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Low Frequency Microwave Spectroscopy Project
A Preliminary Report on the S-Band Spectrum of HDO
Report No. 195.1

Prepared for
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Electronics Branch
Washington, D. C.
Contract No. N000 821 (00)
LOW FREQUENCY MICROWAVE PROJECT

A PRELIMINARY REPORT ON THE S-BAND SPECTRUM OF HDO

REPORT NO. 1951

Prepared by:  

Samuel Weisbaum
Samuel Weisbaum

Wardley Beers
Wardley Beers
Project Director

Gabriel Herrmann
Gabriel Herrmann

Approved by:  

Harold K. Work
Harold K. Work
Director of the Research Division

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014 621 (00)
A Stark-modulated spectrometer has been constructed for operation in the $S$-band region. A search in the range from 2150-2400 Mc/sec has led to the discovery of several lines, three of which have been identified as the $6_1 - 6_2$, $9_0 - 9_1$, and $4_0 - 5_1$ transitions at 2394.6 Mc/sec, 3084.7 Mc/sec, and 2888 Mc/sec respectively. The identification of the $12_1 - 12_0$ transition is not certain as yet, but it is either at 2961 Mc/sec or at 2991 Mc/sec. It was found that the centrifugal distortion formula of Kivelson and Wilson could be used to fit all the known Q-branch lines of HDO.
I. Introduction

Until recently, most of the spectroscopic work in the microwave region has been done at the higher frequencies, that is, in the millimeter range and at K and X-band. The main reasons for this are that intensities are lower at the lower frequencies and the number of molecules expected to exhibit low frequency spectra are less numerous than those with high frequency spectra. However, neither of these reasons is prohibitive, and it appears that much useful work can be done in this region.

The first molecule which we have chosen for investigation in the S-band region is the asymmetric rotor HDO. A search was made for three lines in the absorption spectrum of this molecule. The frequencies of these transitions had been predicted by King, Hainer, and Cross\(^1\), using the parameters \(\kappa = -0.685\) and \(\frac{\ell - \ell'}{2} = 8.195\, \text{cm}^{-1}\), and are shown in Table 1.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency (Mc/sec)</th>
<th>Intensity (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6_1 - 6_2)</td>
<td>3000</td>
<td>(3.6 \times 10^{-7})</td>
</tr>
<tr>
<td>(9_0 - 9_1)</td>
<td>3600</td>
<td>(1 \times 10^{-8})</td>
</tr>
<tr>
<td>(12_0 - 12_0)</td>
<td>4200</td>
<td>(2 \times 10^{-9})</td>
</tr>
</tbody>
</table>

The intensities listed by KHC\(^1\) have been corrected here on the basis of experimental data on the line-width parameter.

Previous investigations\(^2, 3\) of this molecule had not yielded enough data for the evaluation of the structural parameters of this molecule. Therefore it was realized that the discovery of these lines and the measurement of their frequencies would be of considerable significance.
II. Theory

In our present work we have made detailed analyses of Q-branch or "a"-type transitions, for which \( \Delta J = 0 \) and \( \Delta K_{-1} = 0 \). The principal parameters involved are:

\[
\frac{a - c}{2} \quad \text{and} \quad \frac{2b - a - c}{a - c},
\]

where \( a, b, \) and \( c \) are the rotational constants relative respectively to the principal axes of least, intermediate, and greatest moments of inertia. The rigid rotor frequency \( \nu_0 \) may be calculated in terms of these by the method of King, Hainer, and Cross.

