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Title
STUDIES IN MOLECULAR STRUCTURE: I. FEAR-ULTRAVIOLET SPECTRUM OF TETROLALDEHYDE. II. SIMPLE MOLECULAR ORBITAL THEORY OF THE DICHLORETHYLENES. III. HIGH-TEMPERATURE MICROWAVE SPECTROSCOPY

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James S. Muirhead

(Ph. D. Thesis)

January 29, 1964
STUDIES IN MOLECULAR STRUCTURE

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II. SIMPLE MOLECULAR ORBITAL THEORY OF THE DICHLOROETHYLENES

III. HIGH-TEMPERATURE MICROWAVE SPECTROSCOPY

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January 29, 1964

ABSTRACT

Part I

The near-ultraviolet absorption spectrum of tetrolaldehyde vapor has been examined. The weak absorption appearing in the 300-400-\(\mu\)m region has been assigned as the \(\pi^*\pi^*\) transition, and a vibrational analysis places the 0-0 transition at 26,620 cm\(^{-1}\) and yields a value for the C=O stretch frequency in the \(\pi^*\) state of 1036 cm\(^{-1}\).

Two other regions of absorption are observed in the 200-300-\(\mu\)m range, and one of these with center at 47,333 cm\(^{-1}\) is tentatively assigned as the \(\pi^*\pi^*\) transition. The second of these appears as weak structure on the long-wavelength edge of the first and may arise from a space-forbidden \(\pi^*\pi^*\) transition.

Part II

A simple molecular orbital treatment, including overlap, has been employed to compute the electron distribution and energy eigenvalues of the dichloroethylenes. The Coulomb and exchange integrals used were those previously employed for vinyl chloride and were not subject to further adjustment in the present calculations. Comparison with available
photoionization potentials, electric dipole moments, and nuclear quadrupole data show, on the whole, a satisfactory agreement between observed and calculated properties. The results obtained are considered to provide support for the occurrence of lone-pair conjugation in the vinyl halides.

Part III

A high-temperature microwave spectrometer has been assembled to operate in the temperature range up to 1100°C. The absorptions due to OCS and KCl have been observed and the sensitivity of the spectrometer determined. With the present sensitivity of $10^{-7}$ cm$^{-1}$, it should be possible to detect absorptions due to diatomic molecules but not those arising from bent triatomic molecules. The design, construction, and assembly of the spectrometer are described. Several recommendations for design modifications are given. No spectra arising from previously unassigned molecules were found.
I. NEAR-ULTRAVIOLET ABSORPTION SPECTRUM OF TETROLALDEHYDE

A. Introduction

As the result of extensive work on the ultraviolet absorption spectra of unsaturated conjugated aldehydes, cf. McMurray\textsuperscript{1} and Sidman\textsuperscript{2}, one has now come to expect that such a molecule will exhibit two regions of absorption in the near ultraviolet. The first of these is a weak absorption showing long vibrational progressions and lying in the 300-400-\textmu m region. As stated by Sidman in his review article, this absorption is to be identified as the \( \pi \rightarrow \pi^* \) transition and involves excitation of electrons localized principally in the carbonyl group.

The second transition is some hundred times more intense and has a diffuse appearance similar to that of the \( \pi \rightarrow \pi^* \) transition in such molecules as ethylene and butadiene. The position of the second absorption band is somewhat more variable than that of the first but may be expected to lie in the neighborhood of 200 \textmu m for molecules such as acrolein\textsuperscript{3,4} and propargyl aldehyde\textsuperscript{5}.

Examination of the near-ultraviolet absorption spectrum of tetrolaldehyde, \( \text{CH}_3\text{C}≡\text{C}-\text{CHO} \), fully confirms these expectations, there being two absorption regions of the type described above. The similarity of these absorptions to those observed in the case of acrolein\textsuperscript{4} and of propargyl aldehyde\textsuperscript{5} suggests a large degree of similarity in \( \pi \)-electron bonding among these three molecules, and affords the hope that such data may be used in correlating certain of their properties.

As is stated in reference 5, in attempting such a correlation, it is useful to introduce a simplified model for these acetylenic aldehydes.
in which only two of the \( n \) electrons in the triple bond are allowed to interact with the carbonyl group. Although this model stresses the formal similarity to the acrolein \( n \)-electron system, it is apparent, because of the differences in sp and sp\(^2\) hybridized carbon, that the analogy cannot be taken as exact. In addition, as will be seen below, there is some evidence for the existence of a third region of absorption in the acetylenic aldehydes which is not observed in acrolein or crotonaldehyde, and which possibly arises from transitions of the two "unconjugated" acetylenic \( n \) electrons.

B. Experimental

Due to its similarity to propargyl aldehyde, an attempt was made to prepare tetrolaldehyde by a normal chromic acid oxidation from the alcohol. This method did not succeed, presumably because the product underwent further oxidation before it could escape from the hot acid solution.

Various other methods were also tried. These usually resulted in an impure product or no product at all. Finally, a pure sample was prepared by the method of Lunt and Sondheimer.\(^6\) The propyne used was purchased rather than freshly prepared, but the remainder of the synthesis was followed rather closely. The Grignard reagent resulting from the reaction of propyne with ethylmagnesium bromide was allowed to react with ethyl orthoformate to form tetrolaldehyde diethyl acetal. The acetal was then hydrolyzed overnight under an inert atmosphere with a saturated solution of tartaric acid.

After extraction with ether and two vacuum distillations a pure sample was obtained. The boiling point and refractive index of the
tetrolaldehyde and the melting point of the 2-4-dinitrophenylhydrazone were all found to be in excellent agreement with the published values.

It was found that tetrolaldehyde, as well as crotonaldehyde, is stable at room temperature but is very susceptible to autoxidation. This is in distinct contrast with propargyl aldehyde and acrolein, which polymerize at room temperature but are reasonably resistant to air oxidation.

A sample of propargyl aldehyde was prepared by the method of Wille and Saffer and was used for comparison spectra.

C. Interpretation of Spectra

The spectra were recorded on a Cary model 14 double-beam spectrophotometer using a 10-cm absorption cell fitted with removable fused quartz windows. A wavelength calibration curve for the Cary was obtained by scanning the iron arc emission spectrum. With the use of this calibration, the resultant reading accuracy on these recordings was ±0.1 Å.

The more accurate wavelengths were determined by photographic methods using a Baird Associates 3-m grating instrument in first order and with a 25-μ slitwidth. The Kodak type III-0 plates used were sensitized with Eastman Kodak ultraviolet sensitizer No. 2. A Leeds and Northrup microphotometer was used to make tracings for measurement, the wavelengths then being determined by comparison with the iron arc spectrum. The reading accuracy on the tracings was ±0.05 Å with a plate dispersion ~ 5.5 Å/mm. The photographic absorption spectra were obtained using a 1-m cell and a xenon continuum source.

1. n→π* Transition

A recording of the long-wavelength transition of tetrolaldehyde
vapor as obtained with the Cary double-beam instrument is shown in
Fig. I-1. This absorption region exhibits all of the properties normally
ascribed to an $n^\pi^*$ transition and is so assigned: It is the transition
of lowest energy, shows long vibrational progressions, is weak
($\epsilon_{\text{max}} \approx 9$ liter/mole-cm), and exhibits a shift to higher frequency when
observed in solution.

The observed frequencies, corrected to vacuo, are listed in Table
I-1. These frequencies were obtained from measurements on densitometer
tracings of plates made with the Baird grating instrument. Although fre­
quencies could be measured to an accuracy of the order of 1 cm$^{-1}$, diffi­
culties associated with partially resolved rotational structure or with
low intensities precluded actual attainment of such accuracy. It is
believed that most of the frequencies listed in Table I-1 are accurate
to $\approx 4$ cm$^{-1}$, with those marked by an asterisk being accurate to $\approx 10$ cm$^{-1}$.
The relative intensities in Table I-1 are relative extinction coefficients,
in arbitrary units, as measured with the double-beam instrument.

Examination of the spectrum reveals the expected progressions.
By visual inspection, the more intense bands may be grouped into three
series with each member of a series being a doublet. The designation of
bands thus identified is given in Table I-1, where the literal index
identifies the series, the numerical index the member of the series, and
the prime refers to the less intense and higher-frequency member of the
doublet. The validity of these groupings is substantiated by the
measured frequencies, the mean interval in the a series being 1037 cm$^{-1}$,
1034 cm$^{-1}$ in the b series, and 1038 cm$^{-1}$ in the c series. The interval
between a member of the a series and the closest member of the b series
is more variable and ranges from about 275 to 300 cm$^{-1}$, with a mean
Table I-1. Principal absorption bands in the n→π* transition of
tetrolaldehyde.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm⁻¹)</th>
<th>Designation</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26 491</td>
<td>a (0)</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>26 620</td>
<td>a′(0)</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>26 743</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>26 931</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>26 962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>27 076*</td>
<td>a (1)</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>27 540*</td>
<td>a′(1)</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>27 678</td>
<td>b (0)</td>
<td>0.7</td>
</tr>
<tr>
<td>9</td>
<td>27 816*</td>
<td>b′(0)</td>
<td>0.4</td>
</tr>
<tr>
<td>10</td>
<td>27 954</td>
<td>c (0)</td>
<td>0.5</td>
</tr>
<tr>
<td>11</td>
<td>28 077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>28 135</td>
<td></td>
<td></td>
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<tr>
<td>13</td>
<td>28 183</td>
<td></td>
<td></td>
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<tr>
<td>14</td>
<td>28 288</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>28 401*</td>
<td>a (2)</td>
<td>0.4</td>
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<tr>
<td>16</td>
<td>28 581</td>
<td>a′(2)</td>
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<tr>
<td>17</td>
<td>28 707</td>
<td>b (1)</td>
<td>1.3</td>
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<tr>
<td>18</td>
<td>28 873</td>
<td>b′(1)</td>
<td>0.4</td>
</tr>
<tr>
<td>19</td>
<td>29 006</td>
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</tr>
<tr>
<td>20</td>
<td>29 113</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>29 270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>29 334*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>29 390*</td>
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</tr>
<tr>
<td>24</td>
<td>29 490*</td>
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<td></td>
</tr>
<tr>
<td>25</td>
<td>29 611</td>
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<td>26</td>
<td>29 733</td>
<td>a (3)</td>
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<td>29 887*</td>
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<td>c (1)</td>
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<tr>
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<td>30 451*</td>
<td>c′(1)</td>
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<tr>
<td>33</td>
<td>30 572*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>30 666*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>30 779*</td>
<td>a (4)</td>
<td>0.2</td>
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<tr>
<td>36</td>
<td>30 992*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>31 056*</td>
<td>b (3)</td>
<td>0.5</td>
</tr>
<tr>
<td>38</td>
<td>31 202*</td>
<td>b′(3)</td>
<td>0.2</td>
</tr>
<tr>
<td>39</td>
<td>31 347</td>
<td>c (2)</td>
<td>0.4</td>
</tr>
<tr>
<td>40</td>
<td>31 487*</td>
<td>c′(2)</td>
<td>0.1</td>
</tr>
<tr>
<td>41</td>
<td>31 626*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>31 717*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>31 836*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>31 970*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>32 104*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
interval of 289 cm\(^{-1}\); the corresponding mean b to c interval is 279 cm\(^{-1}\).

The doublet, i.e., prime to unprime, interval is also variable within a series and ranges from \(\approx 125\) to 175 cm\(^{-1}\).

Since the \(\pi^*\) transition is formally allowed, it is natural to identify the band \(a(0)\) as the 0-0 transition. The promotion of a nonbonding electron to an antibonding \(\pi\) orbital in the \(\text{C}==\text{O}\) group is expected to lead to long progressions of the \(\text{C}==\text{O}\) stretch frequency in the \(\pi^*\) state. Thus, even though it is some 250 cm\(^{-1}\) lower than the \(\text{C}==\text{O}\) stretch interval found in acrolein or in propargyl aldehyde, the prominent interval of 1036 cm\(^{-1}\) found here is probably the \(\text{C}==\text{O}\) stretch frequency in the excited state. As previously stated, the other two frequencies which also appear are more variable in magnitude but may be taken as having average values of 285 and 150 cm\(^{-1}\). Neither one of these can be unequivocally assigned, but it is perhaps reasonable to think of the higher frequency as associated with a skeletal mode and of the lower, since acrolein also shows doubling whereas propargyl aldehyde does not, as a torsional mode.

