusually weak and diffuse infrared spectra.

With a nearly complete vibrational assignment for TCNE available (5) the problem was to prepare a spectroscopically adequate sample of the anion. This sample should permit the missing infrared fundamentals to be located, and, ultimately,

permit an interpretation of the complete infrared spectrum. It was to this end that the present investigation was initiated. Since the anion derivatives are only sparingly soluble in even highly polar solvents it would be necessary to obtain the crystals, and then to examine them by either KBr pellet techniques or as a film deposited on a suitable infrared window. The extreme sensitivity of the anion salts to water and oxygen made the solution preparations difficult at best. The added contamination encountered in preparing a suitable pellet for infrared sampling forced attention to other methods.

Since only a small amount of pure sample was needed, the vapor phase preparation seemed to hold promise. This preparation can be achieved by crossing beams of the reactants on a suitable crystal plate. The resulting deposit can then be examined spectroscopically. Since the entire preparation and the infrared sampling takes place in a high vacuum this method minimizes contamination of the sample.

Therefore, a simple sampling system, designed around the gas phase preparation, was assembled and the initial results examined. It was obvious, even with this preliminary data, that the missing fundamentals were unusually weak, if even present, in these samples of K^+TCNE^- . Therefore, it was decided that this study should be directed to the perfection of a method of preparation and sampling which would allow a more exhaustive spectral study. During the course of this development enough data has been obtained to permit a tentative interpretation of the unusual spectrum of the potassium and sodium anion salts.

CHAPTER II

EXPERIMENTAL

Apparatus

The apparatus which has been assembled to prepare and sample the anion salts of TCNE is compact and portable while virtually eliminating contamination. The preparation and subsequent spectroscopic examination is accomplished under high vacuum. The units of this system and their functional description follow, with reference to the schematic of the vacuum system in Plate I and the two Plates II, III. These Plates show the details of the main reaction cell.

Since the complete reaction and sampling procedure is done under vacuum a high capacity rotary vacuum pump was chosen as the anchor of the system. This forepump is capable of maintaining a pressure as low as 10^{-3} torr throughout the system, even under adverse conditions produced by small leaks and heated metal surfaces which evolve large amounts of gas. This pump will nearly eliminate all contaminants such as water, grease, and air from the sample cell within a few hours after the cell is assembled. The pressure range in which this pump operates is monitored by a standard hot filament-thermocouple probe. The sublimation manifold shown in the schematic (Plate I) is also evacuated by the forepump thereby providing an auxiliary

system for purifying the commercial samples of TCNE.

Since the preparative reaction requires a lower pressure than 10^{-3} torr, a three stage oil diffusion pump of standard construction was included in the system. This pump, with the use of liquid nitrogen traps, allows a final cell pressure of 10^{-6} torr to be achieved under ideal conditions. The high temperatures ($200-300^{\circ}\text{C}$) which are required to vaporize the alkali metals place further demands on this system. The degassing of the oven containing the alkali metal would, upon heating, quickly raise the pressure of the system to a high level if the vacuum system had not been constructed with large tubing and valves. In the main pumping circuit, there is no constriction which is less than one-half inch in diameter.

The main preparation cell shown in Plate II is a versatile container in which the sample may be prepared by volatilizing TCNE and the metal. Both vapors are directed onto the central crystal plate where the anion salt is deposited. Since this deposition window is suspended on the dewar (Plate II-A), it can later be rotated 90° such that the spectrometer beam passes through it and hence through the deposited sample. The two flanged ports (Plate II-C) are sealed with CsI windows thus permitting this beam to pass completely through the cell. The contact between the dewar and the deposition crystal is made by a Kovar-to-Pyrex tube which terminates in a forked clamp to hold the crystal. To improve thermal contact the addition of indium wire, as a gasket between the clamp and crystal, has been found necessary. Since this window can be easily removed

without physical destruction of the sample it is possible to obtain a qualitative estimate of the pathlength through the sample by the difference in weight before and after deposition.

The copper plates (Plate II-D) at each end of the cell serve a multiple purpose. They permit the clamping action which seals the large "O" ring ends of the main Pyrex body and also act as a support for the entire cell. In addition these plates, being copper, provide an easy method of introducing power leads, thermocouples and gases via soldered tubing and ceramic feedthroughs. The right angle bellows valve shown allows the evacuated cell to be separated from the vacuum system if this is desirable.

It was found necessary to include a liquid nitrogen trap within the cell (Plate II-E) to accelerate the initial degassing process. The degassing speed is a consideration because of the real vapor pressure of the TCNE, which, being one of the reactants, is present during the degassing. Although extended operation of the diffusion pump without the internal trap would eventually degas the cell, the TCNE might no longer be available for reaction.

The ovens for vaporizing the reactants (i.e. TCNE and K) are shown in Plate III. The larger oven (Plate III-A), used for the alkali metal, is of copper construction, this metal being found as durable as any available while still allowing a high thermal conductivity to assure uniform heating. This oven has two chambers which are considered in detail in the next section.

The TCNE is contained in a lead-foil sealed Pyrex tube below the potassium oven (Plate III-B). The temperature required for vaporization of the TCNE (60-80°C) permits the use of the standard power type (10 watt) resistor, in which the Pyrex tube is inserted.

The arrangement of shields and leads is purely a function of the particular preparation being attempted and no general procedure has been used in placing these items. The only major concern was to minimize the radiated heat generated by the large oven, thus facilitating control of temperatures in other areas.

All of the heaters are controlled by variable autotransformers via the leads shown in Plate III. Temperature measurements are accomplished by means of iron-constantan thermocouples and a standard potentiometer. The pressure in the preparative cell is monitored by a cold cathode ionization gauge of standard construction which will permit accurate readings from 10^{-3} to 10^{-7} torr.

The entire system can be moved, thereby allowing the reaction cell to be placed into the spectrometer sampling compartment while still under high vacuum. This mobility also permits visual monitoring of the actual deposition prior to infrared scanning.

