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THE MICROWAVE SPECTRUM OF NITROGEN DIOXIDE AND CHLORINE DIOXIDE

by

James Clyde Baird, Jr.

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY

Houston, Texas
May 1958

Approved Oct. 5, 1958
George B. Bird
ACKNOWLEDGEMENT

I would like to sincerely thank Dr. G. R. Bird for his confidence and encouragement throughout my graduate career, and for many stimulating discussions about this thesis and other scientific topics. I am also deeply indebted to Dr. John Rastrep-Andersen, from the University of Copenhagen, for his explanations and the construction of various essential electronic components used in our laboratory. And to Dr. Chun C. Lin, of the Oklahoma University, for his guidance in the discussion of his theory.

I am also grateful to the Robert A. Welch Foundation for a fellowship during 1957-58.

We would also like to acknowledge grants awarded to this laboratory from the Research Corporation and from the Robert A. Welch Foundation.
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Chemists have always been curious about free radicals. In microwave spectroscopy they again become of interest because of the effect their odd electron has on the molecular rotational energy levels and because of the wealth of information that may be obtained from the microwave measurements. The results of these observations, when correctly interpreted, lead to parameters which are sensitive to the molecular electronic wave function and are useful in determining the electronic structure of the molecule.

The problems encountered in this thesis presumably will be typical of those met when microwave technique reaches the stage, as exemplified by the OH spectrum, when radicals of a more transient nature can be successfully detected and studied.
Chapter I

A DISCUSSION OF THE NITROGEN DIOXIDE AND

CHLORINE DIOXIDE MICROWAVE SPECTRUM

I. Introduction

The two molecules nitrogen dioxide and chlorine dioxide present an intriguing array of energy levels for the spectroscopist to unravel. When considered as a rigid molecular frame the molecules possess rotational levels characterized by the usual asymmetric rotor theory (1). Nitrogen dioxide has been discussed from this point of view and complete structural parameters have been determined (2). However, these relatively simple rigid rotor levels are split by the effects of the magnetic moments of the unpaired electron and the nuclear spin. Therefore, the microwave spectrum is more complex than expected from the rigid rotor point of view.

Ordinarily, one would expect a removal of the two fold degeneracy due to the electron spin and the $2I + 1$ fold degeneracy from the nuclear spin. This arises because of the magnetic interaction between these spins and the field generated by the rotating nuclear frame. For nitrogen dioxide there is a six fold splitting of each rotational level and one would expect a group of transitions as depicted in Figure 3. Since analogous remarks hold for chlorine dioxide we shall only mention that eight fine structure levels will result from these interactions.
Because of the particular magnitudes of the moments of inertia of nitrogen dioxide the rotational spectrum is quite sparse in the microwave region, and only seven rotational transitions have been observed. The first of these, seen by McAfee (3), was noticed to contain six strong lines, see the 26.5 Kmc. group of Figure 2, and he assigned these to be \( 6_{06} \rightarrow 5_{15} \). This assignment failed to predict other rotational transitions and an investigation of the fine structure theory (4) showed that the assignment could not be correct. At this point it was still assumed that the interactions between the electron and nuclear spin, and the nuclear electric quadrupole moment, were much smaller than that between the electron spin and the magnetic moment caused by molecular rotation (spin-rotation). In this coupling scheme six lines should be seen from the transitions \( \Delta F = \Delta J = \Delta N = 1 \), but it was shown by Lin that the spacing between the two triplets should have been at least one hundred times as great as that between the successive members within a triplet. (4).

With the observation by Bird of the set of ten lines at 15.0 Kmc., see Figure 1, not only did the assignment by McAfee become suspect, but so did the theory based on a dominating spin-rotation interaction. Bird's correct assignment placed McAfee's line at \( \frac{23}{2,22} \rightarrow \frac{24}{1,23} \) and supported Lin's idea of a coupling scheme having spin-spin, and spin-rotation interactions on a more equal footing. Such an intermediate scheme, between large spin-spin and large spin-rotation interaction,

* Here, and throughout, \( F \) denotes the total angular momentum; \( N \), the rotational angular momentum; \( S \), the electron spin; \( I \), nuclear spin; \( J = N + S \) and \( G = I + S \).
J-Scheme for Spin-Rotational Coupling in NO$_2$

I.3
would tend to scramble the electron spin states. To elucidate, with large spin-rotation interaction, denoted from here on as J-scheme, the electron spin might be considered as being "parallel" or "antiparallel" to the rotational moment. Transitions which occur tend to keep this orientation of the electron spin and, as mentioned before for NO₂, from six levels only six lines would result. When the magnetic dipole-dipole terms (spin-spin terms), henceforth called G-scheme, dominate then the electron and nuclear spins are strongly coupled and we can imagine that for each orientation of the nuclear spin the electron may be directed along with it or opposed to it. Hence, the levels will appear as three sets of doublets, each representing the two projections of the electron spin, as opposed to the two sets of triplets from J-scheme. This crude picture suggests that in the state intermediate to these there will be a mixing of the electron spin states.

A rather more accurate statement is that the only quantity that is really conserved is the total angular momentum, F, and that transitions with \( \Delta F = \Delta N = 1 \) must occur. Thus, while only six lines exist for McAfee's theory, having \( \Delta F = \Delta N = \Delta J = 1 \), and strong spin-rotation; ten lines exist for the more realistic theory suggested by Lin, having \( \Delta F = \Delta N = 1 \).
During this time Lin (7) derived his intermediate coupling theory in an attempt to fit these experimental observations. Lin and Bird independently proposed that there should be two sets of equal frequency differences among certain of the lines in the nitrogen dioxide spectrum. These equal frequency differences are formed by subtracting certain pairs of lines in a single rotational transition. The combinations which must occur are readily seen by referring to the energy level diagram in Figure 3. Hence, we have a formal rule, independent of the type of interactions, dependent only on the probability of a spectral transition and removal of spin degeneracy.

In nitrogen dioxide there are two possible combination rules, and two ways of taking these rules. One particular difference gives the energy spacing between the upper rotational levels and the other the spacing between the lower rotational levels. The two distinct combinations are labeled A or B in Figure 3. G. R. Bird found that his 15 Kmc. lines exhibited this behavior, thus substantiating Lin's idea and furthermore suggesting that his line was indeed a low rotational transition. Since that time we have found the transition $^9\nu_{19} \rightarrow ^{10}_{0,10'}$ at 41 Kmc., to consist of ten lines and to contain the same types of combination rules as does $^8\nu_{08} \rightarrow ^7_{17}$, at 15 Kmc. From this experience it was felt that another very similar molecule, chlorine dioxide, could be successfully attacked.

The interactions in these asymmetric free radicals can be discussed quite generally. From a qualitative point of view, each rotational
level will be split by the following interactions: spin-rotation, the magnetic coupling between the electron moment and the magnetic field produced by the rotating molecule; dipole-dipole, caused by the nuclear-electronic spin-spin interaction; Fermi coupling, due to the relativistic effects of the "s"-electron interacting with the nuclear spin; and the nuclear electric quadrupole coupling produced by the electrostatic interaction between the nuclear electric quadrupole and the molecular electronic field. These will be further discussed in the next chapter.

Nitrogen dioxide, as we have said, is characterized by its very sparse microwave spectrum. Chlorine dioxide, on the other hand, provides a very dense spectrum, there being on the average a quartet every 410 mc. The majority of the members of these quartets are closely spaced, the usual distance being the order of five megacycles. In this molecule the magnitude of the spin rotational coupling is great, and the fact that there is such an abundance of quartets supports this view. Since the magnitude of this effect is unknown it is difficult, if not impossible, to pair the quartets into the sets of at least eight lines per rotational transition that we require. Some typical quartets are seen as members of some of the atypical multiplets in Figures 4 to 6.

The problem of unraveling asymmetric top free radical spectra hinges upon three factors. First, there must exist some way of predicting a rigid rotor spectrum. Thus, we must rely on the accuracy of infrared, ultraviolet and perhaps electron diffraction data. It is well to note that the microwave predictions are very sensitive to small
uncertainties in these data. Second, because of the larger number of stark levels, and for other reasons not understood at present, resolution of this effect may be impossible except for the very low rotational levels. And thirdly, we propose that at low rotational energies some intermediate coupling scheme will prevail and give rise to sets of combination rules and unusual patterns of lines.

The combination rules will be of great help in connecting two halves of a line split by spin-rotation and in proving its low rotational nature. It is necessary, however, that very accurate measurements be made so that false "combinations" do not arise. Our experience has indicated that many of these have seemingly existed when poor measurements were made and that they disappeared upon more careful scrutiny. In fact, the precision of the microwave frequency measurements is indicated by the agreement of combination pairs.

For dense spectra such as ClO₂ combinations rules are of great help in locating low rotational quantum number transitions, but other methods must also be employed. For example, several lines have been noted to have reversed, or retrograde, stark effects. That is, their stark lobes move to lower frequencies with increasing stark voltage instead of toward higher frequencies as is normal. This effect is caused by perturbation by a nearby level (5). Thus, in ClO₂, the transition 2\( _{02} \rightarrow 1_{11} \), 4,966 mc. calc., shows that it is highly possible for the 2\( _{02} \) to be perturbed by one of the fine structure levels from 1\( _{11} \) and thus cause this effect in part of the 2\( _{02} \rightarrow 2_{11} \), 44,950 mc. calc., multiplet.
MICROWAVE SPECTRUM OF CHLORINE DIOXIDE
Inspection of the group of lines shown in Figure 4 (A) reveals that 44,656.4 has this structure and we would hope that (A) may be a part of this $^2_0 \rightarrow ^2_{11}$ transition. A similar effect should be noticed in $^1_{20} \rightarrow 9^1_{137}$, 12,709 calc., which is perturbed by $^1_{11} \rightarrow 10_{28}$, 4,679 mc., calc.