2. 200-225-\(\mu\) Region

As indicated previously, tetrolaldehyde exhibits intense absorption in the 200-225-\(\mu\) region. Figure I-2 shows a recording of this region obtained with the Cary spectrometer and with a sample pressure of 0.1 mm Hg. In addition to high intensity, \(\epsilon_{\text{max}} \approx 1 \times 10^4\) liters/mole-cm, this transition is characterized by a diffuse triplet appearance, the three partially resolved peaks lying at 49 004\(\pm\)125 cm\(^{-1}\), 47 333\(\pm\)25 cm\(^{-1}\), and 45 440\(\pm\)25 cm\(^{-1}\). The appearance of this region is very similar to one in propargyl aldehyde, \(\text{H}==\text{C}==\text{C}==\text{CHO}\), in which \(\epsilon_{\text{max}} \approx 4 \times 10^3\) liters/mole-cm and for which the vapor phase frequencies are 50 157\(\pm\)20 cm\(^{-1}\),
Although the transition responsible for the 200-225-μν absorption region cannot be identified with certainty, it is reasonable to consider it as N→V in type; i.e., the absorption probably involves excitation from a π to π* state, at least one of which is closely associated with the triple-bond electrons. This assignment is suggested by the intensity of the absorption, by its diffuse appearance, by a redshift on replacing H by CH₃, by a redshift upon solution in 2,2,4-trimethylpentane, and by an occurrence of intervals on the order of 1600-1900 cm⁻¹. In addition, Price has assigned both the region with maximum at 1935 Å in acrolein and the region with maximum at 2030 Å in crotonaldehyde as N→V.

3. 235-250-μν Region

Figure I-3 is a tracing recorded with the Cary at the same sample pressure as that used for the n→π* region. Obviously the positions, intensities, and even the number of bands present cannot be determined due to the extreme slope of the N→V absorption. However, an absorption of the same intensity and essential structure is found in propargyl aldehyde (Fig. I-4). Unfortunately, several of the sharper bands in propargyl aldehyde appear to be due to an impurity since they increase with time. Nevertheless, some of the bands are constant and apparently are due to a third, weak absorption. There are no similar bands in the ethylenic aldehyde spectra, and thus one is led to the conclusion that the bands are associated with the acetylenic part of the molecule. In addition, on the basis of the previously proposed model, it is predicted that a weak transition should occur at a frequency a few thousand wave numbers above that of the N→V (π→π*) transition.

This transition has its origin in the near degeneracy which exists...
between the lowest levels of the in-plane and out-of-plane acetylenic \( \pi \) electrons, the interaction of the out-of-plane electrons with the carbonyl group having relatively little effect on the out-of-plane acetylenic state \( \pi_0 \). A simple semiempirical MO calculation, cf. Goldstein,\(^8\) predicts that the acetylenic \( \pi_0 \) state should lie some 0-0.5 eV lower in energy than the \( \pi_1 \) state, the exact value of course depending on the amount of interaction allowed across the C—C single bond. Moreover, in keeping with these results and the planar model, if it is assumed that the acetylenic linkage possesses \( C_{2v} \) local symmetry (in this respect see Platt\(^9\)), then the transition \( \pi_1 \rightarrow \pi_0^* \) has the symmetry \( B_1 \rightarrow B_2 \) and is forbidden. The actual molecular symmetry is \( C_s \) so that the transition is formally allowed but weak; the situation is analogous to that pertaining to \( n \rightarrow \pi^* \) transitions in carbonyl compounds which do not have \( C_{2v} \) symmetry.

D. Discussion

In discussing the experimental results for tetrolaldehyde it is of interest to consider, first, the effect upon the bonding in an acetylenic aldehyde when acetylenic H is replaced by \( \text{CH}_3 \), and secondly, to what extent the acetylenic aldehyde \( \pi \) system resembles the ethylenic aldehyde \( \pi \) system.

With regard to the effect of replacement of H by \( \text{CH}_3 \), a comparison of the experimental data for tetrolaldehyde with that for propargyl aldehyde\(^5\) shows that in tetrolaldehyde the \( n \rightarrow \pi^* \) transition is shifted 460 cm\(^{-1}\) to higher energy, the \( \text{C—O} \) stretch frequency in the \( \pi^* \) state is 255 cm\(^{-1}\) lower, and the transition tentatively assigned as \( N-V \) lies some 1300 cm\(^{-1}\) lower in energy. All of these effects are attributable to electron release by the methyl group through the inductive effect, cf. Coulson,\(^10\) and through the effect of hyperconjugation.\(^11\) As stated by
Nagakura,\textsuperscript{12} the $n \rightarrow \pi^*$ transition involves transfer of negative charge from the oxygen to the carbon atom and will consequently undergo a blueshift when the electron density in the neighborhood of the carbon atom is increased by adjacent groups. Similarly, the decrease in the $C=O$ stretch frequency may be said to reflect an increased degree of ionic character of the $C=O$ bond in the $\pi^*$ state. And lastly, it is well known, cf. references 10 and 11, that hyperconjugation between $CH_3$ and unsaturated linkages generally leads to a redshift of the $N \rightarrow V$ transition.

Unfortunately, as regards the similarities between the $\pi$ electron systems of the ethylenic and acetylenic aldehydes, no satisfactory general statements can be made. If the problem is approached from the standpoint of semiempirical MO theory, one is impressed by the differences in both Coulomb and exchange integrals for the $sp^2$ and $sp$ cases. Yet, it is experimentally observed that the $C=O$ frequencies for the acrolein and propargyl aldehyde $n \rightarrow \pi^*$ transitions lie within some 300 cm\textsuperscript{-1}, a similar order of agreement being found for crotonaldehyde\textsuperscript{13} and tetroaldehyde. It would thus appear that the state of the $C=O$ group is much the same in all of these molecules and that this degree of similarity can arise only by virtue of weak interaction of this group with the attached ethylenic or acetylenic linkage.
REFERENCES

Part I

13. This is based on an approximate 0—0 frequency estimated from band contours as observed in this Laboratory.
II. SIMPLE MOLECULAR ORBITAL THEORY OF THE DICHLORETHYLENE

A. Introduction

The idea that conjugated systems can be viewed in terms of resonance between two or more participating structures has formed the basis for a widely used and often successful method for the rationalization of molecular properties. Recently, however, Dewar and Schmeising have taken the position that resonance effects are relatively unimportant in the ground states of those organic molecules for which only a single classical structure can be written, and that effects usually ascribed to resonance in such cases are in reality to be accounted for primarily by changes in the state of hybridization of the carbon atoms. This viewpoint has been discussed by other authors who have reviewed a variety of evidence which appears to indicate that hybridization alone is unlikely to be the sole factor responsible for the characteristic properties of conjugated systems.

The haloethylenes comprise a class of molecules which have long been cited as examples of systems whose properties are significantly affected by resonance. In vinyl chloride, for example, an early estimate of \( \approx 20\% \) double-bond character (\( \text{CH}_2\text{-CH=Cl} \)) was inferred from the shortening of the C-Cl bond based upon electron diffraction studies. Further support for the existence of conjugation in the vinyl halides (Cl, Br, I) has been provided by theoretical analyses of the hyperfine structure in the microwave spectra of these molecules, which has its origin in the interaction of the nuclear electric quadrupole with a nonvanishing electric field gradient in the immediate vicinity of the nucleus. This treatment is based upon the formulation of a measure, \( \delta \), of charge
transferred from the halogen atom to the \( \pi \)-electron system, which is to
a very good approximation independent of the \( \pi \)-electron system, and which
can be expressed in terms of the experimentally determined quadrupole
coupling constants. Although the existence of a nonzero value of \( \delta \)
in the vinyl halides is to be interpreted as supporting the idea of
lone-pair conjugation in these molecules, the actual results indicate
that extent of double-bonding is \( \approx 5\% \), which is considerably smaller
than the value of 20\% previously reported.

In the subsequent development of this approach, it was shown that
the quantity \( \delta \) could be used to determine empirically the value of the
carbon- halogen exchange integral, \( \beta_{CX} \), in the simple molecular orbital
(MO) treatment of the \( \pi \)-electron systems of the vinyl halides.\(^6\) Moreover, without further adjustment of any of the parameters involved, the
results of this MO treatment were found to predict other molecular
properties of several vinyl and phenyl halides in rather good agreement
with observation.\(^7,8\)

It is the purpose of this paper to present the results of similar
calculations for the three dichlorethylenes. The MO parameters employed
have been slightly altered to reflect the improved values of the inter-
nuclear distances presently available for vinyl chloride. Apart from
these minor changes, all the calculations were carried out without ad-
justment of the parameters chosen at the outset.

B. Theory

The LCAO-MO calculations, with inclusion of overlap, require that we solve the simultaneous matrix equations

\[
\begin{align*}
T \mathbf{H} \mathbf{\tilde{T}} &= \mathbf{H}^0, \\
T \mathbf{S} \mathbf{\tilde{T}} &= \mathbf{I},
\end{align*}
\]

(II-1) (II-2)
where $\mathbf{H}$ is the Hamiltonian in the AO basis, $\mathbf{S}$ is the overlap matrix in the same basis, $\mathbf{S}^0$ is a diagonal matrix, and $\mathbf{I}$ is the unit matrix. These equations may be rewritten in a form suitable for solution by high speed digital computers as

$$
\mathbf{C} \mathbf{S}^{-1/2} \mathbf{H} \mathbf{S}^{-1/2} \mathbf{C} = \mathbf{H}^0,
$$

$$
\mathbf{C} \mathbf{S}^{-1/2} \mathbf{C} = \mathbf{I},
$$

$\mathbf{S}^{-1/2}$ is readily obtained from a series expansion in powers of $\xi$, where $\xi = \mathbf{S} - \mathbf{I}$. The one-electron MO's are given by

$$
\mathbf{C} = \mathbf{S}^{-1/2} \phi.
$$

We next define an electron density matrix, $\mathbf{n}$, which describes the distribution of electrons among the various one-electron eigenfunctions, $\mathbf{r}$. In the MO basis, $\mathbf{n}^0$ is diagonal and $n_{ij}^0$ is the number of electrons in the state $\mathbf{r}_i^j$. With this definition, the molecular expectation value, $\overline{A}$, of an operator $A_{op}$ is given by the equation

$$
\overline{A} = \text{Tr} \mathbf{n}^0 A^0_{op},
$$

where $A^0_{op}$ is the matrix representative of $A_{op}$ in the MO basis. Transformation of this expression to the AO basis gives:

$$
\overline{A} = \text{Tr} \mathbf{C} \mathbf{n} \mathbf{A},
$$

$$
\mathbf{n} = \mathbf{S}^{-1/2} \mathbf{C} \mathbf{n}^0 \mathbf{C} \mathbf{S}^{-1/2}.
$$

The elements of $\mathbf{n}$ have the significance that $n_{ii}$ is the electron density associated with the $i$th center and $2n_{ij} S_{ij}$ is the corresponding density for the $i$-$j$ region.

Having briefly described the computational method, we now proceed to apply it to the $\pi$-electron systems in the dichloroethylenes. A total of six electrons must be considered and the AO basis consists of
a 2p AO centered on each of the carbon atoms and a 3p AO centered on each of the chlorine atoms. The next steps in the procedure are the evaluation of the matrix $\mathbf{S}$, and the choice of suitable values for the elements of $\mathbf{H}$.

**C. Calculations**

1. **Evaluation of $\mathbf{H}$ and $\mathbf{S}$**

Values of the required structural parameters were taken as $d(C-C) = 1.333$, $d(C-Cl) = 1.724$ Å, and $< C-C-Cl > = 123.6$ deg; these values are based on recent microwave studies\(^9\,\text{to}^\text{10}\) of $CH_2CHCl$ and $CH_2CCl_2$. Using these values, $S_{C-C} = 0.273$ and $S_{C-Cl} = 0.137$ were obtained from published tables for overlap integrals of Slater functions.\(^11\) Values of $S_{Cl-Cl}$ were found to be more than a factor of ten smaller. Accordingly both $S_{Cl-Cl}$ and $H_{Cl-Cl}$ were set equal to zero.