Sample Preparation

The radical anion salts are prepared in the cell shown in Plate II. The cell components are cleaned and then baked

at 150°C to remove trapped contaminants which would interfere with the reaction. For convenience, the cell assembly is done in a room of low relative humidity, rather than in an isolation box. The general results obtained indicate that atmospheric contamination is not a serious problem if a reasonable initial evacuation period is used (4 hours at 10^{-3} torr).

The TCNE is resublimed from practical grade Eastman stock. Large, easily handled crystals are obtained from a modified zone sublimator. Since the TCNE is again vaporized during the actual reaction, this one step purification is sufficient.

This resublimed TCNE is then placed in a Pyrex tube which is fitted with a tight cap of lead foil. This tube is positioned in the lower heater to direct the beam towards the center of the CsI deposition crystal. The orifice in the lead cap, necessary for effusion of the TCNE, is made with a sharp needle just prior to the final assembly of the cell.

The alkali metals have presented the most severe experimental problems. In early trials, using a heated copper tube with pinhole orifice, the potassium vapor tended to stream out of the oven in one burst at a temperature which was much higher than the expected effusion temperature.

These early troubles seemed to indicate two problems with the vaporization of the alkali metal. The first of these problems involves the normal oxide film which develops in the alkali metals even under kerosene. The second effect has its origin in the tendency of the alkali metal vapor to condense at the exit orifice, thereby forming a strong film. The two

phenomena were apparently combining to create a closed cell situation, in which the molten metal would form an oxide coating by reacting with the gases being evolved when the oven was heated. The burst of material at temperatures greater than 300°C indicated that the oxide shell had decomposed. This oxide breakdown then releases a sufficient amount of the pure metal, which in turn creates a pressure in the oven that is three orders of magnitude greater than the pressure of the cell proper. This pressure differential is then capable of breaking the film sealing the oven orifice, leading to the burst of material. This prohibits smooth deposition of product.

To overcome these difficulties the double oven in the following sketch was developed.

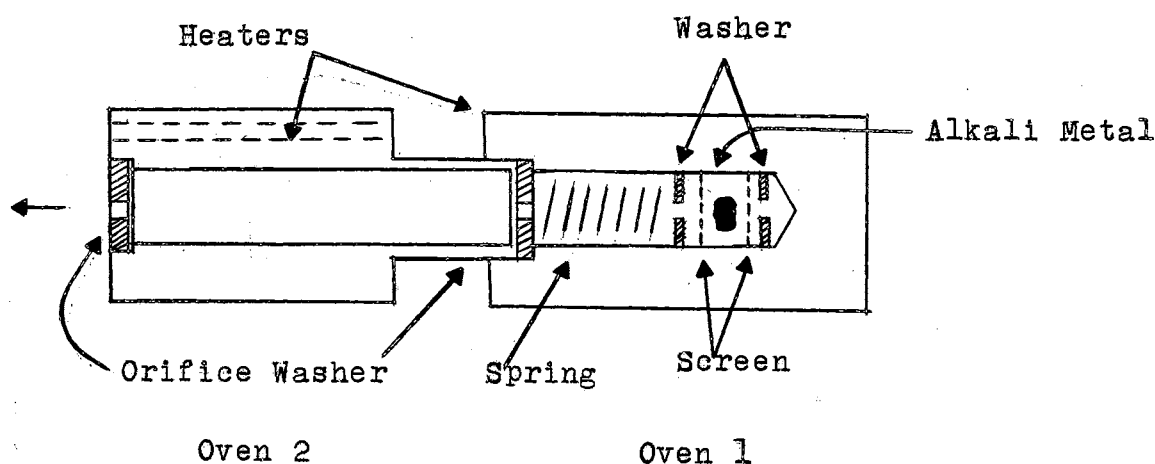


Figure I - Potassium Vaporization Oven

The alkali metal is cut into a cube that will fit the oven opening ($3/8$ " dia.). The sandwich of steel washer, copper screen, potassium, screen, and washer is placed into oven 1. A steel spring with moderate tension is then fixed in position by a larger washer which provides the orifice of oven 1. This first orifice determines the amount of material effusing from oven 1 whereas the larger orifice of oven 2 largely determines the effusion pattern for deposition.

After the cell has been sealed, and evacuated to remove the major contaminants, the heater imbedded in oven 2 is used to quickly raise the oven temperature to 120°C . By heating from this end most of the contaminants within the oven are evolved before the alkali metal becomes molten. As the metal softens the spring forces the mass through the screening. Since the cell is clean and evacuated by this time, the freshly filtered metal can now proceed to vaporize in a normal manner. After the filtration process, a sharp rise in internal pressure is observed followed by a return to the previous level. At 120°C potassium volatility is low, so the temperature of oven 1 is raised to 210°C . If oven 2 is at least 30°C warmer than oven 1 effusion occurs with no observed clogging of the orifice. The sodium procedure is identical except for the final temperatures needed ($330^{\circ}/360^{\circ}\text{C}$) for smooth flow.

In the meantime the TCNE oven temperature should have been raised to at least 60°C to supply an excess of TCNE during reaction. When the onset of reaction is visually

observed, the deposition window is rotated to a position that presents its surface to the effusing vapors. Shields attached to the edges of the CsI window minimize deposition before and after the controlled segment of the reaction.

After the deposition is complete (1/2 hour to 1 hour) the heaters are turned off and the ensuing pressure drop permits the liquid nitrogen reservoir in the cell to act as a scavenger for excess TCNE. In less than an hour all signs of TCNE in the cell disappear, as a thick layer collects on the internal liquid nitrogen trap. Some limitation in sample thickness is caused by the energetic alkali metal vapor, which scatters both reactants and products. This problem can be alleviated, to some degree, by lowering the deposition-zone temperature to 0°C.