There are two effects which make pairing of the two halves of the rotational lines difficult. First, faster rotation increases the magnitude of the rotational magnetic moment and thus leads to greater spin-rotational splittings. However, for higher rotational transitions the percentage difference between the two levels is smaller and therefore leads to less splitting. It would be difficult to predict exactly this dependence, but qualitatively we would suspect that the multiplets would collapse for higher rotational transitions. This is seen in the spectrum of NO$_2$ (6), see Figure 1 and 2, where the trend seems to be for the weaker outside satellites to move to higher and lower frequencies and the more intense group of six to move together. The transition $^8_{08} \rightarrow 7_{17}$ is in the midst of the intermediate scheme while $^9_{15} \rightarrow 10_{0,10}$ is the start of the J-coupling, or strong spin-rotation interaction.

II. Spectrum and Spectral Data for NO$_2$

Since the rotational analysis by G. R. Bird (2) more accurate frequency measurements on the $^9_{19} \rightarrow 10_{0,10}$, 40 Kmc., $^2_{22} \rightarrow 21_{2,20}$, 39 Kmc., and the $^2_{22} \rightarrow 24_{1,23}$, 26 Kmc., lines have been made. These measurements reveal that the 40 Kmc. group consists of ten lines and the
26 Kmc. multiplet consists of more than six; though the relation between these and the ten expected is obscure.

The isotopic species $N^{15}_2O$ was predicted from the original rotational analysis and four lines of the six possible for $9_{19} \rightarrow 10_{0,10}$, 52 Kmc. for this molecule were found (7). Rosenthal and Yardley Beers (8) of New York University have observed the predicted low frequency transition $\delta_{06} \rightarrow 7_{17}^4$, 4 Kmc. Their six lines show the combination rule expected. The frequencies are given in Table I and for completeness all known lines for NO$_2$ are listed.
Table I. Microwave Spectrum of NO₂

<table>
<thead>
<tr>
<th>N¹⁴O₂</th>
<th></th>
<th></th>
<th>N¹⁵O₂</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8₀₈ → 7₁₇ (a)</td>
<td></td>
<td>8₀₈ → 7₁₇ (d)</td>
<td></td>
</tr>
<tr>
<td>14₈</td>
<td>14,929.90 (m)</td>
<td>39,066.70 (m)</td>
<td>3,660.75 (m)</td>
<td></td>
</tr>
<tr>
<td>9₆₁</td>
<td>097.80 (m)</td>
<td>759.69 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15₈</td>
<td>15,025.37 (s)</td>
<td>142.46 (m)</td>
<td>900.57 (m)</td>
<td></td>
</tr>
<tr>
<td>1₃₆</td>
<td>192.94 (m)</td>
<td>4,082.16 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2₄₂</td>
<td>235.98 (m)</td>
<td>2₄₃.₉₄ (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3₄₂</td>
<td>24₇.₂₈ (m)</td>
<td>3₂₁.₅₉ (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4₄₇</td>
<td>5₃₉.₃₂ (s)</td>
<td>2₃₂,₂₂ → 2₄₁,₂₃ (c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5₂₄</td>
<td>6₂₄.₉₀ (m)</td>
<td>2₆₄,₄₈₄ (w)</td>
<td>9₁₉ → 1₀₀,₁₀ (b)</td>
<td></td>
</tr>
<tr>
<td>6₅₃</td>
<td>5₆₃.₂₅ (m)</td>
<td>5₆₉.₂₁ (m)</td>
<td>5₂₁₁₀.₄ (m)</td>
<td></td>
</tr>
<tr>
<td>9₁₉</td>
<td>5₇₇.₀₂ (m)</td>
<td>3₉₈.₄ (m)</td>
<td>4₁₉.₂ (m)</td>
<td></td>
</tr>
<tr>
<td>4₄₀</td>
<td>₆₀₃.₆₅ (w)</td>
<td>6₁₉.₃₈ (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4₆₇</td>
<td>₆₃₃.₈₃ (m)</td>
<td>6₄₇.₁₇ (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6₆₁</td>
<td>₇₀₃.₂₀ (m)</td>
<td>₆₈₁.₄ (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7₁₇</td>
<td>₉₃₁.₁₈ (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9₆₄</td>
<td>₉₉₃.₃₈ (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4₁₆₇</td>
<td>₀₁₄.₀₅ (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2₇₇</td>
<td>₀₁₉.₉₀ (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>₀₂₃.₆₅ (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>₀₂₅.₉₅ (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>₀₃₁.₈₅ (w)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Here (a) and (b) represent measurements made previously to and during this research, respectively, (c) those by K. B. McAfee, and (d) those by Rosenthal and Beers.
III. Spectrum and Spectral Data for ClO₂

A rotational analysis has not been completed for chlorine dioxide, but a rigid rotor spectrum has been predicted (8) from the infrared data of Nielsen and Woltz (9) and the ultraviolet data of Coon, et al. (10) and Ward (11).* The calculated frequencies are listed in Table II.

Observations were made from 30 Kmc. to 44.5 Kmc. but not continuously, and the lines measured are listed in Table III. These data overlap the observations by D. F. Smith, who searched from 6.8 to 33.6 Kmc.** The calculated lines show that the most interesting rotational transitions occur above the region searched by Smith and that if we are to use the ideas stated in Part I we must go to these higher frequencies. In all of the searching no stark lobes were resolved -- with the possible exception of one member of the group at 44.6 Kmc., see Figure 4. Quartets were considered unimportant unless they exhibited some exceptional character, such as great strength, wide separation, or retrograde stark effects.

This research was begun with the working hypothesis that for the lower rotational transitions irregular multiplets with combination rules would be observed. Hence, our starting point was the lower rotational transitions. Particularly interesting were those occurring in the more readily accessible microwave region, \( \frac{3}{13} \rightarrow \frac{4}{04}, 35,200.5 \text{ mc}, \) calc., \( \frac{4}{13} \rightarrow \frac{3}{22}, 45,821.4 \text{ mc}, \) calc., \( \frac{5}{15} \rightarrow \frac{4}{22}, 44,789.3 \text{ mc}, \) calc., and \( \frac{2}{02} \rightarrow \frac{2}{11}, 44,950.0 \text{ mc}, \) calc. Even so, most of these frequencies must be obtained by frequency multiplication.

* Electron diffraction also agrees with these structures, Dunitz and Hedberg, J. Am. Chem. Soc., 72, 3108 (1950).

** Thanks are due Dr. D. F. Smith for sending his microwave data.
Corresponding to our hypothesis, several groups of lines were noted to have strange behavior. Figure 4 (B) shows a portion of a trace in the 32.4 Kmc. region. The usual quartet is noticed towards the right in the figure. About this quartet are a series of doublets, of which three are shown. Strange doublets occur often in this region. Interesting are those at 33,500.9, 33,502.9, 33,516.2, 33,519.6 mc, and at 34,181.9, 34,189.6, 34,251.6, and 34,257.2 mc. Slightly higher in frequency a group exhibiting a pattern characteristic of transitions of the type shown in nitrogen dioxide, see Figure 3, with intensities (w), (s), (s), (w) was observed. The multiplet occurs at 34.4 Kmc, see Figure 5, and shows a combination rule between the weak and strong lines. This looks promising, but at this point in the investigation one cannot have complete faith in these relations.*

Three other striking groups of lines have been seen. These are found at 35.5, a strong quartet and a triplet, at 37.2, see Figure 5, and odd array in the 44.6 Kmc. region, see Figure 4 (A).

The first table contains the frequencies predicted from the moments determined in references (7), (8) and (9). The section following contains the lines measured in our laboratory and the last the measurements made by D. F. Smith of Union Carbide Nuclear Laboratory, Oak Ridge, Tennessee.

* Because of this, even though a multitude of combinations -- though not of this type -- exist among the frequencies reported, they are not listed.
\[
\begin{array}{cc}
\text{Table II} & \\
\begin{array}{l}
\text{Cl}^{35}O_2 \\
(A - \frac{B + C}{2}) = 42,435.3 \text{ mc.} \\
(B + C) = 18,347.15 \text{ mc.}
\end{array} & \\
\begin{array}{l}
\text{Cl}^{37}O_2 \\
41,120.3 \text{ mc.} \\
18,311.4 \text{ mc.}
\end{array}
\end{array}
\]

Transition (calculated)

\[
\begin{array}{ccc}
\text{K} = 0 - 1 & \text{(A)} & \\
0^0 \rightarrow 1^1 & 59,959.0 & \\
2^0 \rightarrow 1^1 & 4,966.37 & 3,708.6 \\
3^1 \rightarrow 4^0 & 35,200.5 & 36,426.8
\end{array}
\]

\[
\begin{array}{ccc}
\text{K} = 1 - 2 & \text{(A)} & \\
4^1 \rightarrow 3^2 & 45,821.40 & 41,850.8 \\
6^1 \rightarrow 5^2 & 636.56 & 3,494.3 \\
7^2 \rightarrow 8^1 & 33,171.13 & 36,233.57
\end{array}
\]

\[
\begin{array}{ccc}
\text{K} = 1 - 2 & \text{(F)} & \\
5^1 \rightarrow 4^2 & 44,797.3 & 41,285.7 \\
7^1 \rightarrow 6^2 & 26,106.4 & 23,206.3 \\
9^1 \rightarrow 8^2 & 10,768.4 & 8,727.8 \\
11^1,11^1 \rightarrow 10^2,28 & 4,678.8 & 3,868.6
\end{array}
\]
Table II (cont.)