However, in such a light molecule, centrifugal distortion effects are large, and therefore the rigid rotor approximation is not adequate. Recently Kivelson and Wilson, using first order perturbation theory, have derived a formula for correction of rigid rotor frequencies.

\[
\nu = \nu_0 \left[ 1 + \frac{2KJ(J+1)S_j}{\mu_H} + \frac{(K-1)J(J+1)D_{JK}}{\mu_H} - \frac{1}{2} \frac{K(K^2+2)}{3} R_5 \frac{\nu_0}{\mu_H} + \frac{1}{3} \frac{K(K^2+1)}{3} R_6 \frac{\nu_0}{\mu_H} \right] \frac{2}{a-c} f^2 \tag{1}
\]

where \( \nu \) is the corrected frequency, \( H \) and \( 0 - F \) are functions of \( \lambda \), and for HDO \( K \) equals the index \( K_{-1} \). \( S_j, D_{JK}, R_5, D_K, \) and \( R_6 \) are centrifugal distortion parameters. Therefore, for complete analysis of these transitions these five parameters and the two above are evaluated by observing at least seven absorption lines and adjusting these parameters to give Equation (1) the best possible fit to the observed frequencies.
Due to the fact that the rotational constants of HDO were known only roughly in the beginning, it was quite difficult to be certain of the identifications of the observed lines on the basis of their positions alone. Although the relative intensities were known fairly well, certain identification was not possible by this method either. For this reason, Stark effect data were invaluable. Applying the results of Golden and Wilson\(^6\) to the problem of HDO it was found that, for purposes of identification, the splitting \(\Delta \nu\) for Q-branch transitions may be written, with sufficient accuracy, as

\[
\Delta \nu = \frac{2M g^2 E^2 M^2 \Phi^2}{J(2J+1)(J+1)\hbar^2 \nu}
\]

(2)

where \(M\) is the component of the electric dipole moment along the molecule-fixed axis, \(E\) is the magnitude of the electric field, \(\Phi^2\) is the line strength for the transition, \(h\nu\) is the transition energy and \(M\) is the magnetic quantum number.

III. Apparatus and Experimental Techniques

The spectrometer employed Stark modulation and, except for the features directly due to its comparatively low operating frequency, was conventional in design. The absorption cell consisted of \(3'' \times 1\frac{1}{2}''\) waveguide and was 20' long. With 707, 726A, 2K29, and 2K56 klystrons, the range from 2150 - 7400 Mc/sec could be covered. The square wave Stark voltage generator operated at 5000 cps., and the voltage was variable between zero and 1000 volts. The detecting system was composed of a 1N21B waveguide crystal detector, a preamplifier, a twin "T" amplifier tuned to 5000 cps., phase sensitive detector\(^7\), and Esterline-Angus record-
ing milliampere. The preamplifier had a measured noise figure of 4 d.

The input stage had a U.T.C. L-5 20 high fidelity 2:1 ratio audio transformer in the input with a 6SJ7 pentode. Undoubtedly, the noise figure could have been improved by the use of a triode, but such an improvement seemed to be unnecessary since the major part of the noise in the system appeared to come from the klystron and the crystal.

One novel technique which has been employed is the Lissajous presentation. A sine wave voltage synchronous with the 5000 cps. Stark voltage generator is applied to the horizontal plates of a cathode-ray oscilloscope, preferably one having a long persistent screen, and the output of the tuned amplifier is applied to the vertical plates. The frequency of the klystron is swept slowly, at a rate of about one or two megacycles per minute, by means of a motor driven potentiometer in the reflector circuit. As the frequency of the klystron passes through the absorption frequency of a line, a 1:l Lissajous pattern is seen to appear and then disappear. The brain of the operator serves as a phase sensitive detector, recognizing the Lissajous pattern and rejecting all else as irrelevant. The sensitivity of this method approaches that obtained with an electronic phase sensitive detector and recording meter since the integration time of a trained operator may be as much as several seconds. In fact, most of the weaker lines which will be listed below can be observed by this method.

A secondary frequency standard has been constructed for frequency measurements. The heart of this standard consisted of
the transmitter of a SCR-522 war surplus aircraft radio. This was used to generate either 90 or 135 Mc by multiplication of a fundamental frequency of 5 Mc. These frequencies were applied to a 1N21 crystal which produced harmonics of 90 or 135 Mc of usable intensity in the S-band region. For interpolation purposes a crystal detector and a SX-63 receiver were used in the standard manner. For accurate measurements a Hilley BCS temperature-stabilised 100 kc crystal oscillator was available. This signal could be multiplied to 5 Mc and could then be synchronised to WWV. However, for most search work, the oscillator in the transmitter was used with a nonstabilised 5 Mc crystal to generate the input frequency because of its convenience and greater freedom from spurious responses. This has been found to agree with the 100 kc unit to within 1 or 2 parts in 10^6, an accuracy which is more than adequate for most search work.