The low temperature preparations, where the deposition zone is maintained at -160°C, present a different set of problems. Control of the exact amounts of reactants, TCNE and the alkali metal, has not been achieved. This results in an excess of TCNE in the brown, non-crystalline deposit observed. Possibly this excess of TCNE could be removed by achieving extremely low pressures while holding the deposit at -160°C. Since this can not be accomplished with the available vacuum system the sample must be warmed. Warming the sample, however, results in a transition from the brown, glasslike deposit to the purple crystalline deposit. Further, this is an irreversible process. The tendency for the sample to "peel" from the window is a further consequence of this transition.

In summarizing the preparations, it appears that the room temperature trials have been successful, whereas the low temperature attempts indicate a need for more sophisticated controls.

Infrared Sampling

A Beckman IR-7 infrared spectrometer was employed for examination of all samples which were prepared. This is a double beam instrument capable of scanning from 200 to 4000 cm^{-1} . The region from 200 to 600 cm^{-1} is recorded using a CsI prism-grating interchange in the monochromator and is hereafter referred to as the CsI region. The region from 600 to 4000 cm^{-1} is scanned with a NaCl interchange. Since CsI is transparent over the region from 200 to 4000 cm^{-1} , as opposed to the lower limit of 600 cm^{-1} of NaCl, all cells are sealed by means of thin CsI crystals. The reference cell is a standard 10 cm gas cell which was periodically evacuated.

The reaction cell proper has two outer CsI windows in addition to the CsI plate upon which the sample has been deposited. The loss of energy due to scattering was minimized by careful polishing of the CsI windows on a flat glass surface prior to each trial.

The recording procedure was that which is commonly employed with this type of instrument. A recent modification which has been used effectively is the Tracking Accuracy Control module which permits the more precise positioning of strong absorption peaks.

After the degassing, but prior to sampling, a spectrum is obtained which represents the normal background due to the windows of the cell and general monochromator optics. This background absorption has been removed from all of the spectra presented. The preparations at reduced temperature (-160°C) were scanned while cold. The repetitive scan facilities of the instrument were employed to scan the 1100 to 1400 cm^{-1} region every eight minutes during the warming of the sample. In this mode of operation alterations occurring within this spectral range could be followed. Since there will be some absorption of energy by the sample this operation may have contributed to "peeling" of the low temperature samples as they approached room temperature. The room temperature preparations exhibited very little change over a period of days. Therefore, it was sufficient to record the spectrum at the end of deposition and again after the excess TCNE had been removed by the interior trap.

After normal observation a few selected samples were exposed to air and changes followed spectroscopically to confirm the position of oxidation product bands. This also provided a sensitive criterion of sample purity as the samples with excess potassium would oxidize almost immediately upon exposure to the atmosphere whereas the better samples could be maintained for longer periods of time if the relative humidity was less than 40%.

CHAPTER III

RESULTS

The major emphasis from an experimental point of view has been on the preparation of a thin film of the optically pure potassium derivative of tetracyanoethylene. The data from preparations carried out at room temperature will be described first.

The anion derivative film appeared to be uniform, with a metallic sheen by reflected light and a red-purple hue when observed by transmitted light. These visual checks are consistent with the descriptions in the literature (8). In general these samples were nearly opaque to visible light. The infrared spectra were recorded over the range of 200 to 4000 cm^{-1} and the major bands for all species investigated are tabulated in Table I. The bands listed are those which appear with regularity and represent major features which are considered to be unique to this species.

The three most intense K^+TCNE^- bands at 1371, 2180, and 2201 cm^{-1} are in good agreement with earlier published values (8), when differences in sampling procedures are considered. Bands appearing at 1187 and 970 cm^{-1} are also included as their intensity is consistent with the intensity of the 1371 cm^{-1} band in the series of preparations using potassium.

A number of secondary bands which appear consistently in the better preparations are included in the table and accompanying spectral reproductions (Plate IV). These are considered in more detail in the discussion section along with similar data obtained from the sodium preparation.

The low temperature (-160°C) data is not as conclusive due to the presence of excess TCNE, the bands of which complicate the assignments. The major features superimposed on the TCNE curve in Plate IV (top) are the bands at 1330 cm^{-1} and 2158 cm^{-1} . The excess TCNE, with many split bands caused by the nature of the low temperature crystal, obscures any weaker TCNE $^{\cdot-}$ absorptions which may be present.

The sodium derivative shows a predictable similarity to the 25°C potassium preparation. The major differences are found in the shift of the 1371 cm^{-1} band to 1390 cm^{-1} and an increase in the splitting observed in the doublet near 2200 cm^{-1} . The physical appearance of the film is essentially the same as that observed in the potassium case. The transmitted hue tends more to a blue tint of purple as opposed to the red-purple of the potassium derivative.

During the many trials necessary to obtain the spectra of pure samples certain other absorption patterns were noted along with their most probable causes. Two broad absorptions often appear at 1510 and 1600 cm^{-1} , indicating reaction of the anion with oxygen and/or water vapor. These bands are enhanced when the deposition window is deliberately exposed to the

atmosphere. During the trials there were occasions when an excess of potassium must have been present. The spectra recorded for these preparations exhibit a series of broad absorptions which decrease in intensity going from 2100 to 1800 cm^{-1} . These features tend to disappear in time if exposed to TCNE vapor. The highly hygroscopic excess potassium present in these particular samples results in almost instantaneous sample decomposition when the cell is opened. In contrast the product having a nearly 1:1 ratio will resist oxidation for much longer periods.

The low temperature preparations present the greatest opportunity for contaminants to complicate the picture. Even CO_2 is observed in some of the spectra. A major complication has been found in the region near 1300 cm^{-1} where the cold TCNE itself has a series of broad absorptions.

CHAPTER IV

INTERPRETATION OF RESULTS

Theory

The anion spectral features of most interest are a) the intense band at 1371 cm^{-1} for the potassium derivative (1390 cm^{-1} for the sodium analog), b) the marked absence of intensity in the 600 to 1300 cm^{-1} region where the strongest fundamentals were expected, and c) the strong doublet in the cyanide stretching region near 2200 cm^{-1} . At this time the proposed explanation of the unusual spectrum hinges entirely upon the origin of the intense 1371 cm^{-1} absorption which is not found in free TCNE.