<table>
<thead>
<tr>
<th>$^{35}<em>{1}Cl</em>{2}$</th>
<th>$^{37}<em>{1}Cl</em>{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 2 - 3$ (A)</td>
<td></td>
</tr>
<tr>
<td>$^8_{26} \rightarrow 7_{35}$</td>
<td>59,199.1</td>
</tr>
<tr>
<td>$^{10}<em>{28} \rightarrow 9</em>{37}$</td>
<td>12,709.3</td>
</tr>
<tr>
<td>$^{12}<em>{24,10} \rightarrow 11</em>{39}$</td>
<td>56,907.0</td>
</tr>
<tr>
<td>$K = 2 - 3$ (F)</td>
<td></td>
</tr>
<tr>
<td>$^9_{28} \rightarrow 8_{35}$</td>
<td>50,952.9</td>
</tr>
<tr>
<td>$^{11}<em>{26,10} \rightarrow 10</em>{37}$</td>
<td>19,541.9</td>
</tr>
<tr>
<td>$K = 3 - 4$ (A)</td>
<td></td>
</tr>
<tr>
<td>$^{10}<em>{37} \rightarrow 9</em>{46}$</td>
<td>110,736.2</td>
</tr>
<tr>
<td>$^{12}<em>{39} \rightarrow 11</em>{48}$</td>
<td>70,752.7</td>
</tr>
<tr>
<td>$K = 3 - 4$ (F)</td>
<td></td>
</tr>
<tr>
<td>$^{11}<em>{39} \rightarrow 10</em>{46}$</td>
<td>93,602.5</td>
</tr>
<tr>
<td>$K = 0 - 1$, $\Delta J = 0$</td>
<td></td>
</tr>
<tr>
<td>$^2_{02} \rightarrow 2_{11}$</td>
<td>44,950.0</td>
</tr>
<tr>
<td>$^4_{04} \rightarrow 4_{13}$</td>
<td>51,248.5</td>
</tr>
<tr>
<td>$^6_{06} \rightarrow 6_{15}$</td>
<td>62,300.3</td>
</tr>
</tbody>
</table>

where (A) represents the most intense transitions and (F) those forbidden in the symmetric top limit.
Table III. Chlorine Dioxide Microwave Frequencies
Measured in These Laboratories

<table>
<thead>
<tr>
<th>Frequency (MHz)</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>17,529.8</td>
<td>34,133.0 (w) q</td>
</tr>
<tr>
<td>966.1</td>
<td>143.0 (w) q</td>
</tr>
<tr>
<td>18,058.29 q</td>
<td>181.9 (w)</td>
</tr>
<tr>
<td>59.8 q</td>
<td>189.6 (s)</td>
</tr>
<tr>
<td>651.16</td>
<td>251.6 (w)</td>
</tr>
<tr>
<td>602.64</td>
<td>257.2 (s)</td>
</tr>
<tr>
<td>667.9</td>
<td>372.7 (w) q</td>
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053.2 (v) q | 444.0 (s) |

088.6 (v) | 456.4 (w) q |

089.9 (v) | 457.0 (w) q |

164.8 (w) | 458.4 (w) q |

251.3 (s) | 460.6 (w) q |

334.0 (w) | 477.4 (s) |

339.5 (w) | 496.4 (s) |

346.6 (v) | 545.2 (w) |

354.8 (w) | 589.7 (w) |

360          | 914.8 q |

500.9        | 915.4 q |

502.9        | 916.7 q |

516.2        | 918.7 q |

519.6        | search stopped |

729.9 (s)    | 36,951.2 (w) q |

785.2 (s)    | |

930          | q |

947.4 q      | |

search terminated

37,167.6 (m) | 182.2 (s) |

193.1 (m)    | 196.1 (m) |

208.8 (s)    | 210.3 (s) |

219.7 (vw) q | 220.9 (vw) q |

221.8 (s)    | 223.7 (vw) q |

226.4 (vw) q | 230.0 (s) |

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search terminated |

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Table IV

Below are listed the measurements on chlorine dioxide made by D. F. Smith.

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Chapter II

THE ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF NITROGEN DIOXIDE IN SOLUTION (12) AND A NAIVE DISCUSSION OF THE ELECTRONIC STRUCTURE OF NITROGEN DIOXIDE

I. Paramagnetic Resonance Spectrum

Difficulties in attempts to fit the nitrogen dioxide data to the fine structure theory of Lin prompted us to try and determine some of the molecular parameters of his theory by another method. The Fermi coupling constant was one such parameter.

Theory shows that the only contribution to the fine structure due to nuclear spin in electron spin resonance in liquids, where random tumbling occurs, is by the Fermi interaction (13). The Fermi interaction is essentially due to "s" electron coupling with the nuclear spin. The classical dipole-dipole term is not applicable here since, because of nuclear attraction, the electron must necessarily have a very great velocity. For this case the relativistic theory must be used (14).

The reason why the other terms average to zero is because the rotational energy is no longer sharp, being perturbed by the nearness of the surrounding molecules composing the liquid. Hence, during a short period of time, the nuclear frame plus the unsymmetrical electron distribution is oriented in all directions. The electron spin then "sees" an average, over all directions, of the electronic field; the spins being fixed in space by the external magnetic field. An average over the radial and angular coordinates is zero for the terms of the dipole-dipole expression, and all except "s" electrons have nodes at the nucleus. Thus, the electron spin-nuclear spin coupling is due to the relativistic effect of the spherically symmetric molecular electrons about the nucleus having spin.
Previous work on the paramagnetic spectrum of nitrogen dioxide in liquids had shown only one broad resonance line (15). This we feel was due to poor resolution and perhaps too great a sample concentration, with resultant exchange narrowing.

Several solutions of nitrogen dioxide were prepared using carbon disulfide and carbon tetrachloride as solvents. Concentrations were determined very roughly by sealing weighed bulbs of NO$_2$ and then breaking them in closed flasks containing the proper amount of solvent. Dilutions from the initial samples were made to give a range of concentrations. These cannot be considered accurate since the vapor pressure of nitrogen dioxide is large at room temperature. The samples giving best resolution were the order of 0.03 to 0.01 percent by volume. The paramagnetic resonance apparatus of the Humble Oil and Refining Co., Baytown, Texas, was used for the measurements.

The electron spin-nuclear spin splittings were observed to be 107 ± 3 gauss (300 ± 9 mc.). No solvent dependence was noted. The g-factor, by comparison with diphenylicrylhydrazyl, was found to be 2.008 ± 0.003 at 9,254 mc. A trace of the second derivative of the spin resonance on nitrogen dioxide in carbon disulfide is shown in Figure 7.

Thus, the value of the Fermi constant, $\sigma = \frac{-16\pi}{3} g_I \mu_I \mu_B |\psi(0)|^2$ is 300 ± 9 mc.*

* Where $g_I$ = nuclear Lande factor; $\mu_I$ = nuclear magneton; $\mu_B$ = Bohr magneton; $\psi(0)$ = value of wave function at the nucleus.
II. Electronic Structure

As a consequence of the electron spin resonance experiment it was thought that a simplified calculation of the Fermi coupling parameter, $|\psi^o|^2$, from the electronic structure of nitrogen dioxide would be interesting. The splittings found above yield an experimental value for $|\psi^o|^2 = 6.3 \times 10^{24} \text{ cm}^{-3}$. This, compared to the value for an atomic 2s-electron, gives 18 percent "s" character to the odd electron distribution about the nitrogen nucleus.

Incidentally, the splitting found in the chlorine dioxide solution paramagnetic resonance spectrum (16) leads to $|\psi^o|^2 = 0.49 \times 10^{24} \text{ cm}^{-3}$. This is to be compared to the value $391 \times 10^{24} \text{ cm}^{-3}$ for a 3s function in a chlorine atom, and corresponds to 0.1 percent "s" character. The structures usually written, with the odd electron available for resonance with the oxygen electrons, attribute no "s" character to the unpaired electron about the nitrogen, or chlorine nucleus.

At present ultraviolet data does not distinguish between the possible ground states for nitrogen dioxide. Chemical evidence does, however, support the structure with the odd electron on the nitrogen atom. This is noted in the discussion given by Walsh (17).
Our first consideration places the electrons of nitrogen in three sigma orbitals and one pi orbital. The terms sigma and pi-orbital are analogous to the use in discussions concerning diatomic molecules. Here they represent orbitals which have symmetry with respect to reflections through the plane of the molecule. The odd electron is contained in the sigma orbital which is in the plane of the nuclei and directed away from the triangle formed by them. For our convenience, we have chosen the same coordinate system as in the calculation of the rotational energies, with the z-axis along that of the least moment of inertia and with the y-axis along that of the intermediate moment of inertia. The coordinate system is shown below.

