Centrifugal Distortion Analysis of Pure Rotational Spectra of \( \text{H}_2^{16}\text{O}, \text{H}_2^{17}\text{O}, \) and \( \text{H}_2^{18}\text{O} \)

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Centrifugal distortion analyses based entirely on high-quality infrared data are carried out for the ground vibrational states of \( \text{H}_2^{16}\text{O}, \text{H}_2^{17}\text{O}, \) and \( \text{H}_2^{18}\text{O} \). As a result of the analyses, the values of 27 rotation and distortion constants for each species are determined. By using these constants it was possible to improve considerably the accuracy of the literature values for rotational energy levels at high \( J \), especially for \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \). The experimental values for the energy levels are deduced from the observed rotational transitions constituting the fitted data.

INTRODUCTION

Several papers dealing with the centrifugal distortion analysis of \( \text{H}_2\text{O} \) have been published during the recent years. For example, De Lucia et al. (1, 2), De Lucia and Helminger (3, 4), and Flaud et al. (5, 6) have been working on the subject. The accuracy and the scope of the infrared data in these studies have varied. The situation has been better, in this respect, for \( \text{H}_2^{16}\text{O} \) than for \( \text{H}_2^{18}\text{O} \) or especially for \( \text{H}_2^{17}\text{O} \). On the other hand, \( \text{H}_2\text{O} \) microwave data are scant and, accordingly, a need for accurate infrared spectra is obvious in the distortion analysis of \( \text{H}_2\text{O} \).

The quality of the available infrared data, particularly the data for \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \), has been considerably improved by measuring the two spectra presented in Refs. (7) and (8). Actually, this paper is a consequence of the difficulties encountered in assigning the latter spectrum, where an isotopically enriched sample was used. It turned out to be necessary to refine the existing predictions for \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) frequencies at high \( J \), in order to successfully complete the assignment of the spectrum. To accomplish this, a least-squares analysis program was written. By means of this program the results of the present distortion analysis have been derived. The analysis is based entirely on the infrared data available in the two spectra mentioned above.

PROGRAM AND EXPERIMENTAL DATA

The program can fit 30 rotation and distortion constants to 400 data points. The maximum \( J \) value that can be used is 15. A double-precision accuracy (three 16-bit computer words or 12 figures) was adopted for every noninteger variable. By properly programming the necessary routines, the memory space occupied by the program could be reduced to 19 kwords, which is an essential fact because the program was written for the minicomputer (Hewlett-Packard 21MXE) connected on line to our Fourier spectrometer (9). The correctness of the pro-
gram code was tested by fitting "spectra" produced computationally by different values of the rotational constants included in the program. These computations also confirmed that our minicomputer is able to handle with sufficient accuracy the large and correlated models used in the model testing.

The \( \text{H}_2^{17}\text{O} \) and \( \text{H}_2^{18}\text{O} \) data were prepared from the spectrum of isotopically enriched water (8). For \( \text{H}_2^{16}\text{O} \), both this spectrum and the spectrum of natural water (7) were utilized and a mean of the two frequencies was taken if the \( \text{H}_2^{16}\text{O} \) line was unblended in both spectra. The numbers of lines in the three sets of data were 368, 282, and 282, respectively, for \( \text{H}_2^{16}\text{O} \), \( \text{H}_2^{17}\text{O} \), and \( \text{H}_2^{18}\text{O} \). Since all the blended and very weak lines were excluded, there was no need to assign different weights to the observations. Figure 1 illustrates the fitted data. As can be seen, the lines selected for the fit provide information on a wide range of rotational energy levels. Most levels are involved in several transitions of different types. The number of \( \text{H}_2^{16}\text{O} \) lines is larger, but the essential coverage of \( J_\tau \) values is the same in the three sets of data. To reach this obviously very advantageous situation, the doublets with \( K_a = 11 \) (those with the line numbers 900, 909, and 932 in Ref. (8)) were removed from the \( \text{H}_2^{16}\text{O} \) and \( \text{H}_2^{18}\text{O} \) data, since the corresponding \( \text{H}_2^{17}\text{O} \) lines were not resolved. Hence the maximum value of \( K_a \) is 10 for each species.