In many conventional charge transfer complexes one observes enhancement of infrared active bands as well as the activation of Raman modes. The normal vibrations of the free TCNE are observed in the spectra of aromatic complexes with little or no shift in position. However, in the TCNE-hexamethylbenzene complex one new feature of interest is the band appearing at 1560 cm^{-1} . This band has been identified as the totally symmetric C=C stretching mode active only in the Raman spectrum of the free TCNE molecule. Surprisingly, polarization studies indicate that the oscillating dipole responsible for this absorption is oriented in a direction perpendicular to the TCNE molecular plane.

While the spectrum of the anion seems completely different from that of the complex, this 1560 cm^{-1} complex band and the 1371 cm^{-1} anion absorption can be shown to have a common origin if interpreted by the recent Ferguson and Matsen (11 - 12) theory of weak complexes. Their quantitative approach to the problem of enhancement and activation is based on the following argument. The ground state of the complex can be described by the wave function where the coefficient (a) determines the amount of no-bond character

$$\psi_n = a \psi_0(D,A) + b \psi_1(D^+A^-)$$

that $\psi_0(D,A)$ contributes to ψ_n . The square of the coefficient (b) approximates the contribution of the dative state $\psi_1(D^+A^-)$. Therefore if $\mu(D^+A^-)$ is defined as the dipole moment of the dative state directed between the donor and acceptor, the equivalent dipole moment of the complex is given by

$$\mu_n \approx b^2 \mu(D^+A^-).$$

This relation requires that a change in dipole accompany a change in the value of (b).

In terms of Q_1 , a normal coordinate such as the C=C stretching mode, it follows that

$$\left(\frac{\partial \mu_n}{\partial Q_1}\right)_{Q_1=0} = 2b\mu(D^+A^-) \left(\frac{\partial b}{\partial Q_1}\right)_{Q_1=0}.$$

Hence a relation exists which implies variation in the dipole directed between donor and acceptor provided (b) changes with Q_1 . By Mulliken's (13) theory of charge-transfer, (b) is directly related to the donor vertical ionization potential (I). Further, changes in the vertical ionization potential are functionally related to variations in scalar polarizability (p).

One can therefore relate, at least in a functional manner, the following parameters

$$\mu_n \propto b \propto b(I) \propto b(p).$$

In terms of the normal coordinate Q_1 , it follows that

$$\left(\frac{\partial \mu_n}{\partial Q_1}\right)_{Q_1=0} \propto \left(\frac{\partial b}{\partial Q_1}\right)_{Q_1=0} \propto \left(\frac{\partial p}{\partial Q_1}\right)_{Q_1=0}.$$

Recalling that for infrared activity the first term, $\left(\frac{\partial \mu_n}{\partial Q_1}\right)_{Q_1=0}$ must be nonvanishing, it is necessary, for infrared activation of Q_1 , that the scalar polarizability change must be non-zero for a change in Q_1 about $Q_1=0$. Mathematically stated, $\left(\frac{\partial p}{\partial Q_1}\right)_{Q_1=0} \neq 0$.

To fulfill this requirement the trace of the polarizability tensor must change as Q_1 changes. There are two ways that a molecular vibration can change the polarizability tensor; either result in Raman activity. The first of these is in terms of the orientation of the polarizability ellipsoid (14). Such modes change only the off-diagonal tensor elements. These off-diagonal elements do not contribute to the scalar

part of the polarizability; hence these motions are of no interest to us in this discussion. The only way to change the trace of the polarizability tensor is to have a totally symmetric vibration. Physically, this is equivalent to varying the size of the polarizability ellipsoid while keeping the principal axis fixed.

In summary this theory predicts that in a weak complex there can be infrared activation of the totally symmetric Raman fundamentals due to the variations in (b) caused by variations in the scalar polarizability. Ferguson and Matsen called this the "electron vibration" model since, on a time average basis, the electron would be pumped back and forth between the donor and acceptor with the frequency of the fundamental. Depending on the geometric relationship between donor and acceptor molecule, this electron vibration mechanism may give rise to an oscillating dipole perpendicular to the nuclear displacements. The intensity (A_i) of the observed infrared band will be a function of the magnitude of the variation in (b) with variations in Q_i and therefore a function of the magnitude of $\left(\frac{\partial p}{\partial Q_i}\right)_{Q_i=0}$. Mathematically this can be expressed by:

$$A_i \propto \left(\frac{\partial \mu_n}{\partial Q_i}\right)_{Q_i=0}^2 \propto \left(\frac{\partial p}{\partial Q_i}\right)_{Q_i=0}^2$$

The 1560 cm^{-1} band arising from the perpendicularly oscillating dipole in the TCNE- hexamethylbenzene complex is quite consistent with this picture. This is one of few solid

state examples where this "electron vibration" effect has been conclusively shown to exist through observation of the infrared dichroism.

Application of Theory to Tetracyanoethylenides

Armed with this seemingly powerful approach to the spectra of molecular complexes, the anion results can now be critically examined. However, certain statements and assumptions must be made concerning the nature of the species. The TCNE radical anion must now be considered as the donor with the alkali metal ion being the acceptor. A new wave function can be written for the anion salt where the coefficients represent the degree of

$$\psi_n = a \psi_0(K^+TCNE^{\cdot-}) + b \psi_1 \text{ (dative)}$$

contribution of the two forms to the total ground state wave function. The term $\psi_1(K^+TCNE^{\cdot-})$ would represent the dative state for the complex formed by $TCNE^{\cdot-}$ and the cation (100% electron transfer). The no-bond wave function, $\psi_0(K^+TCNE^{\cdot-})$ represents the situation where the highly polarizable anion is being perturbed by a "point charge" cation with high polarizing power due to the cation's high electron affinity. To operate within the framework of the Ferguson-Matsen theory it is assumed that $a \gg b$. Variations in the $TCNE^{\cdot-}$ scalar polarizability will cause changes in the dipole moment directed between the donor and acceptor.