With neglect of spin, the electrons of nitrogen in the ground state configuration may be represented by the orbitals,

\[
\begin{align*}
\sigma_1 &: \psi_1 = a \psi_{2s} + b \left[ \cos \alpha \psi_{2py} - \sin \alpha \psi_{2pz} \right] \\
\sigma_2 &: \psi_2 = a \psi_{2s} - b \left[ \cos \alpha \psi_{2py} + \sin \alpha \psi_{2pz} \right] \\
\sigma_3 &: \psi_3 = a' \psi_{2s} + b' \psi_{2py} \\
\pi &: \psi_4 = \psi_{2px}
\end{align*}
\]
The definition of the molecular orbitals $\sigma, \pi$ are shown along with the
eexplicit form of the wave functions. The angle $\alpha$ is determined by the
bond angle of the molecule and the assumption that the molecular
orbitals have their maximum in the bond direction. Using these functions
the conditions for orthonormality lead to the following relations:

\[
\begin{align*}
    a^2 + b^2 &= 1 \\
    a^2 + b^2 \left( \sin^2 \alpha - \cos^2 \alpha \right) &= 0 \\
    aa' + bb' \left( -\sin \alpha \right) &= 0 \\
    a'^2 + b'^2 &= 1.
\end{align*}
\]

Using the bond angle determined by the microwave investigation (2) we
find $\alpha = 23^\circ$. This results in coefficients

\[
\begin{align*}
    a &= 0.6403, \quad b = 0.7681 \\
    a' &= 0.4245, \quad b' = 0.9054
\end{align*}
\]

From the value for $a'$ we determine $|\psi(\alpha)|^2 = a'^2 = 0.1802$, or
roughly 18 percent, precisely the value obtained from experiment.

This fortuitous result does lend confidence in assigning the odd electron
to the $\sigma_3^-$ orbital about nitrogen in the nitrogen dioxide molecule.

Other parameters occurring in the microwave theory are,

\[
\begin{align*}
    \left\langle \frac{1}{r^3} \right\rangle, \quad \left\langle \frac{3 \cos^2 \phi - 1}{r^3} \right\rangle, \quad \left\langle \frac{\sin^2 \phi \left( \sin \phi - 1 \cos \phi \right)^2}{r^3} \right\rangle.
\end{align*}
\]

Here, the angles $\theta$ and $\phi$ and the radial distance $r$, represent the
components of the odd electron in a spherical polar coordinate system
attached to the molecule. A calculation of the above expressions,
with our wave function for the odd electron, gives 29.2, 11.7 and 11.7 mc. respectively.* A discussion of these calculated values will be postponed until the section pertaining to the microwave results.

We should note at this point that a similar calculation for chlorine dioxide gives a value for the atomic "s" character of about 80 percent. We recall that the experimental value was found to be 0.1 percent. From our crude picture we may rationalize this finding by stating that in nitrogen dioxide the three electron $\pi$-bond structure is higher in energy than the $\sigma_3$ structure we support, but that in chlorine dioxide the three electron $\pi$-bond structure is dominant. This amounts to saying that when two additional electrons are added to the valence shell, as in the case of chlorine, they fall first into $\sigma_3$ and then into $\pi$. Thus, $\sigma_3$ contains an electron pair and $\pi$ the odd electron. It must be admitted, however, that in no sense do we consider the discussion of chlorine dioxide accurate or complete.

* We have used hydrogenic functions, the effective nuclear charge being taken from Hartree (18).
Chapter III

SOME ASPECTS OF THE THEORY OF THE FINE STRUCTURE
IN THE ROTATIONAL SPECTRUM OF NITROGEN DIOXIDE

I. Introduction

The splittings caused by the perturbations due to the electron and nuclear spins in a rigid asymmetric rotor may be obtained by the usual application of wave mechanics. This, however, leads to the evaluation of many complex integrals and is therefore laborious. By the use of the matrix formalism and the rules for the addition of angular momentum this labor may be reduced. It was along this line that Lin attacked the problem (4). His method is unique in that he treats the addition of three angular momenta in the molecule directly by way of the coupling schemes in atoms (19). In these schemes a representation for the wave functions diagonal in the symmetric top Hamiltonian, as well as the square of the nuclear and electron spin angular momenta, is required. Hence, if only diagonal elements in the rotation are to be used, it must be assumed that the mixing between the rotation and spin is small. This necessitates the assumption that the rotational part of the energy is independent of the spin. Rigorously speaking, this is not true, and the energy would have to be obtained by diagonalizing the entire matrix. The error in neglecting these off diagonal elements may be found by second order perturbation. Such an error is small in the case of nitrogen dioxide.* We may, however, evaluate this small contribution

* This would be expected since the molecule is a slightly asymmetric top.
of the asymmetry to the spin interactions. This might prove especially useful when using the theory to discuss the more asymmetric chlorine dioxide, and it arose here in connection with attempts to fit the experimental nitrogen dioxide data to Lin's theory.

Lin's theory for nitrogen dioxide leads to energy expressions containing a number of molecular parameters. These quantities cannot be evaluated accurately from first principles and hence must be found by fitting the microwave data. In the normal isotope this leads to eight unknowns. Hence, to determine these, at least eight frequencies must be employed. Because of the nature of the theory most of the information from a single rotational transition (with all its fine structure) cannot be used conveniently and we find that only three equations may be easily obtained. It therefore becomes imperative that we consider the use of the transitions from the isotopically substituted molecule.

Usually isotopic substitution is not necessary in the evaluation of the parameters we have mentioned. It arises here because of the scarce number of observed, low rotational microwave lines. The assumption that must be made for the use of this new source of data is that the constants involved in the spin-rotation interaction must have the same dependence on the moments of inertia between the two molecular species. It is found that this dependence is quite complex and that direct substitution may not be made without error, but that this error is very small. Still it is, in our opinion, best to solve for the molecular parameters using one isotopic species.
II. Energy Expression

The derivation of the total Hamiltonian is given in Lin's thesis. It may be represented by the sum,

\[ H = H^0 + H_{NS} + H_{IS} + H_F + H_Q \]  

where \( H^0 \) represents the rigid rotor energy, \( H_{NS} \) the term for spin-rotation, \( H_{IS} \) the dipole-dipole term, \( H_F \) the Fermi interaction and \( H_Q \) the nuclear electric quadrupole interaction. The rigid rotor energy is evaluated by the usual methods (20). The matrix elements developed by Lin for the rest of the expressions are given below. In these results the dependence on the angular momenta is given explicitly. Integration over the electronic coordinates is assumed, so that terms such as \( (1/r^3) \) designate quantum mechanical expectation values over the molecular electronic wave function.

These results are given for the two coupling schemes qualitatively described in the first chapter. Recapitulating, when the spin-rotation interaction outweighs the sum of the dipole-dipole, Fermi coupling and nuclear electric quadrupole interactions, the electron spin may be thought to add directly to the magnetic moment produced by the rotation. This results in a vector combination of the angular momenta as shown in Chapter I. On the other hand, if the dipole-dipole type interactions override the effect of the spin-rotation coupling, the electron spin may be thought to combine first with the nuclear spin. This resultant may then interact with the rotational magnetic moment and lead to the other vector addition shown in Chapter I. These two diagrams represent the J-scheme and the G-scheme respectively.
In the equations which follow these definitions are used:

\( N \) = rotational angular momentum quantum number.

\( K \) = component of the rotational angular momentum along the molecular axis (in the prolate limit).

\( F \) = total angular momentum including rotation. In J-scheme, \( F = J + I \) and in G-scheme \( F = N + G \).

\( J = N + S \), designating the representation in which there is strong interaction between the electron spin and the rotation.

\( G = I + S \), designating the representation used to depict the coupling between the electron and nuclear spins.

\( S \) = electron spin = 1/2.

\( I \) = nuclear spin angular momentum.

A) \( J \)-scheme

Contribution from the dipole-dipole interaction.

\[
\alpha = \frac{[3(J+1) - N(N+1) - S(S+1)][F(F+1) - J(J+1) - I(I+1)]}{4N(N+1) J(J+1)} x \left\{ (NK|N^2 - 3N_y^2/NK) \lambda + (NK|(N_\gamma + iN_x)^2/NK) \gamma \right\}
\]

where, in the symmetric rotor limit, \( (NK|N^2 - 3N_y^2/NK) = N(N+1) - 3K^2 \), \( (NK|(N_\gamma + iN_x)^2/NK) = N(N+1)(-1)^N \zeta_{ik} \)

and,

\[
\lambda = g_I \mu_I \mu_B \left( \frac{3\cos^2 \theta - 1}{r^3} \right)
\]

\[
\gamma = \frac{3}{4} g_I \mu_I \mu_B \left( \frac{\sin^2 \theta (\sin \phi - \cos \phi)^2}{r^3} \right)
\]

The angles \( \theta \), \( \phi \) and the radial distance \( r \) have previously been described in Chapter II.
Contribution from the spin-rotation interaction.

\[ \beta = \kappa \frac{1}{2} \left[ J(J+1) - N(N+1) - S(S+1) \right] \]

where

\[
\kappa = \frac{1}{N(N+1)} \left\{ \eta_{\delta \gamma} (NK \mid N_{\delta}^2/NK) + \frac{1}{2}(\eta_{xy} + \eta_{xx})(NK \mid N_{x}^2 + N_{y}^2/NK) \right. \\
+ \frac{1}{2}(\eta_{xy} - \eta_{xx})(NK \mid N_{y}^2 - N_{x}^2/NK) + \frac{1}{2}(\eta_{yy} + \eta_{xx})(NK \mid N_x N_y + N_y N_x/NK) \right\}
\]