As recommended by Mulliken,\(^12\) the value of the carbon Coulomb integral was taken as $H_C = \text{8.14 eV}$; $H_{C-C}$ was chosen as $-5.23$ eV so as to reproduce the observed ionization potential of ethylene when used with the $S_{C-C}$ value above. The value of the chlorine Coulomb integral was fixed by the equation $H_{Cl} = H_C + (V_{Cl} - V_C) = \text{-10.64 eV}$, the $V$ being appropriate valence state energies.\(^13\)

Since only nearest-neighbor interactions will be considered in this work the only remaining quantity to be determined is $H_{C-Cl}$. As shown in reference 6, this value may be fixed by using the observed quadrupole coupling constants of $CH_2CHCl$. Since the previously determined value was based on different structural parameters this calculation has been repeated with the results given in Table II-1. The indicated choice is $H_{C-Cl} = 2.35$ eV, and it may be noted in passing that this value
correctly reproduced the observed ionization potential.

Table II-1. Results of CH₂CHCl calculations.

<table>
<thead>
<tr>
<th>-HCl' (eV)</th>
<th>I, (eV)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.30</td>
<td>10.03</td>
<td>0.055</td>
</tr>
<tr>
<td>2.35</td>
<td>10.00</td>
<td>0.061</td>
</tr>
<tr>
<td>2.40</td>
<td>9.97</td>
<td>0.066</td>
</tr>
<tr>
<td>Exptl.</td>
<td>10.00ᵃ</td>
<td>0.061ᵇ</td>
</tr>
</tbody>
</table>

ᵃ Reference 15.
b Reference 9.

This completes the specification of H and S. We are now able to perform a simple MO calculation for the dichloroethylenes in which there are no adjustable parameters. All of the computations described here were performed on an IBM 704 computer and were carried to eight significant figures. The series expansion for S⁻¹/² was carried through the tenth power of S.

2. 1,2-Dichloroethylene

The calculated energy levels are given in Table II-2. Since the nearest-neighbor approximation is used here, these values, and also the value of H, apply equally well to both the cis and trans species. This calculation therefore predicts that the ionization potentials of the cis and trans species are identical and are equal to -E₂, i.e., have the value of 9.66 eV. It is interesting to note that although Walsh¹⁴ has reported ionization potential values for the cis and trans species of 9.65 and 9.96 eV, more recent photoionization work by Watanabe et al.¹⁵ resulted in the values 9.65±0.01 and 9.66±0.03 eV.
Table II-2. Calculated MO energies (eV).

<table>
<thead>
<tr>
<th></th>
<th>CHClCHCl</th>
<th>CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁</td>
<td>3.33</td>
<td>3.29</td>
</tr>
<tr>
<td>E₂</td>
<td>9.66</td>
<td>9.78</td>
</tr>
<tr>
<td>E₃</td>
<td>10.79</td>
<td>10.64</td>
</tr>
<tr>
<td>E₄</td>
<td>11.29</td>
<td>11.35</td>
</tr>
</tbody>
</table>

Pertinent elements in the AO basis of the ground state density matrix are given in Table II-3; the AO's are labelled according to the scheme Cl(3)-C(1)-C(2)-Cl(4). The calculated value of the lone-pair defect is δ = 2-n₃₃ = 0.051. Unfortunately no precise experimental value of δ is available for comparison. However, data from the microwave spectrum of cis 1,2-dichloroethylene indicate the δ has a probable value in the range 0.04-0.06.¹⁶

Table II-3. Electron Density in CHClCHCl.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>n₁₁, n₂₂</td>
<td>0.826</td>
<td></td>
</tr>
<tr>
<td>n₃₃, n₄₄</td>
<td>1.949</td>
<td></td>
</tr>
<tr>
<td>n₁₂</td>
<td>0.768</td>
<td></td>
</tr>
<tr>
<td>n₁₃, n₂₄</td>
<td>0.056</td>
<td></td>
</tr>
</tbody>
</table>

An additional check on the probable validity of the density matrix is afforded by calculating the dipole moment of the π-electron system according to the equation \( \mu_\pi = e \sum_j Z_j R_j - eTr \varphi \varphi^T \), \( Z_j \) being the charge of the \( j \)th nucleus when stripped of its π electron(s), \( R_j \) the corresponding position vector, and \( \varphi \) being the matrix of the electronic position vector. The required elements of \( \varphi \) may be calculated in closed
form from Slater functions and the molecular geometry. The result is that $\mu_\pi$ is opposite to the expected direction of the $\sigma$ moment and has a magnitude of 0.60D.

In order to compare this value with experiment it is necessary to assume independence of the $\sigma$ and $\pi$ moments, and then to estimate the value of $\mu_\sigma$ from the observed moments of suitable saturated molecules. In the present case, in order to reproduce the observed moment of 1.89D, a $\sigma$ moment of 2.5D is required. By using the structural parameters previously given, this is equivalent to a moment of 1.5D lying along each of the C-Cl bonds. Since Smyth gives the value of the C-Cl bond moment as 1.46D, the calculated value of $\mu_\pi$ is in acceptable agreement with experiment, particularly in view of the simplifications and assumptions introduced.

3. 1,1-Dichloroethylene

The computational technique used for the 1,2-dichloroethylenes may also be applied to the case of 1,1-dichloroethylene. The previously given values for the elements of $H$ and $Q$ are appropriate here although the matrices themselves will reflect the fact that the two carbon centers are no longer equivalent. Again, it should be pointed out that there are no adjustable parameters.

The results of the energy-level calculations are given in Table II-2, where they may be compared with those for CHClCHCl. The predicted first ionization potential has the value 9.78 eV. From Rydberg-series data Teegan and Price find the value 9.46 eV; there appears to be no photoionization value available. Since it appears unlikely that the ionization potential of CH$_2$CCl$_2$ is lower than that of CHClCHCl this
experimental value is subject to suspicion.

Results of the electron density calculation for the ground electronic state are shown in Table II-4; the labelling scheme is given by C(1)-C(2)-Cl(3)-Cl(4). In this case the calculated value of δ is 0.060. From their study of the microwave spectrum of 1,1-dichloroethylene, Sekino and Nishikawa\textsuperscript{10} report the value 0.058.

Table II-4. Electron Density in $\text{CH}_2\text{CCl}_2$.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{11}$</td>
<td>0.943</td>
<td></td>
</tr>
<tr>
<td>$n_{22}$</td>
<td>0.716</td>
<td></td>
</tr>
<tr>
<td>$n_{33}$, $n_{44}$</td>
<td>1.940</td>
<td></td>
</tr>
<tr>
<td>$n_{12}$</td>
<td>0.757</td>
<td></td>
</tr>
<tr>
<td>$n_{32}$, $n_{42}$</td>
<td>0.088</td>
<td></td>
</tr>
</tbody>
</table>

As before, the electron density matrix may be used in calculation of the electric dipole moment arising from the six $\pi$ electrons. In this way it is determined that $\mu_{\pi}$ has the magnitude $1.39\text{D}$ and is opposite to the expected direction of the moment resulting from the $\sigma$ electrons. In this case, because large inductive effects between the two C-Cl bond moments are likely, attempts to assign a $\sigma$ moment seem unprofitable. However, reference to Table II-5 would indicate that the calculated $\pi$ moment is substantially in agreement with experiment.

Table II-5. Calculated dipole moments

<table>
<thead>
<tr>
<th></th>
<th>Observed moment</th>
<th>Calculated $\pi$ moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-$\text{CHClCHCl}$</td>
<td>$1.89\text{D}^a$</td>
<td>$0.60\text{D}$</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CCl}_2$</td>
<td>$1.34\text{D}^b$</td>
<td>$1.39\text{D}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reference 17  
\textsuperscript{b} Reference 20
D. Conclusions

The results of the calculations described above indicate that the general approach and the values of the MO parameters employed in the case of vinyl chloride can be successfully transferred to the dichloroethylenes. As far as experimental data are available for comparison, the computed values of $\delta$, $\mu$, and $I$ appear to be in satisfactory agreement with observation. These results further strengthen the contention that appreciable conjugation exists between the lone-pair electrons on a halogen atom and the $\pi$-electron system to which it is bonded, and that the effects of this conjugation are evident in at least some of the important molecular properties of the haloethylenes.
REFERENCES

Part II


III. HIGH-TEMPERATURE MICROWAVE SPECTROSCOPY

A. Introduction

Microwave spectroscopy as a means for determining molecular structure is well known. However, the application of microwave techniques has been, in general, limited to those molecules possessing vapor pressures greater than 0.01 mm at room temperature. The extension of the method to those molecules with insufficient vapor pressure is the principal application of high-temperature microwave spectrometers. The limitations of this type of apparatus are best demonstrated in terms of the molecular complexity of the compounds to be studied, i.e., diatomic, triatomic, and polyatomic.

The peak intensity of an absorption line of a diatomic molecule is given by Townes and Schawlow, their Eq. (1-77), as

$$\gamma_{\text{max}} = \frac{4\pi^2 \hbar N f_{\nu} \mu^2 \nu_0^3}{3 c (kT)^2 \Delta\nu}.$$  (III-1)

By using the parameters listed in Table III-1, a value of $1.6 \times 10^{-4}$ cm$^{-1}$ is calculated for the $J = 3 \leftarrow 2$ transition of KCl. The same procedure gives a maximum absorption coefficient of $2 \times 10^{-6}$ cm$^{-1}$ for AgCl in the K-band region. These values are representative of the diatomic metal halides and, as will be shown, lead to easily observable spectra. Linear triatomic molecules have absorption coefficients of the same order as diatomics and are smaller only because of the vibrational population distribution. Of course, the molecule must have a dipole moment to be observable and many linear molecules, such as HgCl$_2$, will not have observable microwave spectra.

The class of bent triatomic molecules contains many compounds that
Table III-1. Peak intensities for some diatomic molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\theta$</th>
<th>$\omega$</th>
<th>$\mu$</th>
<th>$B_e$</th>
<th>$\Delta\nu$</th>
<th>$J' \leftarrow J$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°K)</td>
<td>(cm$^{-1}$)</td>
<td>(Debye)</td>
<td>(Mc)</td>
<td>(Mc)</td>
<td></td>
<td>(cm$^{-1}$)$^a$</td>
</tr>
<tr>
<td>$^{39}$K$^{35}$Cl</td>
<td>1000</td>
<td>300</td>
<td>10.48</td>
<td>3856</td>
<td>10</td>
<td>3 $\leftarrow$ 2</td>
<td>1.6 $\times$ 10$^{-4}$</td>
</tr>
<tr>
<td>$^{107}$Ag$^{35}$Cl</td>
<td>1200</td>
<td>400</td>
<td>2(est)</td>
<td>2800</td>
<td>10</td>
<td>4 $\leftarrow$ 3</td>
<td>2 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>$^{7}$Li$^{37}$Cl</td>
<td>1000</td>
<td>400</td>
<td>7</td>
<td>21181</td>
<td>10</td>
<td>1 $\leftarrow$ 0</td>
<td>1.8 $\times$ 10$^{-4}$</td>
</tr>
</tbody>
</table>

$^a$ These intensities include the isotope distribution factor but neglect quadrupole interactions.
are stable at high temperatures and they all have dipole moments by symmetry. However, bent triatomics are asymmetric rotors and have lower absorption coefficients than diatomic molecules. The formula for the peak absorption coefficient for an asymmetric rotor is given by Townes and Schawlow,\(^1\) their Eq. (4-28), as

\[
\gamma_{\text{max}} = \frac{8\pi \hbar N f_v (2J+1)|\mu_{14}|^2 \nu^2}{3c (kT)^2 \Delta \nu} \left(\frac{\hbar ABC}{kT}\right)^{1/2} \exp\left(\frac{W_{JK-1 K-1}}{kT}\right) \tag{III-2}
\]

Using the parameters given in Table III-2, the maximum absorption coefficient for the \(3_{31} \leftarrow 2_{20}\) transition in PbCl\(_2\) is calculated to be \(2 \times 10^{-8}\) \(\text{cm}^{-1}\) (neglecting quadrupole interactions). This is four orders of magnitude weaker than the KCl line considered above, and the expected quadrupole multiplets could easily decrease the intensity by another factor of 10. The intensity calculated for the microwave absorption line of H\(_2\)O is given for comparison in Table III-2. It is interesting to note the small temperature dependence of the H\(_2\)O line. This is due (a) to the large rotational constants which make the Boltzmann term small at low temperatures and (b) the high vibrational frequencies which keep the vibrational partition function near unity even at high temperatures.