Since the radical anion has one more electron than TCNE a suitable molecular orbital must exist for this electron to

occupy. Group-theoretic methods indicate that the most likely molecular orbital will provide additional bonding in the region of the C-C single bond and antibonding character for all other pairs of atoms. This qualitative molecular orbital picture of the TCNE radical anion predicts that the C-C single bond in plane stretching modes would be observed at slightly higher frequencies in the anion than in the neutral molecule due to the increased bond order. Other in-plane stretching modes would tend to lower frequencies due to a decrease in the bond order caused by the antibonding electron. This argument is most valid for stretching modes where the bond order has a more direct bearing on the vibrational frequency.

The totally symmetric C=C stretching mode (1569 cm^{-1} in the TCNE Raman spectra), now seems a logical origin for the intense 1371 cm^{-1} band observed in the infrared spectrum of K^+TCNE^- . Since the anion equivalent of the 1155 and 958 cm^{-1} TCNE modes should have comparable activity this singularly intense 1371 cm^{-1} band cannot be the result of a normal infrared fundamental. Therefore consider the arguments for activation of the Raman fundamental. First the intense Raman activity of the totally symmetric C=C stretching mode in TCNE implies a large change in the scalar polarizability. By Ferguson-Matsen theory this large value of $\left(\frac{\partial p}{\partial Q_1}\right)_{Q_1=0}$ would cause an intense infrared band such as the 1371 cm^{-1} absorption in the anion spectrum. Finally the 200 cm^{-1} shift of this band from 1569 cm^{-1} in the TCNE-hexamethylbenzene complex to 1371 cm^{-1} in the anion is reasonable since the qualitative

molecular orbital description predicts that the major anti-bonding effect will be observed in the C=C bond of the TCNE⁻.

The 1390 cm⁻¹ position found in the sodium anion derivative supports this assignment since the Na⁺ electron affinity is greater than that of potassium, thereby weakening the anti-bonding effects on the C=C stretching mode. In the low temperature potassium preparation, which is non-crystalline, this activated C=C stretching mode may account for the band at 1330 cm⁻¹ which converts to the 1371 cm⁻¹ position as the anion salt crystallizes.

It is also possible to assign one band of the doublet at 2200 cm⁻¹ to an activated totally symmetric cyanide stretching motion. Since the splitting does not appear in the non-crystalline sample it is reasonable to presume that the doublet has been caused by crystal effects. This observation was fortuitous since only one totally symmetric Raman mode should be present in this region.

The remaining totally symmetric fundamentals are considerably weaker in the Raman spectrum of TCNE, implying a smaller change in scalar polarizability. Considering this small change in $\langle p \rangle$ plus the lack of detailed knowledge of bond order changes, any further "electron vibration" assignments at this time would be presumptuous.

However, the high polarizability of the anion, necessary to permit the large values of $\left(\frac{\partial p}{\partial Q_1}\right)_{Q_1=0}$ implied by the intense activation at 1371 and 2180 cm⁻¹, does suggest an unusually free electron(s). This unusually free electron(s) offers a

mechanism which may be equally important in interpreting the anion spectra. It is reasonable to consider the radical electron as occupying a potential well having an unusually flat surface extending over the molecular dimensions. This electron which is therefore delocalized within the plane of the entire molecule is capable of reacting to the instantaneous dipole moments which the molecule presents during normal vibrations. This dipole-electron correlation would manifest itself in a decrease in the observed intensity of a particular mode by partial cancellation of the dipole.

This correlation effect, coupled with the shift to higher frequencies caused by a C-C bond order increase, permits identification of the weak anion bands at 1188 and 970 cm^{-1} with the fundamentals (C-C stretching) which give rise to intense absorption in TCNE (1155 and 960 cm^{-1}). These thus correspond to the strongly infrared active fundamentals which would otherwise appear in this region. A comparison of these features for equivalent samples of the anion and TCNE, indicate that this correlation effect is considerable.

Since the extent of electron correlation depends upon the breadth of the shallow region in the potential well it would not be expected to exert as strong an influence on the various out of plane vibrational dipoles where the electron "well" must be considerably more restrictive to electron motion. This is consistent with the rich spectrum observed in the CsI region where out of plane vibrational modes are expected.

It would seem ill-advised at this time to attempt further assignment without the results from thicker samples, Raman data and some firm estimate of the effect of changes in bond order on these low frequency modes.

It is appropriate at this point to qualify the above statements concerning the weaker absorptions. There is yet no absolute proof that these could not be attributed to trapped TCNE even in the room temperature preparations. This is not as serious as it may seem since, even if true, it would not alter the major activation assignments, the interpretation of the shifts in fundamentals, or the need for a model (i.e. the electron-dipole correlation) to explain the absence of intensity in the infrared active planar modes.

CHAPTER V

SUMMARY AND CONCLUSIONS

In summary the Ferguson-Matsen approach to molecular complexes predicts the infrared activation of fundamentals which are totally symmetric. Apparently, because of the unusual polarizability of the anion, this mechanism is the source of the two strongest features observed in the anion spectrum. A further consequence of the high anion polarizability manifests itself in electron correlation with the in-plane infrared fundamentals. The out of plane anion fundamentals and two additional activated totally symmetric modes should be observed in the CsI region. Although this region is rich in observed absorption bands the data is not conclusive at this time. A more thorough investigation with greater sample density would certainly provide more information concerning the infrared active fundamentals of the anion itself. A study of the TCNE⁻ Raman spectrum would permit irrefutable identification of the activated modes. Single crystal studies using polarized light, should facilitate interpretation by determining the directionality of the dipole oscillations involved.

A study of the variations in anion spectral behavior when formed from a periodic series such as Li, Na, K, Rb, Cs or Zn, Cd, Hg would help define the role of the cation in these compounds. The sandwich metal complexes such as ferrocene (dicyclo-

pentadienyl iron) may provide a series of complexes with TCNE which show the transition between the weak aromatic-TCNE complexes and the anion salts.