\((NK \mid N_{\delta}^2/NK) = K^2 \), \((NK \mid N_{x}^2 + N_{y}^2/NK) = K^2 \),

\((NK \mid N_{y}^2 - N_{x}^2/NK) = (-1)^N K^2 \delta_{\delta k} \), \((NK \mid N_x N_y + N_y N_x/NK) = 0 \)

\[ \eta_{\delta \gamma} = 2 \left( F_{\delta} + F_{\gamma} \right) \sum \frac{|\langle 0 | \mathbf{L}_3 | \eta \rangle|^2}{E_0 - E_\eta} + A \delta_{\delta \gamma} \quad \delta_{\delta \gamma} \quad \delta_{\delta \gamma} = \text{rotational constants} \]

\[ F_x = C, \quad F_y = B, \quad F_z = A \]

\( \eta = \text{spin-orbit constant} \)

\[ A_{\delta \gamma} = \text{mechanical effect} \]

Contribution from the Fermi coupling.

\[
\gamma = \sigma \frac{[F(F+1) - I(I+1) - J(J+1)][J(J+1) - N(N+1) - S(S+1)]}{4J(J+1)}
\]

\[ \sigma = -\frac{16\pi}{3} \alpha_x \mu_x / \mu_B |\Psi(0)|^2 \]
Contribution from the nuclear electric quadrupole coupling.

\[ E = \frac{[3C(C+1) - 4J(J+1)I(I+1)]}{I(2I-1)4J(J+1)} \left\{ \frac{3K^2}{N(N+1)} - 1 \right\} h + (-1)^{N+1} h' \]

\[ C = F(F+1) - J(J+1) - I(I+1) \]

\[ h = \frac{1}{8} eQ \frac{\partial^2 V}{\partial x^2}, \quad h' = -\frac{1}{16} eQ \left( \frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right) \]

b) \textbf{G-scheme}

Contribution from the dipole-dipole interaction.

\[ \alpha = \left\{ \frac{3R(N)[R(N)+1] - 4N(N+1)G(G+1)}{2N(N+1)(2N-1)(2N+3)} \right\} \times \]

\[ \times \left\{ (NK|N^2 - 3N^2_y|NK) \lambda + (NK|(N_y+iN_x) \cdot NK) \gamma \right\} \]

\[ R(N) = F(F+1) - G(G+1) - N(N+1) \]

Contribution from the spin-rotation term.

\[ \beta = \kappa \frac{R(N)[G(G+1)+S(S+1) - I(I+1)]}{4G(G+1)} \]

\[ \kappa \text{ defined as before.} \]
Contribution from the Fermi coupling

\[ \gamma = \sigma \frac{1}{2} \left[ G(G+1) - I(I+1) - S(S+1) \right] \]  

(8)

Contribution from the nuclear electric quadrupole interaction.

\[ E = \frac{3c'(c'+1)}{1(2I+1)(2N+3)(2N-1)} \left\{ \begin{bmatrix} \frac{3k^2}{N(N+1)} & -1 \end{bmatrix} \begin{bmatrix} h \end{bmatrix} \right\}, G = I = \frac{1}{2} \]

\[ E = \frac{3c'(c'+1)-4N(N+1)G(G+1)}{1(2I+1)(2I-1)(2N+3)(2N-1)} \left\{ \begin{bmatrix} \frac{3k^2}{N(N+1)} & -1 \end{bmatrix} \begin{bmatrix} h' \end{bmatrix} \right\}, G = I = \frac{1}{2} \]

\[ C' = F(F+1) - N(N+1) - G(G+1) \]  

(9)

\[ h = \frac{1}{8} eQ \frac{\partial^2 V}{\partial x^2}, \quad h' = -\frac{1}{16} eQ \left( \frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right) \]

The energy levels which result on evaluation of the matrix containing the above terms are represented by two groups of equations. First we consider the case when \( F = | N + I + S | \), the maximum value of \( I \) and \( S \) for a given \( N \), and with it the minimum case, \( F = | N - (I + S) | \). These lead to

\[ E(F = | N \pm (I + S) |) = \alpha + \beta + \gamma + \varepsilon, \]

(10)

where the values of \( F \), \( J \), and \( G \) are determined by the maximum and minimum values of \( I + S \); e.g. these are the two states \( F = N \pm \frac{3}{2}, J = N + 1/2 \) and \( F = N - 3/2, J = N - 1/2 \) for \( N^{14}O_2 \). Note that for
this case either J or G representation may be used for the elements.

The second group represents the states,

\[ F = N + I + S - 1, \; J = N + 1/2 \]
\[ F = N + I + S - 2, \; J = N + 1/2 \]

\[ \vdots \]

\[ \vdots \]

\[ \text{etc.} \]

\[ 2\varepsilon = \alpha_1 + \alpha_\Pi + \beta_1 + \beta_\Pi + \gamma_1 + \gamma_\Pi + \varepsilon_1 + \varepsilon_\Pi + \]

\[ \pm \left\{ (\alpha_1 - \alpha_\Pi + \beta_1 - \beta_\Pi + \gamma_1 - \gamma_\Pi + \varepsilon_1 - \varepsilon_\Pi)^2 + \right. \]

\[ 4(\alpha_\Pi + \beta_\Pi + \varepsilon_\Pi)^2 \left\}^2 \right. \]

\[ \beta_\Pi = \frac{1}{4} \left[ (\beta_1 - \beta_2)^2 - (\beta_1 - \beta_\Pi)^2 \right], \quad \gamma_\Pi = 0 \]

\[ \alpha_\Pi = \frac{(\alpha_1 - \alpha_\Pi)(\beta_1 - \beta_2) - (\alpha_1 - \alpha_\Pi)(\beta_1 - \beta_\Pi)}{4\beta_\Pi} \]

\[ \varepsilon_\Pi = \frac{(\varepsilon_1 - \varepsilon_\Pi)(\beta_1 - \beta_2) - (\varepsilon_1 - \varepsilon_\Pi)(\beta_1 - \beta_\Pi)}{4\beta_\Pi} \]

where arabic subscripts 1 and 2 are the states \( F, \; J = N + 1/2 \) and \( J = N - 1/2 \) and the roman subscripts I and II are the states \( F, \; G = I + 1/2 \) and \( G = I - 1/2 \), respectively.
III. First Order Asymmetric Rotor Correction to the Spin Energies

Because the molecule is actually an asymmetric top treated in a scheme dependent on symmetric top functions, a small correction may be made. This is done by determining the asymmetric top wave functions in terms of a suitable basis by first order perturbation theory. We may then substitute the new, approximate, wave functions wherever we find a matrix element determined by the old symmetric top functions.

For example, equation (2) contains the term

\[ (\text{NK} | N^2 - \gamma N_z^2 | \text{NK}) \]

where \( |\text{NK}\rangle \) denotes the symmetric top function and \( (\text{NK}| \) its complex conjugate. Hence, simple evaluation of the effects of asymmetry result.

The most convenient set of functions which may be used as a basis for the solution of the asymmetric top problem are those of the symmetric top. These do not have the same symmetry properties as the asymmetric top functions; however, certain combinations of them do \( (25) \). These are called the Wang combinations and are denoted by

\[ S^{\gamma}_K = 2^{-1/2} (\psi^\gamma_K + (-1)^\gamma \psi^{-\gamma}_{-K}) \quad . \]

Using these as basis functions, the asymmetric top problem, still complicated, becomes simpler. The coefficient \( \gamma \) is either odd or even, depending on the symmetry of the rotational state. For a determination of the parity of \( \gamma \) for nitrogen dioxide we choose a coordinate system in which the z-direction is taken along the axis of the least moment of inertia, the y-direction along the intermediate moment and the
x-direction along the axis of the greatest moment of inertia. This leads to a system designated as $I^L$ by King, Hainer and Cross (24). The coordinates are shown in the diagram below.

\[
\begin{array}{c}
y(B) \\
N \\
0 \\
\end{array}
\quad \quad \quad
\begin{array}{c}
0 \\
\gamma(A) \\
\end{array}
\]

A two-fold rotation about the $y$-axis, above, will bring the atoms back into a position identical with the original one. This operation performed on the functions of equation (12) leads to the relation,

\[
C_2(y) S_K^\gamma = (-1)^N \gamma S_K^\gamma.
\]

A discussion of these symmetry properties is given by Mulliken (25). This operation is entirely equivalent to exchanging the oxygen nuclei. Since we know that the exchange of identical particles having zero nuclear spin must leave the wave function unchanged we have the result that

\[N + \gamma = \text{Even}.
\]

Hence, $\gamma$ has the parity of $N$ and for simplicity we shall replace it by $N$ as it appears in the following equations.
To determine the first order correction to the wave function we write the asymmetric top Hamiltonian as,

\[ 1/2 (C + B)(N_x^2 + N_y^2) + AN_z^2 + H' \]  
\[ H' = 1/2 (C - B)(N_y^2 - N_x^2). \]

In equation (13) the first two terms are diagonal in the symmetric top functions while the third, given by equation (14), is not. This last part is treated as a perturbation. From this and use of the basis functions defined in eq. (12) we obtain the corrected wave function,

\[ \Phi^N_K = S_K^N + a_1 S_{K+2}^N + a_2 S_{K-2}^N, \]  

where

\[ a_1 = \frac{BF(N,K+2)}{8(K+1)}, \quad a_2 = \frac{BF(N,K-2)}{8(K-1)} \]

\[ F(N,K+2)^2 = \left[ N(N+1) - K(K+1) \right] \left[ N(N+1) - (K+1)(K+2) \right] \]

\[ \beta = \frac{c-b}{2a-c-b} \]