MODEL TESTING

The data to be fitted contained several transitions at high \( J \) and \( K_a \). Accordingly, the number of the terms in the Watson Hamiltonian which are expected to yield a significant contribution becomes large. In addition to 24 terms of the degrees 2, 4, 6 and 8, the applicability of the following terms was tested (\( J_{xy}^2 = J_x^2 - J_y^2 \)):

\[
P_{KJ}J_x^4J_z^4, \ P_{KKJ}J_x^2J_z^2, \ P_{KJ}J_x^10, \ P_{KKJ}J_x^2(J_x^2J_y^2 + J_y^2J_z^2)
\]

and

\[
G_{KJ}J_x^4J_z^4, \ G_{KJ}J_x^12, \ G_{KJ}(J_x^2J_y^2 + J_y^2J_z^2)
\]

and

\[
F_{K}J_z^{14}.
\]

The first runs were performed with a model including the following 21 constants: \( P_{K}, P_{KJ}, L_{K}, L_{KKJ}, L_{KJ}, \) and \( l_{K} \) added to 15 constants of the degrees 2, 4 and 6. This model yields the following standard deviations\(^1\) of observations: \( \delta(\text{H}_2^{18}\text{O}) = 2.4 \), \( \delta(\text{H}_2^{17}\text{O}) = 2.6 \), and \( \delta(\text{H}_2^{16}\text{O}) = 2.5 \times 10^{-3} \text{ cm}^{-1} \). An introduction of the term \( G_{K}P_z^{12} \) decreases the standard deviation by 20–30%, e.g., \( \delta(\text{H}_2^{16}\text{O}) = 1.9 \times 10^{-3} \).

\(^{1}\) The standard deviation \( \delta \) was defined as

\[
\delta = \left( \frac{\sum_{i} (y_{\text{obs}}^{i} - y_{\text{calc}}^{i})^2}{n - p} \right)^{1/2},
\]

where \( n \) is the number of lines and \( p \) is the number of parameters.
FIG. 1. The structure of the fitted data. The dots represent rotational levels and the lines connecting the dots represent transitions. J and Kα are quantum numbers. Even and odd refer to the parity of Kα + Kγ. The plots have been drawn from H216O data and H217O data. The structure of H216O data is very similar to that of H217O data.

cm⁻¹. This is not a poor value, but the following indications of the deficiency of this model suggested the need to introduce additional terms: for several transitions even at low J the differences \( \gamma_{\text{obs}} - \gamma_{\text{calc}} \) were comparatively large and to the same direction for all the isotopic species; the ability of this model to reproduce the observed microwave spectra (1–3) was not in agreement with the accuracy of the fitted data, which indicates a significant perturbation among low-order constants.
Even when the effect of a single term proved to be small, the fitting did improve gradually with inclusion of additional terms. Finally, after extensive computation, the following Hamiltonian consisting of 27 rotation and distortion terms was chosen: \((J_x^2 = J_z^2 - J_y^2)\)

\[
H = \frac{1}{2} (B + C)J^2 + \left[ A - \frac{1}{2} (B - C) \right]J_z^2 + \frac{1}{2} (B - C)J_{xy}^2 - \Delta J^4 - \Delta_{JK}J^2J_z^2 \\
- \Delta K J_z^4 - 2\delta_1 J^2J_z^2 - \delta_2(J_x^2J_z^2 + J_y^2J_z^2) + H_{JK}J^4 + H_{JK}J^4J_z^2 + H_{JK}J^2J_z^2 \\
+ H_K J_z^6 + 2h_J J^4J_z^2 + h_{JK}J^2(J_x^2J_z^2 + J_y^2J_z^2) + h_K(J_x^2J_z^2 + J_y^2J_z^2) \\
+ L_J J^8 + L_{JK}J^4J_z^4 + L_{KK}J^2J_z^6 + L_K J_z^8 + 2l_J J^4J_z^2 + l_{JK}J^4(J_x^2J_z^2 + J_y^2J_z^2) \\
+ l_{KJ}J^2(J_x^2J_z^2 + J_y^2J_z^2) + l_K(J_x^2J_z^2 + J_y^2J_z^2) + P_{KK}J^2J_z^2 + P_{KJ}J^2J_z^2 \\
+ P_K(J_x^2J_z^2 + J_y^2J_z^2) + G_J J_z^{12}.
\]

With this model the following standard deviations are obtained: \(\delta(H_2^{18}O) = 1.3\), \(\delta(H_2^{17}O) = 1.6\), and \(\delta(H_2^{16}O) = 1.4 \times 10^{-3} \text{ cm}^{-1}\).

There are high correlations among many of the distortion constants which hardly can be avoided when fitting water spectra. The inclusion of the less significant terms \((L_J, l_J, l_{JK}, l_{KJ})\) increases the uncertainties of the values of the closely related constants of degree 6 by a factor of 2–4. On the other hand, with inclusion of these constants the overall appearance of the fit became closer to that obtained with smaller models by using slightly restricted \(J\), range of data. For instance, removing 10\% of the lines and using the model with the 21 constants mentioned above lead to \(\delta = 1.1 \times 10^{-3} \text{ cm}^{-1}\) for \(H_2^{16}O\).

**RESULTS**

The final values for the rotation and distortion constants are shown in Table I. The rotational energy levels derived from these constants are listed in Table II. The agreement between observed \((I - 3)\) and calculated microwave transitions can be seen from Table III.