A system for stabilising the klystron frequency to differ by some pre-assigned amount from one of the harmonics of the frequency standard has been installed, but it has not been employed to any important extent in the present measurements. In this system, the voltage developed on the F-M discriminator of the SX-63 interpolation receiver is used as an "error" voltage. After dc amplification, it is applied to the reflector of the klystron with proper sign to correct for any deviation from the difference determined by the setting of the receiver. The frequency may be swept through a small range by driving the tuning dial of the receiver with an electric motor. This system fails to operate when the desired frequency is midway between the
harmonics of the standard since the situation is confused by two responses. In this case, it is necessary to change the fundamental frequency by substituting some other crystal in the range from 4.5 to 9Mc. It is partly for this reason that provision is made for operation with high frequency crystals.

IV. Results and Conclusions

The lines which have been observed are listed in Table II. The gaps in Table II suggest several details yet to be investigated. Also, in time, several of these frequencies will be measured more accurately.

The identifications of the $6_1 - 6_2$ and $9_0 - 9_1$ lines were made from the resolved Stark splittings as shown in Figures 1 and 2 respectively. The measured coefficients agreed within a few percent with those calculated by Equation (2) in section II. The observed intensities were also in agreement with the calculated ones. In Figure 2 there is a spurious peak between the $M = \pm 6$ and the $M = \pm 7$ components. The position of this peak was not affected by variation of Stark voltage. Also, it is to be noted from the frequency markers at the top of the Figure that the $M = \pm 6$ and $M = \pm 7$ components are not as widely separated in frequency as might appear at first glance. Except at the ends, these markers are at 1 Mc intervals.

The 2688 Mc/sec line was identified as the $4_0 - 5_{-5}$ transition because its observed intensity was consistent with a calculated intensity\(^1\) of $1 \times 10^{-8}$ cm\(^{-1}\). The rigid rotor frequency of this transition has been recalculated and was found to lie in
Table II. Observed lines

<table>
<thead>
<tr>
<th>Frequency (Mc/sec)</th>
<th>Intensity</th>
<th>Identification</th>
<th>Resolution</th>
<th>Pressure Dependence</th>
<th>Dependence upon cooling with dry ice</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,394.6 ± 0.3</td>
<td>Strong</td>
<td>6_1 - 6_2</td>
<td>Excellent</td>
<td>Strong</td>
<td>Disappears</td>
</tr>
<tr>
<td>2,836 ± 2</td>
<td>Weak</td>
<td></td>
<td>None</td>
<td>Weak</td>
<td>Persists</td>
</tr>
<tr>
<td>2,888 ± 2</td>
<td>Medium</td>
<td>4_0 - 5_5</td>
<td>None</td>
<td>Moderate</td>
<td>Persists</td>
</tr>
<tr>
<td>2,961 ± 2</td>
<td>Weak</td>
<td>12_1 - 12_0 (?)</td>
<td>Uncertain</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>2,997 ± 2</td>
<td>Weak</td>
<td></td>
<td>Uncertain</td>
<td>Weak</td>
<td>Disappears</td>
</tr>
<tr>
<td>3,044.7 ± 0.3</td>
<td>Strong</td>
<td>9_0 - 9_1</td>
<td>Good</td>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>3,074 ± 2</td>
<td>Weak</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the S-band region. The calculated Stark coefficient for the \( \ell_0 - 5 \) transition was so small as to make resolution impossible, while for the 2886 Mc/sec line no Stark splitting could be observed. This identification has been confirmed from infrared rotation-vibration data\(^1\).