In this treatment \( a_2 \) is dropped for the case \( K = 1 \). The functions (15) are seen to be normalized if terms of order \( a_1^2 + a_2^2 \) are neglected. Our theory is only good to this approximation. It is now necessary to apply the above function (15) to the appropriate matrix elements in the Hamiltonian; i.e. to equations (2) through (9). Note that we do not consider the asymmetric correction to the quadrupole interaction. This is because the quadrupole effect is already quite small in nitrogen dioxide.
The asymmetric corrections which result may be easily applied to
the equations provided by Lin by replacing his terms, on the left below,
by their counterparts to the right.

\[
\begin{align*}
\text{Term appearing in Lin's} & \quad \text{To be replaced by} \\
K & \quad \left\{ g(\eta) + f(\eta) \frac{K^2}{N(N+1)} + (\eta_{yx} - \eta_{xx}) \right\} \\
& \times \frac{1}{2} \sum_k N(N+1) + a_1 F(N, k+2) + a_2 F(N, k-2) \\
\left[ N(N+1) - 3K^2 \right] \lambda + N(N+1) \zeta & \quad \left\{ \left[ N(N+1) - 3K^2 \right] \lambda + \left[ (-1)^N N(N+1) \delta_{ik} + \right. \\
& \left. a_1 F(N, k+2) + a_2 F(N, k-2) \right] \zeta \right\}
\end{align*}
\]
IV. A Note on Spin-Rotation

The spin-rotation Hamiltonian, describing the magnetic interaction between the electron spin and the field produced by the rotating molecular frame, is taken from Van Vleck (22). It may naively be seen to originate from the two classical problems of the motion of (a) an electron, \( i \), about another electron, \( j \), and (b) a nucleus, \( K \), about an electron, \( j \). A diagram defining the variables in the Hamiltonian is given below.

![Diagram](image)

The motions are referred to space fixed axes, but we may assume that the molecular fixed axes are as good since we have already invoked the Born-Oppenheimer approximation. Thus, the total spin-rotational Hamiltonian is written by Van Vleck as,

\[
H_{NS} = \frac{g_e}{c} \sum_{k,j \neq j} \frac{Z_k e}{r_{kj}^3} r_{jK} \times (\frac{1}{2} V_j - V_k) \cdot S_j + \frac{g_e}{c} \sum_{i > j} \frac{e}{r_{ij}^3} r_{ij} \times (\frac{1}{2} V_j - V_i) \cdot S_j
\]

(16)
where the indices $i, j$ refer to electrons and $K$ to nuclei, the other quantities are defined later. The first part of expression (16) is due to the mechanical effect, i.e. the rotation of the nuclei about the electron, and the second, to the motions of the other electrons (or the orbital effect). Lin discusses in detail the origin of the orbital part of the spin-rotational interaction and its contribution to the Hamiltonian. We shall discuss only the effects of the first term above. It is to be noted that the term $\eta$ in equation (3) contains a parameter $A_{jj}$. This term represents, in Lin's work, the effect of the first part of equation (16). By inspecting $\eta$ we readily see that its first part is simply multiplied by the $j$-component of the moment of inertia. Our interest now lies in the inertial dependence, or the effect of the change in the center of mass between the two isotopic species, of this $A$-part. We shall keep only the terms in (16) which depend on $V_K$ because we wish the contribution from the rotational angular momentum depending on the change in the center of mass. This is because $V_K$ may be written as $\omega \times r_K$, where $\omega$ is the angular velocity of the molecule, and is consequently proportional to the rotational angular momentum, and $r_K$ is the distance from the origin, at the center of mass, to nucleus $K$.

If we take our molecule in a coordinate system like that used in Part III, then expansion of (16) plus integration over the electronic coordinates gives,
\[
\frac{g_\beta e}{m_c} \sum_i \left\{ \frac{Z_N C_N^2}{r_{3j}^3} + \frac{2 Z_O a_o^2}{r_{3j}^3} - \frac{Z_N C_N^2}{r_{3j}^3} \right\}
\]
\[+ 2 Z_O a_o \left\{ \frac{y_{ij}}{r_{3j}^3} \right\} \left( \omega_x S_{xj} + \omega_y S_{yj} \right) \]

(17)

Here the following definitions are used.

\( g \) = the Lande g-factor (= 2)

\( \beta = \frac{\hbar}{2m_e c} \) = Bohr magneton

\( c \) = speed of light

\( e \) = electron charge

\( Z_K \) = the charge on nucleus K

\( C_N \) = the distance from the center of mass to the nitrogen nucleus

\( a_o \) = the distance from the center of mass to the oxygen nucleus, along the y-axis

\( r_{jk} \) = the radius vector from the jth electron to nucleus K, see the diagrams at the beginning of this section

\( S_{yj} \) = the y-component of the spin angular momentum of the jth electron

\( y_j \) = the y-component of the jth electron measured from the center of mass

Since the term \( y_j \) is measured with respect to the center of mass coordinate system we will gain somewhat in simplicity if we shift to the nitrogen nucleus. Hence we let
\( y_j = y_{jN} + c_N \), \hspace{1cm} (18)

where now \( y_{jN} \) is measured relative to the nitrogen nucleus. Substitution of (18) into (17) leads to

\[
g_{\tilde{F}C} = \sum \left\{ 2 Z_a a_0 (a_0 - c_N) \left( \frac{1}{r_{j0}^3} \right) - Z_N C_N \left( \frac{y_{iN}}{r_{j0}^3} \right) + 2 Z_a a_0 \left( \frac{y_{iN}}{r_{j0}^3} \right) \right\} \times (\omega_x S_{xj} + \omega_y S_{yj} + \omega_z S_{zj}). \hspace{1cm} (19)
\]

The great simplification which has resulted since equation (16) is due to the symmetry of the nitrogen dioxide molecule. In this particular case the \( x \)-components of \( r_K \) are all zero since the molecule is contained in the \( y,z \) plane. Averages over the electronic coordinate in the \( x \)-direction and in the \( z \)-direction are also zero since there is as much charge on one side of these axes as on the other.

With the following assumptions we are now in a position to make an order of magnitude calculation of the averages in (19). From the results of the paramagnetic resonance experiment and the discussion of the electronic wave function of nitrogen we know that the quantity \( r_{j0} \) must have roughly the minimum value 1.2 \( \AA \), the bond length between oxygen and nitrogen. We further assume that the spin is attached to one particular electron, i.e. the electron described by the odd electron
orbital \( \sigma_3 \) of Chapter II. And lastly we must consider that

\[
\left\langle \frac{\gamma_{32}}{r_3^3} \right\rangle \sim \left\langle \frac{\gamma_{23}}{r_2^3} \right\rangle.
\]

These yields, for the mechanical effect in \( N^{14}O_2 \), a value equal to 37.3 mc. due to the least moment of inertia, and a value equal to 34.9 mc. for the same effect in \( N^{15}O_2 \). This difference of 2.4 mc. between the isotopic species is larger than the error made in microwave measurements. However, these measurements are for a rotational transition and therefore it is not quite fair to make a comparison at this point. A determination of this difference between two sets of isotopic transitions shows it to be only 0.3 mc. Since the theory is no better than this we must assume that the isotopic data may be mixed. In the case of chlorine dioxide this result will be more favorable toward the use of isotopic data since the chlorine atom is much heavier.
Chapter IV
RESULTS FOR NITROGEN DIOXIDE AND CONCLUSIONS

I. Results

Since there are ten components, due to fine structure, per rotational transition in \( ^{14}\text{N}_{2} \) it would seem that there is ample information for obtaining the eight molecular parameters and the pure rotational frequency, \( \nu_0 \). However, because of the combination relations there are two redundancies. Hence, we have only eight equations. From the energy expression (11) we see that the splitting in the combination lines is due to a square root term. This is shown in the diagram below.

Rotational State \( \text{N}_J \)

\[
\begin{align*}
E(F = N + 3/2) & \quad \alpha + \beta + \gamma + \epsilon \\
E(F = N + 1/2, \quad J = N \pm 1/2) & \quad \sqrt{(1)} \quad \alpha + \beta + \gamma + \epsilon \pm \sqrt{(1)} \\
E(F = N - 1/2, \quad J = N \pm 1/2) & \quad \sqrt{(2)} \quad \alpha + \beta + \gamma + \epsilon \pm \sqrt{(2)} \\
E(F = N - 3/2) & \\
\end{align*}
\]

Direct solution of the eight independent equations from the ten observed frequencies leads to,

\[
\begin{align*}
\sum a_{ijk} x_i x_j &= D_k, \quad k = 1, \ldots, 6; \quad i, j = 1, \ldots, 8 \\
\sum a_{ijk} x_i &= D_k, \quad k = 7, 8; \quad i, j = 1, \ldots, 8.
\end{align*}
\]
These six simultaneous, quadratic, inhomogeneous equations, along with the two linear inhomogeneous equations from the $F = N + 3/2$ states, are very difficult to solve, even by machine. Hence, we have been forced to use another method. To the first approximation we assume negligible quadrupole interaction. This reduces the number of unknowns to six, plus the pure rotational frequency. Since we have determined the Fermi constant, by means of paramagnetic resonance, we need only consider five unknowns.