It would also be helpful to investigate the crystal structure of the anion salts to obtain their true molecular geometry. Knowledge of the angles and intermolecular dimensions would simplify the interpretive problem. With or without the geometric data, there is a need for more theoretical consideration of the actual molecular orbitals which are involved in the electron transfer.

Finally, what has been accomplished to date is essentially a preliminary study. Methods have been developed for preparation and sampling of various salts of the anion of TCNE which give a reasonable measure of success. It is not deliberately implied that these techniques are the best, but rather to present them as convenient for preparing the anion in a form suitable for infrared sampling.

A tentative interpretation of the observed data is offered based on the relationship of the dative coefficient (b) to donor scalar polarizability which was derived as an extension of the Ferguson and Matsen theory. It is not the intent or purpose of this thesis to offer this as a final answer, but rather a model which can be used as a guide to further experiments and thus ultimately lead to a conclusive interpretation of the anion spectrum. This model, or some modification derived from further data, may provide a lever which will be useful in studying similar complexes involving highly polarizable anions, which are now becoming available.

TABLE I

Frequencies in cm^{-1} of the Major Bands in the IR Spectra

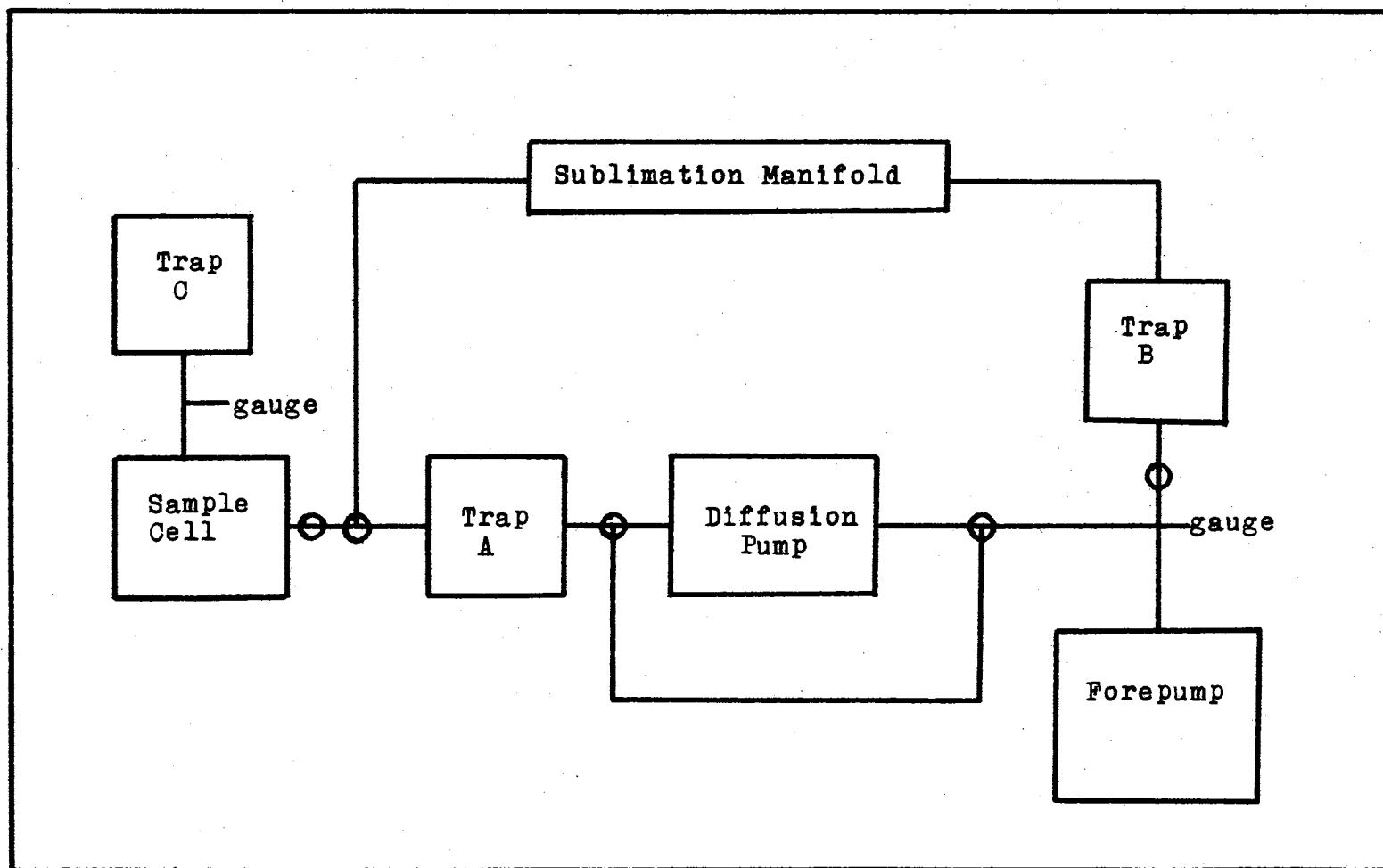
| <u>K^+TCNE^- (@ 23°C)</u> | | | <u>K^+TCNE^- (@ - 160°C)</u> | |
|---|----|-----|--|------|
| 970 | | 270 | | |
| 1187 | | 460 | | |
| 1371 | s* | 472 | | 1330 |
| 2180 | s | 523 | s | 2158 |
| 2201 | s | 537 | | |
| 2260 | | 552 | s | |
| 2270 | | | | |

| <u>Na^+TCNE^- (@ 23°C)</u> | | |
|--|---|-----|
| 970 | | 270 |
| 1187 | | 458 |
| 1390 | s | 467 |
| 2185 | s | 521 |
| 2210 | s | 530 |
| 2260 | | 554 |
| 2280 | | s |

| <u>TCNE (5)</u> | |
|-------------------------------------|---|
| 958 | s |
| 1155 | s |
| 2228 | s |
| 2260 | s |