It is to be assumed that one of the remaining lines is the \( 12_{-1} - 13_{0} \) transition, which is predicted to fall in this region according to Table I. The most likely choices, on intensity considerations, are the 2961 Mc/sec and the 2991 Mc/sec lines. It is uncertain whether positive identification by Stark effect can be made since, with such a high J transition, resolution is difficult and the components, if resolved, have intensities hardly any bigger than noise. The observations of the Stark splittings of these two lines were inconclusive. However, the line at 2961 Mc/sec showed a pressure dependence similar to that of the \( 6_{1} - 6_{2} \) and \( 9_{0} - 9_{1} \) lines. On the other hand, the 2991 Mc/sec line was insensitive to pumping, although it disappeared upon cooling with dry ice. Therefore, it is possible that this latter line, as well as the one at 2836 Mc/sec which showed a similar behaviour, may be due to a heavy contaminant.

Calculations were made to fit the centrifugal distortion formula of Kivelson and Wilson to all known Q-branch lines. These calculations also favor the 2961 Mc/sec line over the one at 2991 Mc/sec as the \( 12_{-1} - 13_{0} \) transition and exclude the possibility of either the 2836 or 3071 Mc/sec line having this identification. The results of these calculations together with the values of the prin-
Principal parameters are shown in Table 3. It will be seen that both fits are reasonably good but the one employing 2961 Mc/sec is somewhat better.

The authors wish to thank Prof. Strandberg and Mr. Posener of M.I.T. for helpful discussion and for access to their unpublished results. They also wish to thank Mr. Leen Arnall and Mr. Leonard Yarmus for help in building some of the electronic circuits and to Mr. Howard Greenberg for help in performing some of the calculations.

Table 3

Comparison of Calculated and Observed Frequencies

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed Frequency (Mc/sec)</th>
<th>Observed - calculated frequency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2\textsuperscript{1} - 2\textsuperscript{2}</td>
<td>10,278.99</td>
<td>+0.03</td>
<td>See Note A</td>
</tr>
<tr>
<td>3\textsuperscript{0} - 3\textsuperscript{1}</td>
<td>50,236.90</td>
<td>-0.10</td>
<td>See Note A</td>
</tr>
<tr>
<td>4\textsuperscript{1} - 4\textsuperscript{2}</td>
<td>Unpublished</td>
<td>-0.05</td>
<td>See Note A</td>
</tr>
<tr>
<td>5\textsuperscript{0} - 5\textsuperscript{1}</td>
<td>22,307.67</td>
<td>+0.17</td>
<td>See Note A</td>
</tr>
<tr>
<td>6\textsuperscript{1} - 6\textsuperscript{2}</td>
<td>2,391.6</td>
<td>-0.06</td>
<td>See Note A</td>
</tr>
<tr>
<td>7\textsuperscript{0} - 7\textsuperscript{1}</td>
<td>Unpublished</td>
<td>+1.0</td>
<td>See Note A</td>
</tr>
<tr>
<td>8\textsuperscript{1} - 8\textsuperscript{0}</td>
<td>Unpublished</td>
<td>-1.3</td>
<td>See Note A</td>
</tr>
<tr>
<td>9\textsuperscript{0} - 9\textsuperscript{1}</td>
<td>3,011.5</td>
<td>-1.7</td>
<td>See Note A</td>
</tr>
<tr>
<td>12\textsuperscript{1} - 12\textsuperscript{0}</td>
<td>2,991</td>
<td>+1.7</td>
<td>See Note A</td>
</tr>
</tbody>
</table>

Note A: Calculation based upon the assumption that the asymmetry parameter \( \kappa = -0.6827 \); that \((\alpha - \epsilon)/2 = 8.495 \text{ cm}^{-1} \); and that the 2,961 Mc/sec is the 12 \textsuperscript{1} - 12 \textsuperscript{0} transition.

Note B: Calculation based upon the assumption that the asymmetry parameter \( \kappa = -0.6821 \); that \((\alpha - \epsilon)/2 = 8.450 \text{ cm}^{-1} \); and that the 2,991 Mc/sec line is the 12 \textsuperscript{1} - 12 \textsuperscript{0} transition.
This report contains essentially the subject matter of a contributed paper, No. 86, at the Meeting of the American Physical Society in Cambridge, Massachusetts, on January 22, 1953. However, since the abstract for that meeting went to press some time in advance it does not completely represent the paper as given.