There are several ways that averages of frequencies may be taken which eliminate the square root terms and lead to equations linear in the unknowns. One such method is to average all the frequencies of a given combination group. This is seen, for one case, by making the following identification:

$$
\sqrt{2} = E(F = N' + 1/2, J = N' + 1/2) - E(F = N + 1/2, J = N + 1/2) \\
\sqrt{3} = E(F = N' + 1/2, J = N' + 1/2) - E(F = N + 1/2, J = N - 1/2) \\
\sqrt{4} = E(F = N' + 1/2, J = N' - 1/2) - E(F = N + 1/2, J = N + 1/2) \\
\sqrt{5} = E(F = N' + 1/2, J = N' - 1/2) - E(F = N + 1/2, J = N - 1/2)
$$

Then the sum,

$$\sqrt{2} + \sqrt{3} + \sqrt{4} + \sqrt{5} = \sum a_i x_i + 4 \sqrt{0}, \quad i = 1, \ldots, 8.$$

This process reduces the amount of information, from all the combination parts of the rotational transition, by four equations. Combining the equations formed by the sum and the difference between the $F = N + 3/2$ and $F = N - 3/2$ transitions to these we find that four linear equations result. By subtracting out the rigid rotor frequency we see that three
linear equations, in only the molecular parameters, may be obtained per rotational transition. Thus, for two such transitions, we may procure six linear equations. This should be sufficient for solving the fine structure problem.

The detailed calculation reveals one other difficulty; that of assigning the various lines to the quantum states $F, J$. This is no simple problem, but because of our method of averaging we need only consider four possibilities. These are, two due to the uncertainty in $F = N + 3/2, F = N - 3/2$ and two due to the uncertainty in assigning $F = N + 1/2, F = N - 1/2$. Further aid in delegating the actual observed frequencies to the energy levels is facilitated by the connection between them due to the combination rules. The best set of results, at present, from procedures of this description are given below.

$$\eta_{yy} = -6,342 \text{ mc.}$$

$$\frac{1}{2}(\eta_{yy} + \eta_{xx}) = -69.84 \text{ mc.}$$

$$\eta_{xy} = 50.29 \text{ mc.}$$

$$\lambda = 23.1 \text{ mc.}$$

$$\tau = 20.1 \text{ mc.}$$

$$\omega = 300 \text{ mc. (paramagnetic determination)}$$
II. Discussion

Inspection of the experimental hyperfine constants $\lambda, \tau, \sigma$ for nitrogen dioxide shows good agreement with the values calculated from the naive electronic structure.

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Observed ($N^{14}O_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>11.7 mc.</td>
</tr>
<tr>
<td>$\tau$</td>
<td>11.7 mc.</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>300 mc.</td>
</tr>
</tbody>
</table>

An approximate calculation, based on the experimental value for $\lambda$, gives the distance from the nitrogen nucleus to the odd electron as being close to nitrogen. This supports our contention that the odd electron is placed in an orbital on nitrogen rather than in a configuration allowing resonance with the oxygen electrons. The other view would give a value for this distance of roughly the bond length. A general discussion of the relation between hyperfine constants and molecular structure is given by Townes, et al. (26).

It is of further interest at this point to consider the parameters from the spin-rotation interaction. First, we may neglect the mechanical effect, $A_{ij}$, since this has been shown to be small. To arrive at the form given by Lin for the parameter eta we must discard terms in the spin-rotation Hamiltonian such as,

$$-\frac{1}{m_e} \frac{1}{r_{ij}^3} L_i \cdot S_j + \frac{1}{2} \frac{1}{r_{jk}^3} r_k \times v_j \cdot S_j + \frac{1}{r_{ij}^3} \left( \frac{1}{2} r_i \times v_j + r_j \times v_i \right) \cdot S_j.$$
If this approximation is accepted then the spin-orbit constant is

\[ j = \frac{1}{2m_e} \sum_j \left( \frac{1}{r_{jk}^3} - \frac{1}{r_{kj}^3} \right). \]

The sign of this quantity may be predicted providing certain definite statements may be made about the electronic distribution. For the following arguments the sign of \( j \) is unimportant; however, the fact that it must be the same for each of the three \( \eta \)'s is. This means that since the spin-rotation constant contains the sum of the absolute values of the orbital motion, and \( j \), all three of them must be identical in sign. The variables obtained by a fit of the experimental data clearly indicate that some of the approximations used are not valid. It therefore would be instructive to insert the quadrupole coupling expression in the calculation and to use the isotopic species \(^{15}\text{N}_2\). Still it can be seen that the parameters we have determined are of the right order of magnitude.

The gross features of the nitrogen dioxide spectrum, described in Chapter I show that the lines eventually collapse with increasing rotational quantum number. In the first approximation we find from the theory that this may be investigated by looking at the difference in the frequencies of the strongest lines of the multiplet, \( F = N + 3/2 \). We find that

\[ \Delta \nu = q(\eta)(N+2) + f(\eta) \frac{1}{N(N+1)} - \frac{1}{2}(\eta_{yy} - \eta_{xx}). \]
giving a maximum (or a minimum) at,

$$\frac{g(\eta)}{f(\eta)} = \frac{2N + 1}{N^2(N + 1)^2}$$

This relation shows, as found experimentally, that the quantity $f(\eta)$ must be greater than $g(\eta)$. Solving this equation for nitrogen dioxide we find that a maximum occurs at the reasonable value, $N = 6$. This would furthermore imply that $r_{jk}^3 > r_{ij}^3$.

The results of the above discussion ought to allow us to speculate about the form of the chlorine dioxide spectrum. We would expect that the same type of behavior as seen in $\text{NO}_2$ should exist with this molecule, the only major difference being that the position of the maximum should be shifted. An order of magnitude for the eta type terms might be obtained from observations of the chemical shift in the nuclear magnetic resonance spectrum of chlorine dioxide since this effect is dependent on the same kind of interaction (27). We propose that the quartets of higher rotational multiplets may be combined to form the group of eight lines per rotational transition. This conclusion is supported by the observation of retrograde stark effects on a group of two quartets, separated by 500 mc., in the 38,340 - 38,400 mc. region. The problem of chlorine dioxide, unsolved at this point, still remains mysterious.
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Chapter V

APPARATUS

I. Introduction

The spectrometer is of the usual Wilson design. It employs Stark modulation and phase sensitive detection. The concepts involved in the use of such a system are explained in the references cited (1).

The system is composed of five main elements. These are, (1) a source of microwave radiation, consisting of klystrons, or other suitable tubes, and power supplies for the tubes; (2) a sample cell, consisting of a wave guide vacuum sealed at each end and connected to a vacuum and sample handling system; (3) a Stark modulator, in our case a square wave generator; (4) microwave detectors and low frequency amplifiers; and finally (5) a frequency measuring device. These components are shown in the block diagram, Figure 1.

II. Radiation Source

Klystrons purchased from Varian Associates, Palo Alto, California, and the Raytheon Manufacturing Co., Waltham, Massachusetts, are used as microwave sources. These tubes cover the range from 7 to 45 Kmc. and are capable of very stable operation. With stability being desirable for high resolution spectroscopy, very highly regulated power supplies are required.

For obtaining higher frequencies a series of crystal multipliers must be used. Doublers of this type are manufactured by the F-R Machine Works, Woodside, New York, and by DeMornay-Bonardy, Pasadena, California.
III. Power Supplies

Klystrons require several types of voltages. These are, repeller, beam and filament, and for high frequency tubes, a focus or grid voltage. In our laboratory the repeller, focus and filament voltages are contained in a single supply. The circuit diagram for this unit is shown in Figure 3.

In the diagram, T denotes a 120 volt to 12 volt step down transformer having 7000 volts secondary insulation. The silicon diodes $D_1$ and $D_2$ are manufactured by Transitron Electronic Corporation, Wakefield, Mass. Those used in full wave rectification, $D_1$, are a common low voltage, high current type. $D_2$ consists of two diodes in series to act as a safety device in keeping the repeller always negative. Their specifications are: peak inverse voltage = 400; inverse current at 25° = 1 a; maximum rms. voltage = 280; maximum average forward current = 200 ma.

The filament voltage employed is rectified in order to reduce even this possible source of ripple. Batteries are used for the production of the repeller and focus potentials since there is little drain and no ripple. The beam supplies, delivering 10 to 50 ma. current, are highly regulated, manufactured items. For the Raytheon tubes we use Furst Electronic Company's Model 810-V 1000 to 2500 volt variable power supply, having less than 5 mv. rms. ripple. And for the Varian tubes we employ the Hewlett Packard Model 712B zero to 500 volt supply, having 1/2 mv. rms. ripple.
IV. The Stark Cell

Careful design of the sample cell is necessary. The usual pitfalls are poor microwave transmission, with the production of standing waves and other anomalous effects, and wave guide vibration -- forced vibrations caused by the modulating square wave (2). Our guide features very close tolerances in the machining of the teflon electrical insulation and Stark septum support, and in the width of the brass Stark septum. The septum is fishtailed at each end in order to present a more gradual transition from simple to divided waveguide (Figure 4A). Two such cells were made and used in this laboratory. One is constructed with X-band guide and is 12 feet in length; the other, with K-band guide, is about five feet in length. The transmission properties have generally been good. For the X-band guide, the teflon strips were 0.0635" thick, having a 0.0230" deep groove of 1/16" width at the center. The width of the strip was 0.400". The septum had a thickness of 1/16" and a width of 0.814". Electrical connection of the 100 kc., 1000 volt square wave to the Stark electrode is made by a phosphor-bronze alloy wire. Good vacuum is maintained by kovar to glass to kovar and silicone "O"-ring seals. The phosphor-bronze wire makes a very tight taper fit into the septum and was chosen because of its tough, springlike qualities. This wire resists the shearing forces which might arise between the electrode and the guide wall when the cell is cooled to low temperatures. The "O"-ring connection facilitates demounting the Stark septum (Figure 4 B).
Near the Stark connection, a six inch slot was made along the
electric node of the TE_{01} microwave mode (in the center of the broad
side of the guide). This slot, 1/16" wide, serves as the vacuum inlet
to the cell. The waveguide end flanges were grooved from about 0.110"
to 0.115" deep to drop fit 1 1/4" I.D. by 1 1/2" O.D. silicone "O"-rings.
The entire assembly was silver soldered and mounted in an insulated metal
trough. Two permanent waveguide connectors were made in the metal trough;
one fixed and one sliding through a liquid-tight, brass, silicone
"O"-ring fitted joint. The waveguide absorption cell was then fastened
within this heating, or cooling, system. Since teflon is the lowest
melting material in the cell, sample temperatures up to 250°C may be
used.