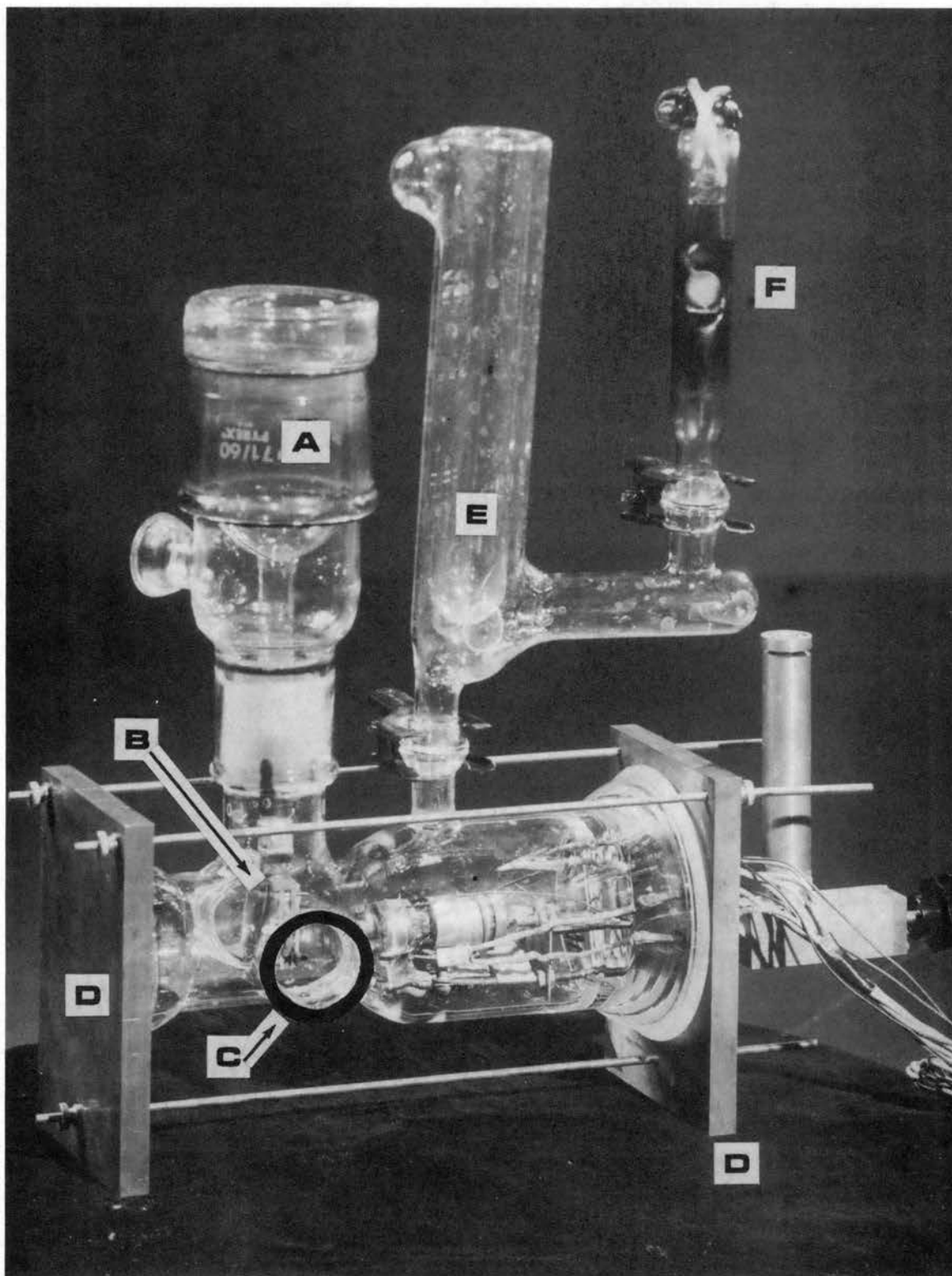
* s = strong absorption, all others weak