The effect of small rotational constants and low vibrational frequencies on the predicted strength of the PbCl\(_2\) lines can be seen from the calculated intensity at 300\(^\circ\)K given in Table III-2. As will be shown, this factor of 40 in intensity takes the lines from the class of easily observable all the way down to the extreme lower limits of our sensitivity.
Table III-2. Peak intensities for some triatomic molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>T (°K)</th>
<th>$f_v$ (Debye)</th>
<th>$\mu$ (Gc)</th>
<th>A (Gc)</th>
<th>B (Gc)</th>
<th>C (Gc)</th>
<th>$v$ (Gc)</th>
<th>$J_{K'<em>{-1},K</em>{-1}}$</th>
<th>$J_{K'<em>{-1},K</em>{-1}}$</th>
<th>$\gamma$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>300</td>
<td>1.0</td>
<td>1.94</td>
<td>833</td>
<td>435</td>
<td>299</td>
<td>22.2</td>
<td>6.16</td>
<td>5.23</td>
<td>9 X 10$^{-6}$</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>1100</td>
<td>0.88</td>
<td>1.94</td>
<td>833</td>
<td>435</td>
<td>299</td>
<td>22.2</td>
<td>6.16</td>
<td>5.23</td>
<td>2 X 10$^{-6}$</td>
</tr>
<tr>
<td>Pb$^{208}Cl_{35}$</td>
<td>800</td>
<td>0.21$^b$</td>
<td>3.16</td>
<td>6.4</td>
<td>1.6</td>
<td>1.3</td>
<td>25.0</td>
<td>3.31</td>
<td>2.20</td>
<td>2 X 10$^{-8}$</td>
</tr>
<tr>
<td>Pb$^{208}Cl_{35}$</td>
<td>300</td>
<td>0.72$^b$</td>
<td>3.16</td>
<td>6.4</td>
<td>1.6</td>
<td>1.3</td>
<td>25.0</td>
<td>3.31</td>
<td>2.20</td>
<td>9 X 10$^{-7}$</td>
</tr>
</tbody>
</table>

---

a All intensities in this table are calculated by assuming a line-width parameter of 10 Mc.

b The vibrational partition function is evaluated with estimated frequencies of 300, 600, and 650 cm$^{-1}$. Somewhat lower values are suggested by Brewer, Somayajulu, and Brackett.$^2$

c Neglecting quadrupole interaction and nuclear spin statistics.
Several high-temperature microwave spectrometers have been assembled for the purpose of studying those molecules that have insufficient vapor pressure at normal temperatures. The general design of these spectrometers has usually been a simple modification of a conventional spectrometer. That is, the microwave source, the method of Stark modulating, and the detection systems have all had the same characteristics as room-temperature spectrometers.

The absorption cell for a conventional system consists of a section of waveguide with mica or Mylar windows at each end, which allow microwave transmission while providing sample isolation. It is necessary that the total pressure in the cell be kept below 1 mm to prevent line-broadening due to molecular collisions. Provision for Stark modulation is normally made by installing a thin conducting sheet, called the Stark septum, inside the absorption cell. The septum is placed parallel to the broad face of the rectangular guide and extends the entire length of the cell. Modulation is accomplished by applying a zero-based square wave to the septum, which must be exactly centered between the broad faces of the cell to allow accurate dipole moment measurements. In a room-temperature spectrometer the septum is usually supported by grooved Teflon strips running along the narrow faces of the waveguide. The temperature range of a conventional spectrometer is therefore generally limited by the stability of the materials used for the windows and the Stark septum insulators.

The first three heated cells were designed to operate in the neighborhood of 150 to 250°C. These cells are described by Mays and will not be elaborated on here.
The first spectrometer designed for very high temperatures was constructed by Stitch, Honig, and Townes at Columbia University. They chose to use gold-plated nickel for their waveguide and Stark septum. Nickel was chosen because of its structural strength at high temperatures; the cell was gold-plated to improve its chemical inertness. The cell was mounted vertically so that the septum required support in only a few places rather than continuously along its length. Forsterite, a steatite, was used both for the supports and for the cell windows. The whole section of waveguide was placed in a vacuum furnace. This prevented air oxidation of the hot parts and also simplified the problem of cell leaks. Since the only pressure on the cell windows was the sample pressure, considerable leakage could be tolerated. The window, which was under atmospheric pressure, was at room temperature and therefore could be made of mica.

A mechanical system was used for sample control. This provided a convenient means for confirming the validity of observed absorptions simply by removing the sample and noting the disappearance of the lines.

This spectrometer was very successful in obtaining spectra of most of the alkali halides and later the Tl, In, and Ga monohalides.

Another spectrograph was assembled by Tate and Strandberg at MIT. It consisted of a stainless steel waveguide and Stark septum with quartz insulators. The waveguide was enclosed in a Vycor tube with quartz windows sealed to the tube. A clearance of 7 mm was left between the waveguide and the windows to allow for the difference in expansion coefficients. Vacuum and electrical connections were made through a Vycor sidearm which was kept near room temperature. The
sample was admitted by heating another sidearm. A commercial tube
furnace was used to heat the absorption cell.

Happ\(^8\) used a brass cell with mica windows to study TlI and BiCl\(_3\). Only the central 1-m section of the 3-m cell was heated. The Stark septum was also only 1-m long and was supported with quartz insulators. The sample was admitted in the middle of the cell and was allowed to condense on the walls of the waveguide outside the heated region. The attenuation of microwaves by the condensed salt was apparently no problem. This result is reasonable as long as the deposits are thin films outside the modulation region, since the microwave electric field is primarily in the center of the waveguide and is quite small at the edges. If molten salt were to be collected on the mica windows, however, the attenuation should be quite noticeable because condensation puts a conducting layer in the path of the microwaves.

Fitzky,\(^9\) and later Hoeft,\(^10\) used a system similar to Happ's except that they used a frequency-stabilized source. Fitzky did a superb examination of all the isotopic species of the thallous halides. Hoeft gave a similar excellent treatment of the indium monochloride isotopes. The spectrometers of Happ and Fitzky were designed to operate in both the 1.5- and 3-cm wavelength regions.

The cell which might be considered the direct predecessor of the one described here was built by Professor John Howe during his tenure as a graduate student at Harvard University. It is of a different type from those previously described in that the waveguide is a dielectric rod.\(^11\) The cell consisted of a quartz tube sealed around a quartz plug at each end. The microwaves then travel along a quartz rod connecting the two plugs. According to the theory of dielectric
rod waveguides, part of the microwave power is transmitted within the rod and the remainder is transmitted in the space surrounding the rod. The sample is contained in the quartz tubing so no further window material is needed. The Stark electrodes used were a pair of external parallel plates. Due to the abnormally large spacing required for this arrangement, extremely high Stark voltages were needed to get the desired field strengths. The resulting capacitance of the system was also considerably larger than that usually encountered. The high voltages and large capacitance necessitated extremely high charging currents to provide a good square wave; these currents led to severe coupling problems between the modulator and detector systems.

Howe also experienced trouble with spurious signals, which he attributed to either a glow discharge within the cell or nonreproducible molecular absorptions. Due to the observed dependence of the signals on sample temperature it was impossible to ascertain the cause of the signals.

Two new spectrometers have been assembled since the initiation of this thesis project. The only published description of these two to date has been in a joint paper on the spectrum of LiCl. The spectrometer of Gold and Cahill at Columbia University is very similar to the ones built by Happ and Fitzky. They use nickel waveguide and septum with ceramic insulators for the Stark electrode. The waveguide is 38-1/2-in. long but the septum is only 22-in. long. The septum is located entirely within the hot region of the waveguide, which is the 28-in. section inside the furnace. The ends of the waveguide outside the furnace are water-cooled sufficiently well to allow the use of mica windows. A pressure of about 1 mm of N₂ is left in the cell as a
buffer gas to keep the salt vapor from effusing to the cold portions of the cell. The buffer gas causes line widths on the order of 1 to 2 Mc, due to pressure broadening. The frequency range of this cell is apparently from 10 Gc to at least 42 Gc. The LiCl spectrum is the only reported observation to date on this spectrometer.

Lide's spectrometer was constructed at the National Bureau of Standards in Washington, D.C. It has a new innovation with respect to applying Stark modulation. The waveguide is of stainless steel and has been split down the narrow face. The halves are separated by ceramic spacers and the voltage is applied between the two halves. The resulting internal dimensions are 5 by 20 mm and, according to the report, the Stark field is sufficiently uniform to give well-resolved Stark components of the type $\Delta M = \pm 1$. This spectrometer also uses a "flow" type sample system with only a portion of the cell contained within the furnace. Lide reports that his best results are obtained with a buffer gas in the cell. Due to the small dimensions of the waveguide, the cell is usable only above 30 Gc. Since the intensity of absorptions increases as the cube of the transition frequency for a diatomic molecule [see Eq. (III-1)], this high-frequency requirement may be an advantage rather than a limitation.

Lide has also reported on the spectrum of AlF$^{15}$ and AlCl$^{14}$ in addition to LiCl. Unlike the majority of the compounds examined to date, AlF and AlCl were not obtained simply by heating a pure sample of the salt. These compounds were formed in the high-temperature cell by the reaction of the aluminum trihalide with excess aluminum. From the viewpoint of high-temperature chemistry, the observation of a diatomic molecule in the gas phase can be used to establish the
amount of polymerization in the gas$^{16}$ or the thermodynamic stability of an unusual oxidation state, as in AlF. Lide$^{14}$ has used the observed strength of the absorption for AlF to establish limits on the thermodynamic properties of AlF.

The original design of the spectrometer described in this thesis is due to Professor John Howe, now of Bell Telephone Laboratories, Murray Hill, New Jersey. Mr. William Chamberlain of the Lawrence Radiation Laboratory did the actual mechanical design. Basically, the spectrometer is a parallel-plate waveguide, the plates also serving as Stark electrodes, enclosed in a ceramic tube. The cell is entirely enclosed in a vacuum furnace.

The use of a parallel-plate waveguide was originally described by Gordy.$^{17}$ In principle the parallel plate is ideal in that there is no obstruction of the microwave path by either septum or insulators. Also, the problem of field uniformity should be solved with little difficulty. The practical limitations will be discussed in a later section.

The choice of ceramic materials for construction was dictated by a desire for high temperature stability (the cell was designed to operate up to 1100°C) and the need for chemical inertness. Platinum was chosen as the material for the metal surfaces mainly because of its chemical inertness and high work function with respect to thermionic emission.$^{18}$ The various components of the system will be discussed individually, where possible, with respect to design, fabrication, and modifications, past and future.

At the time of this thesis the only molecules to have been assigned
by high-temperature microwave spectroscopy have been diatomic halides. The assigned molecules are listed in Table III-3. References to molecular beam studies are also included.

B. System Components

1. Vacuum Furnace

The furnace is contained in a 7-1/2-in. steel pipe mounted vertically on a 4-in. support pipe. The heated region is 4-1/2-in. in diameter and 69-in. long and is surrounded by a mullite tube. Mullite is one of the principle construction materials. It is a compound containing 30% SiO₂-70% Al₂O₃, which decomposes at 1800°C. The choice of mullite for many of the parts may not have been advisable, as will be seen later.