It was also possible to deduce the rotational energy levels from the experimental frequencies. As can be seen from Fig. 1, the calculation of the \(H_2^{16}O\) levels with even \(K_a + K_c\) can be initiated from the rotational ground state. The other half of the \(H_2^{16}O\) levels was calculated by fixing the value of the level \(1_{0,1}\) to that obtained in the fit. For \(H_2^{17}O\) as well as for \(H_2^{18}O\), it was necessary to fix the values of both the level \(1_{0,1}\) and the level \(1_{1,1}\). The propagation of the calculation was toward higher energies. Before proceeding forward from any level, a mean of the energy values resulting from all the possible routes leading to that level, was calculated. An exception to this scheme of calculation was caused by the levels which could not be reached without going downward on the energy scale. Those levels were preferably obtained by making a step toward smaller \(K_a\) within the same \(J\) value. After picking up the desired level the calculation was continued normally.

The method outlined above is still very sensitive to inaccurate data points, especially if these are located at the bases of the "trees" in Fig. 1. Therefore, it is unfortunate that in \(H_2^{16}O\) spectrum of Ref. (7) there seem to be several systematic
measurement errors in low-J lines within the lowest wavenumber region 30–60 cm\(^{-1}\). The accumulation of these errors (typically +0.002 cm\(^{-1}\)) made the whole chain of experimental H\(_2\)\(^{16}\)O levels too high when compared to the set of the levels derived from the fit. The situation was corrected by replacing our measured line positions for H\(_2\)\(^{16}\)O lines with line numbers 1–18 in Ref. (7) by the values obtained from the energy levels given in Ref. (5). Because the results of a least-squares fit are rather insensitive to a few less accurate data points it can be expected that calculated energy levels quoted in columns H\(_2\)\(^{16}\)O, H\(_2\)\(^{17}\)O, and H\(_2\)\(^{18}\)O of Table II
TABLE II

Ground-State Rotational Levels of H$_2^{16}$O, H$_2^{17}$O, and H$_2^{18}$O (cm$^{-1}$)

<table>
<thead>
<tr>
<th>$J$</th>
<th>$E_J$</th>
<th>$\Delta E_J$</th>
<th>$E_J^\prime$</th>
<th>$\Delta E_J^\prime$</th>
<th>$J'$</th>
<th>$\Delta J$</th>
<th>$\Delta E_J$</th>
<th>$\Delta E_J^\prime$</th>
<th>$E_J'$</th>
<th>$\Delta E_J'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.0</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.1</td>
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<td>0.001</td>
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<td>0.002</td>
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<td>0.2</td>
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<td>3</td>
<td>0.3</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
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<tr>
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<td>0.4</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.4</td>
<td>0.4</td>
<td>0.004</td>
<td>0.004</td>
<td>0.4</td>
<td>0.004</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.5</td>
<td>0.5</td>
<td>0.005</td>
<td>0.005</td>
<td>0.5</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Note. The levels resulting from the fit are listed in the columns H$_2^{16}$O, H$_2^{17}$O, and H$_2^{18}$O. The levels deduced from the experimental wavenumbers are listed in the columns OBS. DIFF refers to the difference between the two sets of levels in 10$^{-4}$ cm.

are more reliable than experimental levels listed in columns OBS. It is also seen from Table II that the standard deviations obtained for energy levels are somewhat larger than the standard deviations obtained for the fitted transitions. Columns DIFF of Table II yield: $\delta$(H$_2^{16}$O) = 1.6, $\delta$(H$_2^{17}$O) = 2.1, and $\delta$(H$_2^{18}$O) = 2.1 x 10$^{-3}$ cm$^{-1}$.

DISCUSSION

It was found out during this work that the ability of the different sets of H$_2$O constants found in the literature to predict transitions outside the $J$, range of the original analysis is very limited. Especially if the range of $K_a$ is extended, the pre-
PURE ROTATIONAL SPECTRA OF WATER VAPOR

TABLE III

Observed and Calculated Microwave Transitions of H\textsubscript{2}\textsuperscript{16}O, H\textsubscript{2}\textsuperscript{17}O, and H\textsubscript{2}\textsuperscript{18}O (MHz)