Our K-band guide was built about the same principles. However,
since heating was not contemplated, soft solder was employed. The
teflon tape had a width of 0.169" and a groove depth of 0.020" and a
groove width of 0.030". Waveguide flanges for the K-band had to be
machined to fit the "O"-ring system described above. These flanges
were 2" in diameter and about 3/16" thick. "O"-ring seals, it is to
be noted, should have approximately 0.020" projecting above the sealing
surface and should drop fit into position.
V. Amplifiers and Detectors

The detection system begins at the silicon crystal diode. The signal is then preamplified by a double tuned voltage amplifier (4). This device is designed about a 12AT7 double triode tuned to 100 kc. It is the purpose of this unit to provide a signal of sufficient potential to drive the phase sensitive detector and to act as a medium band pass noise filter, see Figure 5 A. This output is fed to the grid of a 6K7 beginning a chain of three double tuned, pentode, voltage amplifiers in the lock-in detector. The amplified 100 kc. output is phase-detected in a 1N34A crystal bridge. Here, the phase of the signal is compared with the 100 kc. reference. Since the spectral lines and their Stark components are out of phase (due to the phase of the square wave) they may be distinguished in this bridge (5). This enables the detector to present an output in which the absorption lines are displayed as positive voltages and the Stark components as negative voltages with respect to the D.C. level of the bridge. Hence, the spectral lines are displayed up or down with respect to the Stark components. Fine adjustment of the phase is controlled by two 100 mfd. capacitors with rotors mechanically connected 180° out of phase, and stators connected to two successive points of a 0°, 90°, 180°, 270° phase dividing circuit (12AT7).

The best method for obtaining maximum signal is to tune on a known spectral line. In our work sulfur dioxide is particularly convenient. The correct microwave frequency for a rotational transition is obtained
SQUARE WAVE HIGH VOLTAGE CONNECTION

KOVAR

GLASS

KOVAR

1/4"

1 1/4"

3/8" BRASS

1/8" TEFLOM

1/32" PHOSPHOR-BRONZE

TEFLON

1/16" BRASS SEPTUM

1/2"

1 1/4"

V.4.B
and the coarse phase adjustment on the lock-in detector is varied to
give the maximum signal to noise ratio. The fine phase is similarly
tuned. At this point the preamplifier, already crudely tuned to 100 kc.,
is adjusted to give maximum signal.

VI. Frequency Measurement

There is no substitute for a set of well-calibrated wave meters.
We purchased two to cover the region from 7 kmc. to 18 kmc. and con-
structed one to serve the K-band. This was designed from the description
given by Beringer in, "Technique of Microwave Measurements," p. 327 (3).
The bore was 0.375" and the tube 3.5" in length. We did not employ the
horseshoe strap described in the text. The finished wave meter worked
well in its designated band and surprisingly well outside it. Measured
frequencies were often found within 2 mc. of the actual frequencies.

The frequency standard begins with a General Radio crystal controlled
100 kc. oscillator whose stability is better than 5 parts in $10^9$ per day.
This unit is standardized against National Bureau of Standards Station
WWV, whose accuracy is better than 1 in $10^3$ per day. A beat between the
crystal oscillator and the WWV signal may be of the order of a cycle
per minute, as seen on the signal strength meter on the communications
receiver. This gives an accuracy of the order of 0.01 mc. or better at
20,000 mc. Following the 100 kc. reference is a conventional 100 kc.
to 5 mc. tuned multiplier (3), employing a passive crystal filter.
This has been used successfully in producing a pure 5 mc. output, free
of modulation sidebands. The next stage offers a choice between 5 mc.
to 40 mc. or 5 mc. to 75 mc. multiplication. The 40 mc. or 75 mc. output, harmonic rich, goes then to the high frequency unit of the measurement system. This is the Gertsch signal generator FM 4, which produces a signal in the 500 - 1000 mc. range, and phase locks this 10 mc. above or below a reference signal. Thus, if the 13th harmonic of 40 mc. is present the Gertsch unit will take either 510 or 530 mc. and generate all harmonics of the chosen side band. In this way we may, for example, select 510 mc. and therefore have all the harmonics of this frequency -- with the exclusion of all others. These harmonics are mixed in a crystal diode with the microwave frequency from the klystron. Suppose the klystron frequency to be 12,725 mc. Then we note that the 25th harmonic of 510 mc. is 12,750 mc. The difference between these two, as they are mixed in the crystal, is 25 mc. -- a signal which may be conveniently detected and amplified in a communications receiver. Hence, the mixed signal is returned to a National HR0-60 receiver. The difference frequency, 25 mc. in this case, is detected, amplified and fed simultaneously with the output from the phase sensitive detector to the display oscilloscope. Therefore, the absorption line will have a frequency marker superimposed upon it. Since the communications receiver may be tuned over the r.f. band, a movable frequency marker results. For the details of the frequency standard circuits see Figure 6 A and 6 B.
VII. Square Wave Generator

The high voltage square wave generator was designed by the staff of the Columbia University Radiation Laboratory. We quote here the Instructions provided by their Laboratory.

"In setting the square wave generator in operation it would be advisable to first trace the pulse signal through the system. To do this, apply the 300 V. to tubes $V_1$ through $V_4$ and removing the blocking oscillator tubes $V_5$ and $V_6$ and keeping all other B voltages off. The cathode resistors in the phase-inverter $V_2$ should then be adjusted until symmetrical signals appear at the grids of $V_5$ and $V_6$. The blocking oscillator tubes are then inserted with the "SYM. ADJ." in center position and the "B.O. Bias" at maximum. These two controls are located near the grid and cathode of tube $V_6$. Gradually reduce bias until pulses appear at the 829B grids. These are symmetrized by means of the "SYM. ADJ.". Then apply the 450 v. to the 829B stage and check the pulses at the grids of the switch tubes. This plate voltage is fairly critical. With 75 V. bias, we have found 450 V. a good value. The high voltage is then applied to the switch tubes and a square wave output should be seen at the monitor jack. Experimenting with the 715 screen resistor may improve the trailing edge somewhat.

"The negative supply in the cathode of the 715 tubes is used to pull the bottom of the square wave slightly below ground so that the 5V4 clamp tubes can conduct. This need not be used in the initial adjustment described above. After square waves are obtained this negative voltage
is applied. It is gradually increased by means of the 40 ohm rheostat in the primary of the negative supply until the square wave suddenly becomes zero based indicating that clamping is taking place.

"In construction, it would be wise to keep the two channels well separated and shielded from each other to prevent any interaction."

The square wave circuit elements are mostly shown in the drawings, see Figure 7 A. The pulse transformers, $T_1$ through $T_4$, are war surplus General Electric type 68G-627.

The power supplies for the generator, see Figures 7B, 7C, and 7D, employ the following transformers and inductances.

**The high voltage supply**

$D_1 = D_2$ : Federal $1804A$ selenium rectifier

$T_1$ : Thordarson, T21 F02, 2.5 volt CT at 10 amps., 7500 volt rms.

$T_2$ : Thordarson, T21P83, primary 440 v.a. (1 amp.), 300 v.a. (c.c.s.),
1560-1250-0-1250-1560, D.C. V, 1250, 1000; D.C.M.A. 300 ma. I.C.A.S.,
200 ma. c.c.s.

**Low voltage supplies**

$T_1$ : Thordarson, T22R12, 120 V., 75 ma., D.C., 6.3 V. 1.5 amp.

$T_2$ : Thordarson, T22R12, supplies -75 V. at 50 ma.

$T_3$ : Thordarson, T21P89, 550-0-550, 450V. D.C., 250 D.C.M.A. ICAS.

$C_1$ : Thordarson, choke, T20C56.

$T_4$ : Thordarson, TS24R06, 750 V. C.T. at 150 ma. Supplies +300 V.

$C_2$ : Thordarson, T20C56.
Negative 150 voltage supply

T₁ : Thordarson, T22RB5, 400-0-400 V., 340 ma., 5V-6A, 6.3 V. 7A C.T.

T₂ : Thordarson, T21F04, 5 V. C.T. 8A., 2500 V. R.M.S.

Choke: Thordarson, T20C56, 10 h at zero amp., 7 H at 300 ma. D.C.,
       600 ohms, 3500 V. Rms.

VIII. Frequency Sweep

Microwave frequency sweep is determined in two ways when using
klystrons. First, small ranges of the order of 5-30 mc may be electron-
ically swept by modulating the repeller voltage. Second mechanical tuning
of the klystron cavity results in ranges of the order of hundreds of
megacycles -- depending on the lengths of microwave modes in the tubes
used. Electronically, we employ either saw tooth or triangular sweep
modulation. The advantage of triangular over saw tooth sweep is that
an average over the time delays in the circuitry is made and hence more
accurate frequency measurements can be obtained.

The mechanical drive is simply a series of 3:1 reduction gears
powered by a very slow and smooth running, reversible induction motor.
This either turns a micrometer screw in the case of the Varian tubes,
or depresses a tuning lever in the case of Raytheon's oscillators.
References to Chapter V