The mullite tube around the hot region serves two main purposes: (1) it is used as the support to hold the heat shields, and (2) it serves as a barrier to keep any gas that escapes from the absorption cell from condensing on the heat shields. The effectiveness of this barrier can be noted from the fact that, after 40 high-temperature experiments (in which many grams of salt were lost from the cell into the furnace area), the furnace only dropped in temperature about 25°C per hour at 600°C after the heater input was turned off. The power input required for 600°C steady state is about 350 W. Stitch et al. reported a steady-state input of 500 W for the same temperature with "new" radiation baffles and 900 W with "old" ones. The heat shields used in this furnace are 0.0005-in. tantalum-foil sheets hanging in concentric rings around the mullite tube. Due to the inaccessibility of these sheets, they have not been examined since installation.
Table III-3. Assigned high-temperature molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>References</th>
<th>Molecule</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>g</td>
<td>CsF</td>
<td>a</td>
</tr>
<tr>
<td>LiCl</td>
<td>p</td>
<td>CsCl</td>
<td>a</td>
</tr>
<tr>
<td>LiBr</td>
<td>a,e</td>
<td>CsBr</td>
<td>a,e</td>
</tr>
<tr>
<td>LiI</td>
<td>a,e</td>
<td>CsI</td>
<td>a,e</td>
</tr>
<tr>
<td>NaF</td>
<td>h</td>
<td>GaCl</td>
<td>b</td>
</tr>
<tr>
<td>NaCl</td>
<td>a</td>
<td>GaBr</td>
<td>b</td>
</tr>
<tr>
<td>NaBr</td>
<td>a,e</td>
<td>GaI</td>
<td>b</td>
</tr>
<tr>
<td>NaI</td>
<td>a,e</td>
<td>InCl</td>
<td>b,o</td>
</tr>
<tr>
<td>KF</td>
<td>f</td>
<td>InBr</td>
<td>b</td>
</tr>
<tr>
<td>KCl</td>
<td>a,m</td>
<td>InI</td>
<td>b</td>
</tr>
<tr>
<td>KBr</td>
<td>a,e,n</td>
<td>TlF</td>
<td>b,d</td>
</tr>
<tr>
<td>KI</td>
<td>a,e</td>
<td>TlCl</td>
<td>b,d,i;j</td>
</tr>
<tr>
<td>RbF</td>
<td>k,l</td>
<td>TlBr</td>
<td>b,d</td>
</tr>
<tr>
<td>RbCl</td>
<td>a,k</td>
<td>TlI</td>
<td>b,c,d</td>
</tr>
<tr>
<td>RbBr</td>
<td>a,e</td>
<td>AlF</td>
<td>q</td>
</tr>
<tr>
<td>RbI</td>
<td>a,e</td>
<td>AlCl</td>
<td>r</td>
</tr>
</tbody>
</table>

References for Table III-3


c) H. Happ, Z. Physik 147, 567 (1957).


References for Table III-3 (cont.)

The heat shields at the ends of the tube consist of stacks of "dimpled" and "plain" sheets of 0.010-in. tantalum alternated to give minimum thermal contact. These stacks are readily accessible and do show some signs of contamination and corrosion. However, they have not been replaced and probably will not need to be for quite a few more runs.

The heaters are 0.004- by 0.25-in. tantalum ribbon. The wiring arrangement is shown in Fig. III-1. Each of the elements is a 12-ft section with both ends clamped at the top of the furnace. The strips are kept taut at all times by the weight of the lower end insulator. This insulator holds all four elements in place and also provides a hanger for the bottom stack of heat shields. It has been found that the length of each heater strip is extremely important to trouble-free heating. If any one heater is as much as 1/4-in. longer than the ones adjacent to it, when it gets hot it will sag or bow enough to allow it to short out to the metal supports on the absorption cell. A new type of clamp with a more accurate method of adjusting the length of the heater strips would be a tremendous advantage in overcoming this fault.

It would also be advantageous to have a larger hole in the lower end insulator and heat shield stack. If the absorption cell axis does not exactly coincide with the furnace axis, the heat shield stack binds against the sample tube assembly and therefore does not hang on the heaters. This allows the heater strips to sag and short out.

The resulting short circuits burned out the silicon rectifiers being used in the dc power supplies. For convenience the supplies were replaced with two 20-A Variacs. The wiring scheme, as shown in Fig. III-1, has been quite satisfactory and a similar circuit is used.
Heating elements

Heater support (typical)

20-A Variac

20-A Variac

115 V ac

MU.33368
for the heaters involved in sample control.

The furnace and sample temperatures are measured by five thermocouples connected to a multipoint Leeds and Northrup recorder. Three thermocouples are used for the furnace and absorption cell area and the other two thermocouples are used for recording the sample temperature. Initially, noble-metal thermocouples (commercially available under the name "Platinel" from Engelhard Industries) were installed. The alloy employed reproduces the output of a chromel-alumel couple over the temperature range of interest. This gives the maximum available sensitivity over these temperatures and also provides some protection from chemical attack. Unfortunately, the mechanical strength of the Platinel is not suited to the relatively strenuous treatment involved in installation in this particular apparatus. After several experiments had to be terminated owing to failure of vital thermocouples, chromel-alumel couples were installed.

The first set of chromel-alumel thermocouples were removed after 25 high-temperature experiments. They appeared to be in good operating condition and were replaced only because the cell had to be dismantled for repairs to other sections. The thermocouples are mounted inside ceramic tubes fastened to the outside of the absorption cell. The thermal contact of the couples with the cell is hard to maintain when the dimensions change on heating. Somewhat erratic readings are obtained when the components are moving with respect to each other but these false readings cause no serious difficulties.

The normal procedure for making a vacuum feedthrough for a chromel or alumel wire is to completely tin the end of the wire with hard solder. This tinned area can then be soft-soldered into the feedthrough. The
feedthroughs used in this apparatus are metal-ceramic-metal junctions known as Advac seals. Due to the problems involved in obtaining a perfect inning of the thermocouple wire, a somewhat different procedure was followed in making the vacuum seal.

In the modified procedure only a small area on the wire needs to be tinned with hard solder. This is then crimped to a copper wire and is soft-soldered. The copper wire is inserted through the Advac seal and soft-soldered to it. Since the thermocouples-to-copper junction is very close to the furnace wall it is essentially at room temperature and can be corrected for by use of similar junctions in the reference cell circuit.

The power for the auxiliary heaters used for sample control is also brought into the furnace in the same manner. The heater wires are 0.020-in. tantalum and are also very hard to tin with hard solder. In addition, the copper wire used has a considerably lower resistance and therefore generates less heat in the vacuum seal. Because of the high temperature of the heater wire, solder is unsatisfactory for the copper-tantalum junction and a screw-type mechanical clamp is used to connect the two wires.

The vacuum system consists of a VMF-20 diffusion pump (20 liters/sec) with silicone oil backed by a Welch 1397 mechanical pump (5 liters/sec). Pressure measurements are made using two standard thermocouple gauges or an ion gauge, depending on the pressure region. The system as designed does not have a cold trap. It would be convenient to add a trap in order to increase the effective pumping speed when outgassing and to prevent contamination of the pump oil.

Generally speaking, the furnace has been designed so conservatively
that under all the conditions encountered to date it has performed very well.

2. **Absorption Cell**

As in all types of absorption spectroscopy, the purpose of the absorption cell is to contain the sample in the path of the radiation. In the microwave-frequency region of the spectrum it is necessary to provide a waveguide to keep the power localized. The alternative method of using optics to focus the microwaves is made impractical by the large dimensions required to operate in this wavelength region. Some means of modulation, such as Stark or Zeeman effect, is also necessary in order to observe any except the very strongest of absorptions.

A parallel-plate configuration was chosen for the waveguide in this spectrometer. The particular advantage of this arrangement is the ease with which a uniform electric field can be applied to the sample. This arrangement also avoids placing any dielectric material in the microwave field and thereby eliminates losses which occur in ceramics at high temperatures. Unfortunately, at least for the dimensions used in this spectrometer, the losses due to scattering out the sides of the parallel plate far exceed those due to the attenuation of microwaves by the spacers in a system with a Stark septum.

The microwaves are fed into the cell via the brass transition piece and oval tantalum waveguide shown in Fig. III-2 (upper right). The portion on the right side is a buffer pressure region containing a transition from the normal rectangular waveguide to an oval waveguide. There is a Mylar window at each end of the brass section, and the region between the windows is kept at a pressure of 1/2 atm. This
pressure distribution decreases the probability of a window rupturing. This is important since the heaters and most of the heat shields would be destroyed if a large volume of air was admitted to the cell while at elevated temperatures.

The tantalum waveguide is used to guide the microwaves into the hot region of the furnace. The oval shape was chosen in order to allow fabrication since it is extremely difficult to form tantalum into a rectangular tube. The outer end of the upper tantalum guide is hard-soldered into a water-cooled copper block. The lower tantalum guide is also shown in Fig. III-2. It is not water-cooled and is shown disconnected from the lower transition piece.

The microwave path is via the brass transition piece, the upper tantalum guide, and through an alumina horn into the cell. The power transmitted by the cell passes out through a similar arrangement to the detector. The microwave horns are ground to the shape pictured in Fig. III-3 and are installed by press-fitting them into the alumina heads as shown in Fig. III-4. In the cell the broad end of each horn is inserted between the faces of the parallel plate.

The parallel-plate assembly is constructed from eight blocks, each of which has a flat surface 2-1/4 by 14 inches. These blocks are fastened together in pairs to make a hollow "sandwich" type structure. The waveguide consists of these four sandwiches stacked end to end. The sandwich structure is shown in Fig. III-5 with the spacers and pins used for alignment shown extending from the right end of the upper block. In addition to the completed waveguide sections, Fig. III-5 shows a cross-sectional view of the blocks with the platinum surface added.
In order for the ceramic blocks to serve as a waveguide it was necessary to have them covered with several mils of metal. Platinum was selected for its chemical inertness and high thermionic work function. The process for applying platinum to ceramic in the thickness required by this application was developed under contract by Dr. Leonard Reed of Bitel-McCullough (Eimac).

The process involves two types of platinum "paint" which may be applied either with a brush or by spraying. The paint is then heated in air to remove the solvent and organic binder, and the piece is fired to form the ceramic-to-metal bond. The bond is actually a graded seal type union of the two materials.

There are two base metal oxides present in the first coat of paint. When fired these oxides wet both the ceramic piece and the platinum powder suspended in the paint. The bond thus formed may be broken by severe mechanical treatment but under normal circumstances the bond remains very strong. The second coat of paint contains only platinum powder suspended in an organic lacquer. Upon firing, the platinum is sintered to the previously applied platinum to give a soft velvety surface. This second type of paint may be applied repeatedly to give the desired thickness of platinum. If a smoother surface is desired the platinum may be machined to a very thin layer without flaking off.

The first coat is 90% platinum powder-10% base metal oxides. Using Dr. Reed's notation this is called Pt-3 and the exact formula is:
28 g Pt (-325 mesh)
1.7 g MnO₂
1.0 g SiO₂
0.6 g manganese stearate
2 ml Beckersol 458A grinding resin
20 ml 20A solvent (equal parts by volume of methyl-ethyl-ketone and ethylene glycol monoethyl ether)
5 ml ethylcellulose.

This paint can either be sprayed or brushed on and then fired in air. The exact temperature to which the paint is fired does not seem to be of critical importance. However, the report from Eimac said to fire to 1300-1350°C and it was found that test pieces fired at our Laboratory to a temperature of 1310°C were overfired. When the pieces got too hot the glaze (metal oxides) flowed and caused the paint to ball up. Since the platinum seemed to be well bonded when fired to 1200°C, the blocks were coated at this lower temperature.

The Eimac report also specifies that the paint be ball-milled before mixing in the thickener (ethyl cellulose). The first attempt at our Laboratory was run on a single batch (28 g of Pt). This was such a small amount that extreme difficulty was encountered in recovering the paint from the balls. This resulted in water being adsorbed on the oxides. When the blocks were heated under vacuum the water was desorbed and caused bubbles to form on the platinized surface. No difficulty with bubbles has been observed except for those blocks painted with this first small batch of Pt-3.
The second coat is just a suspension of very fine platinum powder in a standard lacquer. The formula given by Dr. Reed for this paint (Pt-4) is:

\[
\begin{align*}
28 \text{ g Pt} & \quad (-325 \text{ mesh}) \\
9 \text{ ml } 20A \text{ lacquer} & \quad (\text{Solvent } 20A \text{ with } 2\% \text{ nitrocellulose by weight}) \\
1 \text{ ml Beckersol } 458A & \\
3 \text{ ml ethylcellulose.} \\
\end{align*}
\]

This coat is then fired to the same temperature as the first coat. If greater thickness is needed, more coats of Pt-4 may be added, with each coat being fired before the addition of the next. The use of the platinized blocks as a parallel-plate waveguide requires a metal surface of about 0.005 inch. This thickness was usually obtained with one coat of Pt-3 followed by two coats of Pt-4.