Plate I



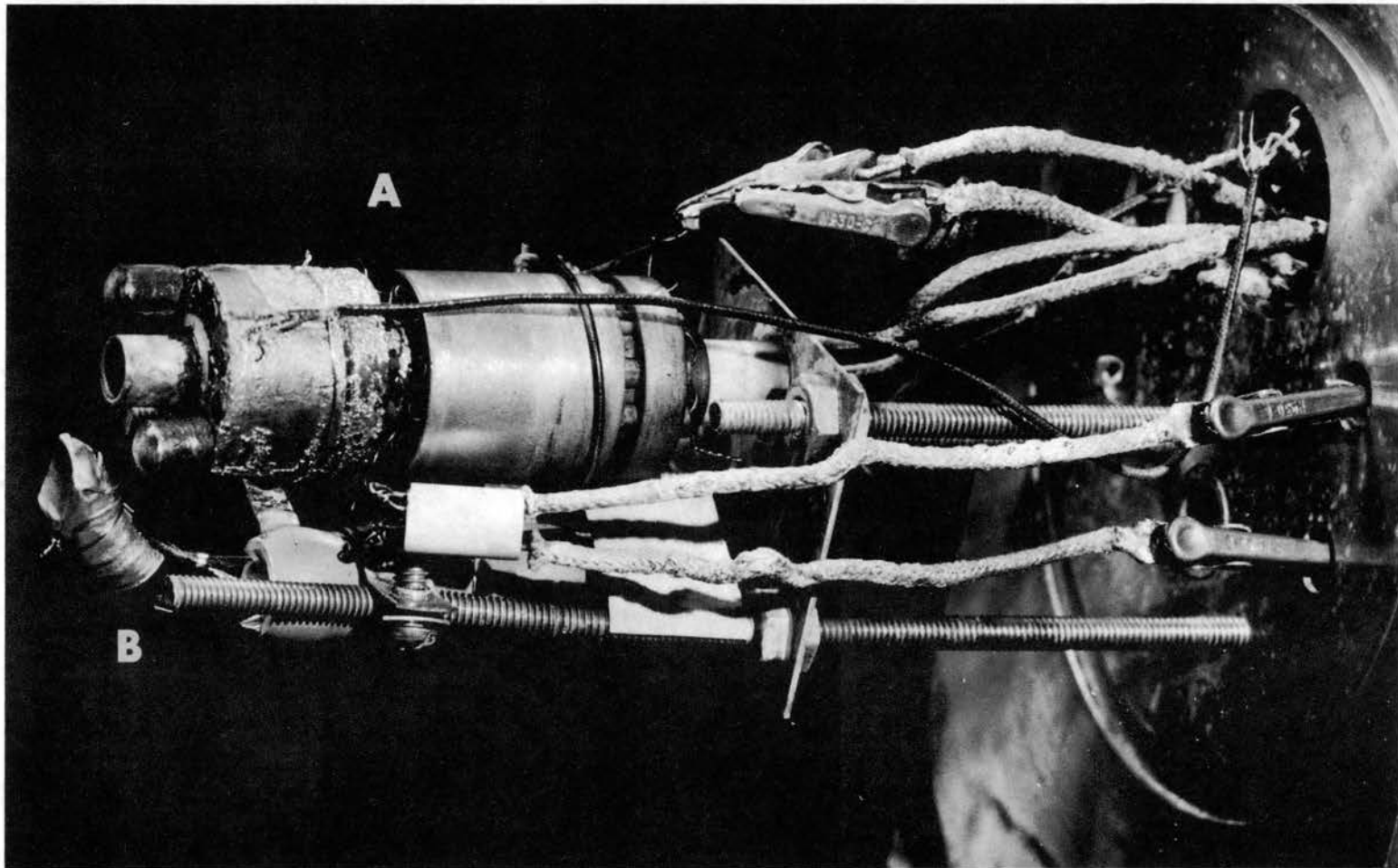
Schematic of Vacuum System

Plate II

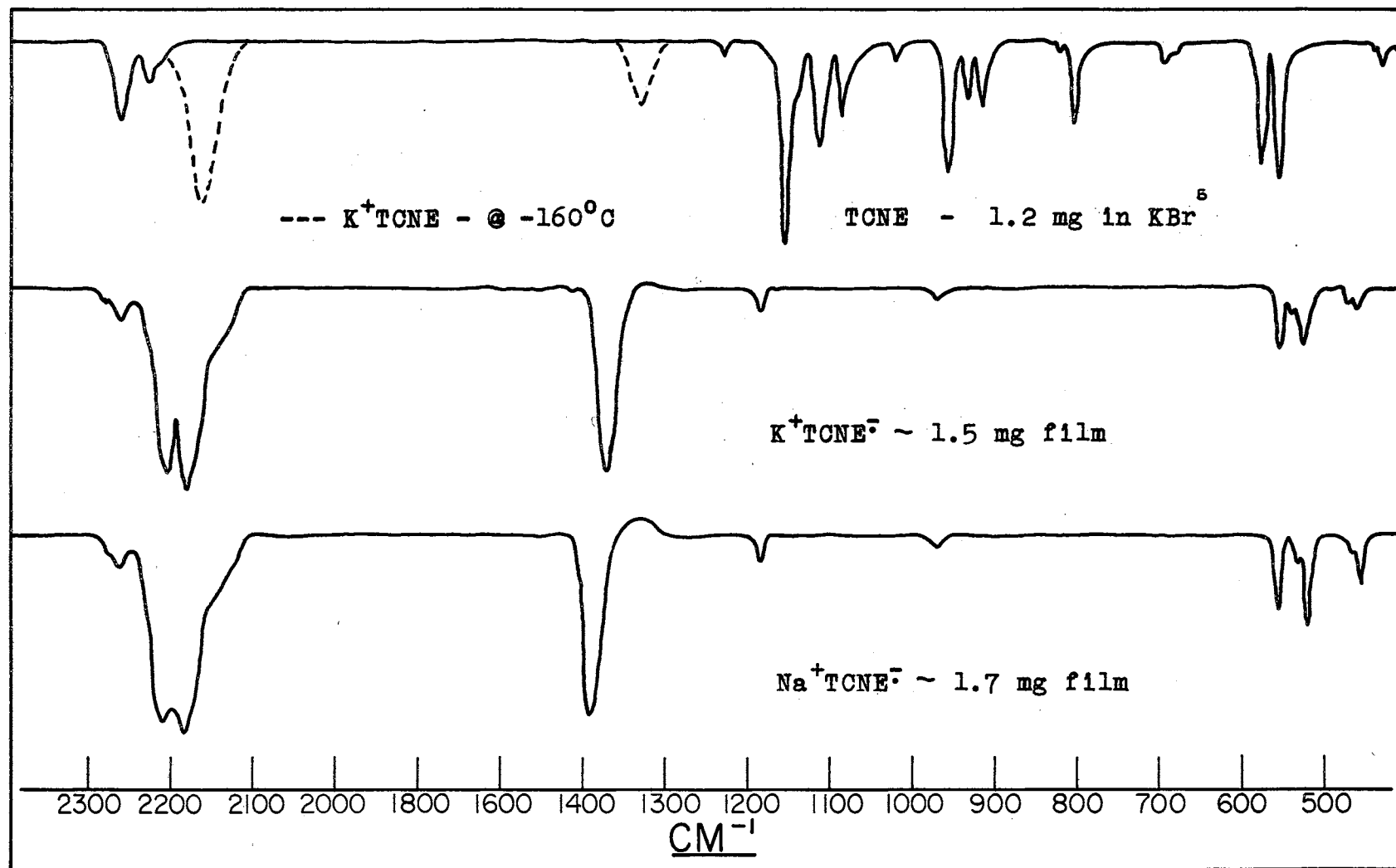


Sample Preparation Cell

Plate III



Vaporization Ovens (Interior of Plate II)



Spectra of TCNE and TCNE^- Derivatives

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