<table>
<thead>
<tr>
<th>Transition</th>
<th>H\textsubscript{2}\textsuperscript{16}O</th>
<th>H\textsubscript{2}\textsuperscript{17}O</th>
<th>H\textsubscript{2}\textsuperscript{18}O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>observed</td>
<td>obs-calc</td>
<td>observed</td>
</tr>
<tr>
<td>6\textsubscript{16} - 5\textsubscript{23}</td>
<td>22235.080</td>
<td>-14.136</td>
<td>13536.02</td>
</tr>
<tr>
<td>3\textsubscript{13} - 2\textsubscript{20}</td>
<td>183310.117</td>
<td>+9.851</td>
<td>194002.998</td>
</tr>
<tr>
<td>10\textsubscript{29} - 9\textsubscript{36}</td>
<td>321225.644</td>
<td>+2.411</td>
<td>321525.919</td>
</tr>
<tr>
<td>5\textsubscript{15} - 4\textsubscript{22}</td>
<td>380197.372</td>
<td>-4.485</td>
<td>385784.860</td>
</tr>
<tr>
<td>4\textsubscript{14} - 3\textsubscript{21}</td>
<td>448001.075</td>
<td>+25.133</td>
<td>469808.134</td>
</tr>
<tr>
<td>7\textsubscript{32} - 6\textsubscript{60}</td>
<td>470989.947</td>
<td>-9.710</td>
<td>520157.32</td>
</tr>
<tr>
<td>6\textsubscript{43} - 5\textsubscript{50}</td>
<td>439150.812</td>
<td>-29.918</td>
<td>520157.32</td>
</tr>
<tr>
<td>7\textsubscript{52} - 6\textsubscript{61}</td>
<td>440101.295</td>
<td>-12.631</td>
<td>520157.32</td>
</tr>
<tr>
<td>1\textsubscript{23} - 3\textsubscript{30}</td>
<td>448001.075</td>
<td>+25.133</td>
<td>469808.134</td>
</tr>
<tr>
<td>6\textsubscript{42} - 5\textsubscript{51}</td>
<td>470989.947</td>
<td>-9.710</td>
<td>554059.07</td>
</tr>
<tr>
<td>5\textsubscript{33} - 4\textsubscript{40}</td>
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<td>+17.260</td>
<td>537337.57</td>
</tr>
<tr>
<td>6\textsubscript{24} - 7\textsubscript{17}</td>
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</tr>
<tr>
<td>1\textsubscript{10} - 1\textsubscript{01}</td>
<td>556936.002</td>
<td>-0.442</td>
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</tr>
<tr>
<td>5\textsubscript{32} - 4\textsubscript{41}</td>
<td>620700.807</td>
<td>+21.078</td>
<td>692079.14</td>
</tr>
<tr>
<td>2\textsubscript{11} - 2\textsubscript{02}</td>
<td>752033.227</td>
<td>+3.618</td>
<td>74858.254</td>
</tr>
</tbody>
</table>

Predictions soon become very poor. This remark is obviously valid for any set of rotation and distortion constants of H\textsubscript{2}O because of the slow convergence of the Watson Hamiltonian. To illustrate this, let us recall that the value obtained for \( G_K \) (term in \( P_1^5 \)) is about \(-5 \times 10^{-12} \text{ cm}^{-1}\). Therefore, even the smallest contribution of \( P_2^2 \) terms is approximately \(-5 \times 10^{-12} \text{ cm}^{-1} \times 10^{12} = -5 \text{ cm}^{-1}\) for the level \( 10_{10,0} \), and \(-16 \text{ cm}^{-1} \) and \(-45 \text{ cm}^{-1}\), respectively, for the levels \( 11_{11,0} \) and \( 12_{12,0} \). It is not surprising that the errors in the excluded doublets with \( K_a = 11 \) proved to be \( 0.05-0.15 \text{ cm}^{-1}\) when calculated by the constants of Table I.

It is, however, interesting to compare the abilities of the literature constants to reproduce our spectra. The comparison is better justified if the \( J \), range of our observations is restricted according to the analysis in question. Thus, omitting lines with \( J > 8 \) leads to \( \delta(\text{H}_2\textsuperscript{16}O) = 3.6, \delta(\text{H}_2\textsuperscript{17}O) = 6.7, \) and \( \delta(\text{H}_2\textsuperscript{18}O) = 3.0 \times 10^{-3} \text{ cm}^{-1}\) when the present data are predicted by the constants found in Ref. (4). In this case the agreement proved to be very good, typically 0.001 cm\(^{-1}\), at low \( J \), but became considerably poorer toward higher \( K_a \). A better overall agreement (\( \delta = 2.0 \times 10^{-3} \text{ cm}^{-1}\) was obtained with the \( \text{H}_2\textsuperscript{16}O \) analysis found in...
Ref. (5), where the \(J\) range covers 90% of our transitions. When the 21 constants were refined according to the present data, \(\delta\) was reduced to \(1.1 \times 10^{-3} \text{ cm}^{-1}\) and the predictions for the excluded 10% of the transitions became much more accurate.

Considering the facts that microwave data have not been included in the analysis and that the expected measurement error of the fitted infrared data is about 30 MHz, the standard deviation \(\delta = 24\) MHz obtained in recalculating the 34 microwave transition frequencies shown in Table III is reasonable. This together with good fitting of high \(J\) infrared transitions guarantee that the values of the constants given in Table I are essentially correct and that the energy levels derived from them can be safely used in practical spectroscopy.

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REFERENCES