The sandwiches are held together with a glaze consisting of the oxide portion of Pt-3. This glaze is applied to the spacers in a pasty form and the blocks are stacked while the glaze is still wet. This gives a very strong seal once the bond is formed. Unfortunately, much trouble has been caused by the spacers' failing to stick the first time they are fired in place. Recent experiments suggest that in the future the blocks and spacers should both be prefired with glaze to give a surface that will guarantee reliable bonding.

When the cell was assembled for the first time it was found that, for practical purposes, it would not transmit microwaves. The estimated attenuation was more than 40 db. The testing period that followed was designed to salvage an already constructed system and should not be
taken as a guide for redesign. The tests should have been run on mock-up systems before construction but these were bypassed due to a shortage of time.

During the waveguide tests, the blocks were mounted horizontally on a crude test bench. It should be noted that the blocks were designed to be assembled only in a vertical arrangement, and every attempt to align them while in a horizontal position has resulted in the sandwiches being split open at the spacers. The apparent reasons for this behavior are the extreme hardness of the ceramic and the very small tolerances associated with the alignment spacers. When the spacers from one block are inserted between the blocks of the next sandwich there is virtually no room for motion without applying tremendous leverage to force the sandwich apart. Therefore, it is recommended that the spacers to be used for alignment have one end tapered slightly (a few mils should be sufficient). This would also make the alignment during the vertical assembly much less critical.

Since the glazed sandwiches always came apart, the blocks were fastened in place with plastic tape during the tests. The tape gave support and allowed rapid assembly and disassembly without danger of damage to the blocks. The tests were performed with the same waveguide as used to feed the cell. It was found that the horns were transmitting reasonably well but that nearly all of the microwaves were emerging from the sides of the parallel-plate assembly. The position and number of spacers seemed to have an effect on the direction and amount of scattering but no simple relationship was observed. A very rough antenna pattern was measured for the horn with and without the parallel-plate guide. The results seemed to indicate that the guide was not guiding at all.
and that the power reaching the receiving horn was nearly independent of the presence of the guide. Tests were then run using a smaller distance between the horns. It was found that by shortening the cell to a length equivalent to three sandwiches instead of four the power transmitted reached what was deemed to be an acceptable level. Thus the problem became a choice between trying to effectively shorten the cell or else completely redesigning the waveguide. Of course, the former was chosen. The method selected for shortening the cell was the one that required the smallest amount of refabrication. Coincidentally, the method also turned out to be the quickest.

For test purposes horns were constructed from K-band waveguide by removing the broad faces. The remaining narrow faces were then flared out to form the sides of a "horn". Sheets of copper were soldered to the top and bottom to complete the horn. This horn was excited with the original ceramic horn arrangement, and the copper horn then fed a brass parallel-plate waveguide constructed to the dimensions of the ceramic system. The transmission was comparable to that obtained without the use of the copper horn. The conclusion was that the effective length of the cell could be decreased by putting "fences" in the end sandwiches in the same shape as the copper horns. The arrangement used is shown in Fig. III-6 with the ceramic horn in place.

The fences are elongated spacers of the same height as the spacers along the sides of the sandwiches. It was found to be more convenient to have the fences made with a wider base to give them more stability when positioning prior to firing. A platinum layer comparable to that on the blocks is put on the side of the fences facing the microwaves. Good electrical contact is required at all points along the fences so
the microwave fields will be the same as in a rectangular metal waveguide.
If the contact is not continuous along the joints, there will be resist-
tance to the flow of the current due to the microwave field and this
will cause attenuation of the microwaves. However, this contact between
the parallel plates would short out the Stark field. Therefore, it was
necessary to isolate the ends of the blocks containing the fences. Isola-
tion was attained by cutting a slot completely through the platinum
surface at the end of the fences, as is shown in Fig. III-6.

A prerequisite for any redesign should be an extensive testing
program. Based on the geometrical sensitivity observed with the present
components, it would seem advisable to assemble a mechanically rigid
test area including adjustable mounts for horns and waveguide. It should
also be remembered, however, that exact positioning in the cell is
extremely difficult due to the large expansion on heating. In the
present cell the length is calculated to be increased by about 0.4 in.
at 1000°C.

The platinizing process is also employed as the means for applying
the Stark voltage to the parallel plates. Electrical connection to the
platinum surface is through a 3/8-in. hole drilled in the center of the
broad face of each block. The inside of the hole is platinized with Pt-3
at the same time the main surface is fired. A plug which has been
platinized with both Pt-3 and Pt-4 is pressed into the hole before the
application of Pt-4 to the block. The block and the remainder of the
hole are then platinized with Pt-4. The thin cylinder of platinum between
the plug and the block makes a very good conductor and no difficulty has
been caused by this arrangement.

A springy platinum-clad molybdenum wire is used to carry the
voltage from the upper head of the cell down to the blocks. The wire connects the four blocks on one side of the stack to a feedthrough on the head. Connections are made by pressing slightly oversized loops in the wire into the platinized holes. The feedthrough in the head consists of a tapered platinized hole with a seal plug in the center. A loop in the wire from the blocks is pressed into the bottom of the hole and another similar wire loop is pressed into the top. The top wire is insulated with ceramic beads and passed out of the vacuum chamber via an Advac ceramic-to-metal seal. Since the wire is platinum-clad, it can be soft-soldered to give a good vacuum-tight connection. An identical pair of wires is used for the other side of the parallel plates.

A niobium ring with a platinum foil cover formed around it was used as the seal plug in the Stark feedthroughs. Niobium was chosen in an attempt to match thermal expansion coefficients so that a vacuum-tight seal would be maintained throughout the experiments. Platinum expands slightly more than the alumina, and the niobium slightly less. Due to fabrication difficulties these rings are being replaced by oversized platinum disks when the rings become corroded.

The same type of seal plugs are used to cover the bolt heads, which are countersunk in the cell heads. Figure III-7 shows the inside faces of the heads with the seal plugs in place. The plugs in the Stark feedthrough holes can also be seen. These plugs are used to protect the bolts from corrosive vapors and to provide a rough vacuum seal. As a further aid to maintaining sample isolation, a water-base castable ceramic, sold by American Thermocatalytic Corporation, under the name Astroceram, has been used at various times.

Astroceram is the trade name for three types of cements available.
Two of these, Astroceram A and Astroceram A-LP, are silicate refractories. The third is a phosphate called Astroceram B. All three have been used in the cell at some time. The two silicates have behaved very well, the LP (low porosity) giving the better seal. The phosphate, however, was the cause of considerable trouble.

These cements are of an experimental nature and therefore there is not very much information on their chemical activity. It was found in the course of several experiments that some gas that was corrosive to platinum was being evolved, presumably from the Astroceram B or from a reaction between the cement and some ceramic. The effect on the platinum was to form a low-melting alloy. At least this is the interpretation that best explains the completely destroyed platinum foil, platinum coating on the molybdenum wire, and platinel thermocouples. One inconsistency, and the only good thing that can be said for Astroceram B, is that it did not appear to attack the platinum coating on the parallel plates. The presence of traces of this cement may have been the cause for many of the Platinel thermocouple failures that were observed after Astroceram B was used. It is strongly recommended that Astroceram B be avoided until extensive tests have been made on its chemical activity. The Astroceram A-LP appears to give a better seal and more mechanical strength in any case.

The problem of making a vacuum seal between the heads and the mullite tube which serves as the main body for the cell has been approached from several angles during the course of the many experiments. In the original design the tube was to be enclosed in a cage of eight bolts or tie rods. These tie rods passed through the holes shown around the heads in Figs. III-4 and III-7. A 0.007-in. platinum wire was formed into a circular
gasket and placed between the tube and the lower head. A similar wire was placed between the tube and the upper head. Ceramic spacers were placed on the tie rods separated from the heads and from the nuts by platinum washers. A torque wrench was then used to tighten the nuts enough to flatten the wire gaskets. This procedure was tried several times but never succeeded in sealing the joints.

When molybdenum nuts were used on the molybdenum bolts, galling occurred and the nuts could not be unscrewed. The molybdenum nuts were therefore replaced with tantalloy nuts. Tantalloy is an alloy containing approximately 90% tantalum and 10% tungsten. No problems with galling have arisen since this material change was made.

Since the tube-to-head seal could not be made satisfactorily by using the small platinum wire, an attempt was made to use 0.025-in. wire as gasket material. This system did not hold a reasonable vacuum either. As a last resort the joints were sealed by applying Astroceram as a caulking compound. This method yielded a considerably lower leak rate than the wire techniques and was used for the majority of the experiments. In the most recent assembly 0.015-in. platinum foil was used on both ends of the cell. The nuts were tightened to 60 in.-lb and the cell appeared to be reasonably well sealed.

When the seal was made with Astroceram there was no need to squeeze the heads tightly against the tube and the four tie rods, which had been used only for clamping the heads, were not installed. The remaining four tie rods were designed to serve both as clamping rods and as supports for hanging the cell from the upper cover of the furnace. Only four tie rods were used in the last assembly with the platinum gaskets.
since the vacant holes in the upper head were found to be extremely convenient as a route for getting the thermocouples past the head and down into the hot region of the furnace. The thermocouples are attached to the cell and are removed from the furnace when the cell is hoisted out.

The entire absorption cell with all electrical connections can be removed intact from the furnace by use of a pulley-and-winch arrangement. This portion of the apparatus is called the hoistable subassembly and is shown in detail in Fig. III-8. It includes the cell with waveguide, the microwave input guide, the tie rods and associated hardware, the thermocouples and Stark system feedthroughs, and the sample-handling system.

The order of assembly is not unique, but sequencing is critical in some instances. Since the stack of sandwiches must be supported manually during assembly, it is advisable to have as much of the assembly completed as is possible before they get stacked. Some of the operations which should be done in advance are the installations of all the horns and bolts into both heads.

It is preferable to insert the bolts and seal plugs before the horns to avoid the danger that the horns might be damaged when the plugs are forced in by hammering. The horns are then inserted into their platinized holes, with particular care being given to insure correct angular alignment.

The orientation of the lower head with respect to the furnace is predetermined by the position of the sample tube. This means that both the head and the tantalum waveguide are in fixed positions. Thus, when the horn is inserted into the lower head it must be oriented so that it will pass into the oval guide when the subassembly is lowered into the
furnace. The alignment of the upper horn is similarly restricted since it must fit into the upper tantalum guide and also be aligned with the parallel plates containing the lower horn. Visual alignment by comparison with the holes present in the heads has always been sufficiently close to allow assembly, and misalignment has not been found to be the cause of any difficulty.

The platinum gaskets and Stark lead wires can also be prepared in advance. The loops in the Stark leads are formed by wrapping the wire around an anvil of the appropriate diameter. The distance between the loops is best determined by laying the blocks end to end and then matching the loops to the holes. A larger anvil is required for the double loop that is inserted into the upper head. The gasket for the lower head should be placed on the head before the blocks are stacked to avoid the difficult maneuvers involved in lowering it over the stack without allowing the blocks to move.

A convenient support for the cell during its assembly is a piece of brass pipe with an outside diameter slightly less than the diameter of the circle formed by the inside of the tie-rod nuts. The pipe should be long enough to provide protection for the sample tube and horn that protrude from the bottom of the lower head. However, for mechanical stability the pipe should not be any higher than is necessary. An O-ring may be used on the end of the pipe to protect the head but it is not really needed. With the head resting on the pipe and the lower gasket in place the cell is ready for assembly. From this point on, until the cell is hung from the furnace cover, the operation requires three people at all times and the assembly must be carried to completion or returned to this point before stopping. The time required is generally
about 30 to 45 minutes.

The first step in the assembly is the stacking of the sandwiches. One person does the stacking while the other two support the stack. Each block should be steadied individually with one hand. Extreme care should be taken since any bending of the stack will usually cause the sandwiches to split apart. In the original system the bottom sandwich was designed to rest in a gimbal arrangement to allow for some motion. This is the reason for the conical section on the lower end of the block shown in Fig. III-5. When the blocks were modified with fences, it seemed unnecessary, and even unadvisable, to have this provision for motion, due to the small clearance between the fences and the horns. The gimbal has been left out during recent assemblies.

The next step in the assembly is to insert the Stark lead loops into the holes in the blocks. Again caution is required to avoid lateral motion when pushing on the wire. When the wires are all in place, the cell is ready to be enclosed in the mullite tube.

The tube is lowered by hand over the stack. It must be kept very steady and exactly vertical to prevent damage to the stack. Once the blocks are within the tube there is relatively little danger of motion in the stack since the clearance is only 1/8-in. on the diameter. It is still important to keep the tube vertical, though, or else the pipe base may have a tendency to tip over. As long as two persons are holding the tube they can usually detect any leaning and correct it. The upper end platinum gasket is now placed in position. During the mounting of the head, care should be taken to avoid shorting out the Stark leads to the gasket.

When the head is lowered onto the tube, the horn is positioned
between the parallel plates with the alignment necessary to provide the proper polarity for the Stark feedthrough holes. Initially the head will rest on the springy coils of the Stark leads which protrude from the end of the tube. The coils are then pushed into the holes in the lower side of the head. This can best be accomplished by using a long thin screwdriver or similar tool to push individually on each loop of the double loop connection. For the length of Stark leads normally used this operation is slightly difficult, due to the small space between the tube and head. Unfortunately, if longer leads are used there is too much slack in the wire inside the cell after assembly, and the possibility of shorting between the wires is greatly increased. As it is, care should be taken to use the minimum length of wire. Since the insertion of the Stark leads into the head normally involves prying against the mullite tube, it is usually necessary to reposition the platinum gasket before the tie rods are installed.

The tie rods are lowered one at a time into the proper set of holes. The ceramic spacers and tantalloy nuts are then attached.

The ceramic spacers are separated from the heads and nuts by platinum washers to avoid cracking the heads or spacers when the nuts are tightened. The danger of cracking arises from the property of ceramics that the entire load is placed on the highest point of the bearing surface. There is absolutely no "give" or smoothing out under pressure without crumbling. This crumbling can be just the breaking off of a high spot or it can cause the entire piece to break up. The soft platinum washers distribute the load uniformly over the ceramic surface. In the current assembly with 0.015-in. gaskets between the tube and heads, thin washers (0.003-in.) were used with the spacers.
on the upper end of the tie rods. Since the torque wrench is applied to the nut at the bottom, 0.015-in. washers were used to protect the lower tie-rod spacers. These thicker washers provide some lubrication during the turning of the nuts.

The next steps involve locating the upper stack of heat shields and connecting the furnace cover to the tie rods. The hanger assembly is shown in view C-C of Fig. III-8 (upper right, center) and consists of a swivel hanger nut with two molybdenum straps going to pins mounted in blocks on the cover. The straps are locked on the pins by wires passing through the pins. The four tie rods not presently used were originally installed at the same time as the other rods and had the same type of nuts on the upper end as on the lower. The original design called for heat shields around the ends of the tie rods, which extend beyond the limits of the absorption cell. These heat shields have been left out for two reasons. The lack of thermal gradients indicates that they are not really necessary, and they are nearly impossible to install. The upper stack of heat shields is tied together with string and placed on the hanger nuts, again observing the correct orientation, prior to connecting the cover.

The hoistable subassembly is now moved to the support bracket mounted on top of the furnace and is then bolted to the bracket to provide stability during the remainder of the assembly process.

The continuous procedure mentioned at the start of the assembly has now been completed and the further assembly can be done by one person with no requirement for continuity. The disassembly obviously has the same continuity conditions between the different states of the apparatus.
The following steps have no particular order except that it is probably best to install the upper tantalum waveguide first to protect the tip of the upper horn. The tantalum waveguide must be separated from the transition piece shown in Fig. III-2 in order to gain access to the clamping bolts. The transition piece should not be attached until after the cell has been lowered into the furnace. The external Stark leads and thermocouples are then mounted on the cell and the vacuum feedthroughs are soldered. The exhaust pipe (which will be described in the next section) should also be installed at this time. The cell is then ready to be lowered into the vacuum furnace.

The cell must be lifted to its extreme upper limit before the sample-cell clamping bolts will clear the upper end of the furnace. Even then the clearance is less than $\frac{1}{4}$-in. The support bracket on which the cell was hanging can be removed at any time during the hoisting process. Two people are generally required for this operation since the cell must be manually supported to prevent it from scraping against the furnace. Once the cell has reached its upper limit and has swung into position above the furnace the cranking is repeated, in reverse this time. The O-ring for the upper cover must be in place before the cell is lowered. Care should be taken to avoid making the cell vibrate by cranking too vigorously.

It is necessary to guide the cell past several critical clearance points while it is being lowered. The first point is when the lower head of the absorption cell passes the main heater supports. If the cell comes to bear on one of these it will usually cut the heater strip so that all of the heaters will have to be removed and the damaged one(s) replaced. The same danger exists when the lower head passes the top of the ceramic cleanliness barrier.
The cell can then be lowered, carefully, for the majority of its length without problems. The next point of encounter is when the upper head comes to the heater supports. Immediately after this point is passed the sample-cell support bolts will reach the lower end insulator on the main heaters. It is always necessary to wiggle the insulator to keep the cell from hanging-up on the heaters. This is done by reaching up from the bottom of the furnace and lifting the insulator and heat shield stack up about 1/4-inch. This allows one to rotate the stack freely and also to stop the cranking before the entire weight of the cell is supported by the heaters. The lowering should be done with extreme caution at this point to avoid damaging the cell or heaters. Once the ends of the sample-cell support bolts have cleared the bottom of the lower heat shield stack, which is hanging from the lower end insulator, the upper cover is rotated to align the bolt holes and the cell is lowered until the cell rests on the furnace.

The lower tantalum waveguide is not in place during the lowering process since it would be very difficult to insure the alignment of the microwave horn when the two parts engage. The waveguide can now be put in place so as to complete the microwave plumbing. It is best to check microwave transmission at this point in order to adjust the lower tantalum guide for maximum transmission. This is a fairly critical adjustment and should not be omitted. The final step in preparing the cell is the bolting in place of the bottom cover of the vacuum furnace. This step should not be done until the sample-handling system has been installed and the heaters have been checked for shorts.

The dismantling procedure is essentially the reverse of the
of the above operations, without the testing steps. There is in general no difficulty involved in raising the hoistable subassembly out of the furnace. However, if the heaters become oxidized they have a good chance of breaking and can cause the lower head to bind inside the cleanliness barrier. This can be corrected by repeated vertical oscillations of the hoistable subassembly.

The absorption cell as a unit has performed in a quite satisfactory manner except for the extremely poor transmission characteristics of the parallel-plate assembly. This lack of power through the cell limits the sensitivity of the cell to the extent that its usefulness is questionable. A modification to the basic parallel-plate arrangement, such as the split waveguide used by Lide,¹³ which should give marked improvement in transmission, would greatly enhance the sensitivity of the spectrometer.
3. Sample-Handling System

For the purposes of high-temperature microwave spectroscopy a sample-control system should provide the facilities for outgassing the cell and sample at elevated temperatures and should also make it possible to change the sample pressure in the cell rapidly. Since valves for operation at high temperatures are difficult to construct, the normal method of sample control in apparatus of this type is by variation of the temperature of the sample.

In the spectrometer described herein the sample is contained in a ceramic test tube clamped to the lower end of the absorption cell. The tube is usually sealed to the head by using either Astroceram A-LP or the platinum-gasket technique described earlier. The temperature of the sample tube is controllable over a range of temperatures near the temperature of the absorption cell.

Since the sample tube is firmly connected to the lower head of the absorption cell, the sample receives considerable heat from the main heaters. However, the lower end of the sample tube is in reasonably good thermal contact with the heat shields surrounding it. These heat shields are outside the hot region of the furnace and are exposed only to the cold walls of the bottom cover. This positioning results in enough radiative heat transfer to keep the sample relatively cool with respect to the absorption cell. The difference in temperature between the cell and the sample naturally depends on the temperature of the cell, but for a typical operating temperature in the neighborhood of 700°C the sample is about 200°C cooler than the cell. This difference in temperature allows the cell to be heated to operating temperature without any sample entering the cell. The sample is then introduced by
increasing the temperature of the sample tube.

The sample tube is shown in place on the lower end of the absorption cell in Fig. III-8. The entire hoistable subassembly is shown in position inside the vacuum furnace in Fig. III-9. The sample-tube heater consists of a length of tantalum wire insulated with standard thermocouple tubing; this is placed inside the sample-tube heat shields. This arrangement allows for rapid heating of the sample tube with respect to the cell, but relies on radiative cooling to lower the temperature. The principal disadvantage of the present system is the relatively long time, up to an hour, required for the sample to cool. This problem could probably be overcome by establishing a conductive heat leak from the heat shield to the wall of the furnace. The power available for heating is sufficient to allow for a reasonable leak rate.

The vaporized sample passes from the sample tube into the absorption cell through a hole in the lower head. The location and size of the original opening is shown in Fig. III-7. Due to the difficulty in obtaining a really good vacuum seal between the test tube and the lower head, it was observed in the early experiments that the sample leaked around the end of the test tube into the furnace rather than entering the absorption cell. In subsequent experiments with a larger hole through the head no further difficulties arose in getting the sample into the cell.

The original design for the system called for two separate vacuum systems: One for the furnace and one for the absorption cell. Two systems have not been necessary up to this time because of the poor vacuum seals on the absorption cell. The vacuum connection to the
absorption cell was to be via a platinum tube which could be clamped
to the upper head with the bolts shown in Fig. III-4. The upper end of
the platinum tube was hammer-welded in the center of a platinum diaphragm
to provide a vacuum seal which allowed for vertical motion when the
cell was heated. The tube was surrounded by heat shields and a separate
heater to prevent the sample from freezing around the valve rod. A cold
stainless steel baffle arrangement served to collect the sample vapors
and allowed for convenient removal of the distilled sample.

The valve consisted of a long ceramic rod with a tapered end which
rested in the small hole in the upper head. The rod was raised with a
standard bellows-type vacuum valve mechanism. At the present time only
the platinum tube is used. The leak rate to the stainless steel baffles
appears to be considerably less than that for leakage from the cell into
the furnace region. The exhaust pipe heater and heat shield assembly are
also omitted in the present apparatus. The omitted parts are included
in Figs. III-8 and III-9 and will have to be replaced if it is desired
to study compounds formed at high temperatures from normal gaseous species.
The need for two vacuum systems for this type of study is due mainly to the
severe damage to the heaters and heat shields which results from exposure
to any gas while the metal parts are hot.

Construction of the sample tube from some material other than mullite
should be given considerable attention. The reactivity of mullite with
fluorides and the solubility of oxides in the ceramic make it imperative
to have a different sample container in order to examine oxide or fluoride
molecules. Some possible materials are platinum-clad molybdenum, molybdenum,
tantalum, or perhaps a more inert ceramic such as zirconia or titania.
For the most part the sample system has given satisfactory performance. The enlarged entry port allows good sample flow and there is never any problem getting the sample out once the sample tube cools.

4. Stark Modulator

The original Stark modulator for this spectrometer was of the same design as the one used by Howe for his spectrometer at Harvard. It employed a hydrogen thyratron switching network and gave a very good square wave into any pure capacitive load. However, under the high-temperature conditions prevalent in the present apparatus, the conductivity of the ceramic blocks was sufficient to cause severe distortion of the waveform. The resulting modulation waveform was zero-based but the top of the square wave was actually an exponential decay curve with a time constant $RC$, where $R$ is the resistance between the electrodes and $C$ is the cell capacitance. At the higher temperatures, above 700°C, the decay was so severe as to render the modulation useless. This necessitated the construction of a modulator with a higher output power capability.

The present modulator unit is a conventional hard-tube circuit with a 304TL high-power triode as the output tube. The 304TL was chosen to give the required current and voltage characteristics for driving the low-impedance load found when the cell is hot. The high-voltage power supplies are of conventional design. Provision for biasing the square wave above zero-based has not been included but the required modifications would be minor. The biased square wave is more convenient for dipole moment measurements than the zero-based form. The frequency of the modulation is determined by the input square wave from the master oscillator, and the phase relative to a reference sine
wave may be adjusted at the master oscillator. The present modulator performs quite satisfactorily and should not require major modification.

5. Microwave Source and Detection System

The spectrometer is designed for use with 4.5-kc Stark modulation and uses the normal arrangement of tuned amplifiers and phase-sensitive detection. A LN2926 silicon diode has been found to give the best signal-to-noise ratio under the low-power conditions encountered thus far. Some difficulty with false signals was had due to coupling of the preamplifier with the square wave generator. This problem was corrected by carefully grounding all the components at a single point. This procedure eliminates all of the so-called "ground loops" and should be followed rigorously during any modifications.

The output is available for either chart or oscilloscope presentation. There are provisions for both electrical and mechanical sweep of the klystron output frequency.

6. Estimated Spectrometer Sensitivity

An estimate of the practical sensitivity of a high-temperature spectrometer may be obtained by comparison with an existing room-temperature spectrometer operating in the same frequency region and employing the same frequency Stark modulation. For example, consider the 5-kc Stark spectrometer used by Professor Gwinn's group at Berkeley. Gwinn's apparatus has an optimum operating sensitivity of $10^{-11}$ cm$^{-1}$ when using a frequency-stabilized klystron.$^{19}$

For normal everyday conditions with a reasonable time constant, a value of $10^{-9}$ cm$^{-1}$ is probably more accurate. By comparing the relative sizes of the absorption cells and the amount of microwave power available in the two systems, an expected sensitivity of $3 \times 10^{-8}$ cm$^{-1}$ for the
high-temperature system would be predicted. Thus, nearly all diatomic molecules possessing dipole moments should be easily observable, while almost all of the bent triatomics should be just on the borderline of detection. There are many lines for the asymmetric rotors that are stronger than those listed in Table III-2, but these lines are due to transitions between states with high values of J. These high-J transitions are not very useful in obtaining an assignment of the spectrum because of the complexity of the Stark effect.

C. High-Temperature Experiments

1. Test Molecules

In order to determine the actual operating sensitivity of the high-temperature absorption cell, 10 of the 40 high-temperature experiments run were on molecules whose spectra had been previously assigned. The room-temperature spectrum of carbonyl sulfide, OCS, was examined to ascertain the minimum detectable absorption line under the low-power conditions present in this system. The Stark field uniformity can also be confirmed by observing the width of the Stark lines as a function of applied voltage. In the event that accurate dipole moment measurements are desired it should be possible to determine the cell constant by the Stark splitting in OCS. By using the absorption intensities for OCS tabulated by Kisliuk and Townes, the sensitivity of the spectrometer at room temperature was found to be about $10^{-7} \text{ cm}^{-1}$. This value is in reasonable agreement with that obtained by comparison with Gwinn's spectrometer.

The $\text{H}_2\text{O}$ line at 22.2 Gc has been used many times to insure that the cell was operating properly. Since water is generated during the curing of the Astroceram, it is usually present in observable quantities until
the cell has been heated for several hours. The extremely slow Stark effect of this line leads to the disadvantage that the Stark lobes cannot be entirely displaced from the absorption line. This means the full intensity of the line is never realized, and also that the intensity of the line increases steadily with applied voltage. Thus, it is difficult to obtain any quantitative intensity data on the water line for comparison with values given in the literature. However, the water absorption has been observed at 800°C at quite low pressure, probably $10^{-3}$ Torr, with a signal-to-noise ratio of 4. From the data given in Table III-2 one might conclude that the sensitivity is about $10^{-7}$ cm$^{-1}$ at higher temperatures as well as at room temperature. This is expected and there would appear to be no significant loss of sensitivity due to heating the cell.

The only salt which has been observed in this cell is KCl. The experiments on KCl were run at various times during the development of the cell, for several purposes. Initially, a KCl experiment was run to determine whether or not sample was flowing from the sample tube into the absorption cell. It was not, so another experiment was run with the sample placed inside the absorption cell. This experiment resulted in the first observation of a high-temperature species with this spectrometer. After the cell was dismantled and the hole between the sample tube and the cell enlarged, the KCl experiment was repeated to test the sensitivity under the desired operating conditions.

An example of the spectra obtained is shown in Fig. III-10. The three Stark lobes for the $v=0$ component of the $J=3\rightarrow2$ line of KCl are shown as they appear near the zero-field absorption line at several values of the Stark field. The voltages given are the peak voltages
KCf \hspace{1cm} V = 0 \hspace{1cm} \text{Stark effect}

50 volts

75 volts

100 volts

250 volts

(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d)
applied to the cell. The cell spacing is approximately 0.2 in, but the exact spacing required for dipole moment measurements has not been determined. The half-width of the main absorption line is approximately 1 Me. It should be noted that the amplifier gain setting for the 75- and 250-V sweeps, Fig. III-10 (b) and (d), was decreased by a factor of 2 from that used for the other two sweeps.

The vibrational satellites of the KCl J=3-2 line have been observed up to v=6 with a signal-to-noise ratio of 15 to 1. Due to difficulty with the klystron, the higher excited vibrational states have not been observed. The intensity of the v=6 line is calculated to be 1.2 X 10^{-5} \text{ cm}^{-1}. This would indicate that several more states should be observable if the sensitivity of the spectrometer is 10^{-7} \text{ cm}^{-1}. Since probably no new information would result from these observations, the experiment has not been repeated.

The mechanical performance of the cell during the high-temperature tests was quite satisfactory. The principal difficulty was getting the sample into the cell. This was overcome by enlarging the sample port. The extremely slow cooling rate of the furnace resulted in relatively long periods of shutdown between experiments. The high-temperature experiments normally involved a time period of from 2 to 3 days of more or less continuous activity.

2. Unassigned Molecules

No spectra arising from previously unassigned high-temperature species have been observed. The basic reason for this failure has been the poor sensitivity of the spectrometer. The lack of sensitivity resulted from the low microwave-power transmission of the cell. Other experimental difficulties have also contributed to the failure of many
of the experiments.

During the early attempts, many runs were terminated due to mechanical or electronic difficulties. The failure of large numbers of noble-metal thermocouples, especially after Astroceram B was introduced into the system, caused several runs to end prematurely. The most unfortunate aspect of these failures was the long wait while the furnace cooled sufficiently to allow repair.

Attempts to aid the cooling processes by admitting argon to the cell to break the vacuum resulted in a second type of difficulty. When tantalum foil, such as that used for the heater strips, is exposed to impure argon at a temperature above approximately 400°C, the impurities adsorb on the metal and cause embrittlement. The same problem also occurs with molybdenum and tungsten. It was found to be more expedient to wait for the furnace to cool than to waste the time and money involved in replacing the heaters. Some trouble was also observed with false signals which became pronounced only at high temperatures.

There have been two types of false signals which have occurred during the course of the high-temperature experiments. The principal difference between the two is their dependence on microwave power transmitted by the cell. One type is entirely independent of microwave power and results from either ground loops or radiative coupling of the square wave with the preamplifier. This type of signal can usually be eliminated by proper grounding and shielding of the circuits. Normally this can be done while the cell is at room temperature; however, the increased currents arising from the conductance of the ceramic blocks at high temperatures can magnify the effect considerably. The conditions must then be eliminated while the cell is at operating temperature.
The second type of false signal has a nearly linear dependence on the microwave power received at the crystal detector. This type is commonly known as "hills" and shows all the customary traits of a real line. That is, it is frequency-dependent (although not usually as sharp as a line), the intensity is a function of the Stark voltage, and many times it is reproducible. The principal means of separating the hills from the lines in a normal spectrometer is to pump out the sample and watch for the line to disappear.

In the case of high-temperature spectrometers there is apparently a mechanism for causing hills which is also dependent on sample being present. Whether or not the hills appear seems to be a random function of an undefined variable. In one instance the source of the hills was found to be mechanical vibrations of the blocks, which were allowed only because all of the sandwiches had split apart. At the present time the intensity of the hills is sufficient to make the observation of a $10^{-6}$ cm$^{-1}$ line problematical. The present source of hills will have to be eliminated before any useful work can be done in this system.

There have also been problems associated with high-temperature chemistry. The first example of this type of difficulty was observed when the mullite sample tube reacted with a PbO sample, or vice versa. The resulting sample tube had a transparent bottom and apparently none of the oxide had ever gotten out of the sample tube. A similar problem was encountered with PbF$_2$.

After three attempts to find a line due to PbCl in the region between 22 and 25 Gc., which presumably failed due to lack of sensitivity, it was decided to try PbF$_2$. The larger rotational constants and absence of quadrupole interactions should result in stronger absorption lines.
The reactivity of fluorides with silica and/or alumina at high temperatures is well known. However, the temperature required for the PbF$_2$ experiment was only 600°C, and it was felt that the system should be reasonably stable up to these temperatures. When PbF$_2$ was heated to 600°C the walls of the sample tube were eroded almost completely through and the bottom $\frac{1}{2}$ in. of the tube dissolved and flowed down over the supporting clamp.

On the basis of these experiences it was concluded that the present ceramic system could not be used for any oxides or fluorides without a change in the material used for the sample tube and absorption cell. The problem of choosing a new material is worthy of considerable study since there are a reasonable number of fluorides and oxides that are of chemical interest and that have not been studied.$^{2,21}$

Several attempts have been made to observe the spectrum of AgCl. Three of these experiments were run under what appeared to be good operating conditions and yet no lines were seen. The region from 22 to 25 $\text{cm}^{-1}$ was searched, with particular interest being given to the region near the frequency predicted from Barrow's assignment of the ultraviolet spectrum.$^{22}$ The region where Howe observed some transient lines$^{11}$ was also investigated. The absence of lines can be explained in two ways. There is a possibility of dimerization as in the alkali halides$^{16}$, but to prevent the observation of any lines this effect would have to be much greater than that observed for the alkali salts. The most probable explanation is that the AgCl decomposed to the metal and Cl$_2$. The same phenomenon was observed with AgI but to a much larger extent. In the AgI case, there was a considerable amount of silver metal remaining in the test tube. In both cases silver metal was found deposited on the
cell parts.

Another molecule that was not observed due to decomposition of the sample was KCN. The residue in the sample tube was black and gave no detectable odor of cyanide. Attempts to find lines of CsHgO₂ and CdCl₂ were abandoned because of the severe hills and should be repeated when the sensitivity of the spectrometer is improved.

D. Conclusions and Recommendations

From the results already in the literature it is apparent that a successful high-temperature microwave spectrometer can be assembled. The problem remains whether one can be constructed with sufficient sensitivity to observe the weak lines due to bent triatomic molecules. The principal limitation to the sensitivity of the present spectrometer lies in the low microwave power transmitted by the cell. With a redesigned waveguiding system within the absorption cell it should be possible to attain the sensitivity required for these molecules.

The materials used for the construction of this new waveguide should be chosen for high-temperature inertness toward the molecules under consideration, as well as for high-temperature structural stability. A program of material testing should be carried out before the construction is initiated. Of course, the platinizing procedure given in this thesis could be used to protect almost any ceramic material for chemical attack.

The present temperature limitation of the platinizing process is the melting point of the glaze contained in the first coat. Substitution of a higher-melting oxide mixture should give an increased temperature limit for the spectrometer, and thereby increase the number of molecules available for study. If higher temperatures are to be employed, the heat shield arrangement should be examined to avoid thermal gradients in the cell.
Therefore, with an improved waveguide and possibly a higher temperature capability, it should be possible to obtain molecular parameters and thermodynamic properties with this spectrometer.
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REFERENCES

Part III


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