Millimeter-Wave Spectra and Global Torsion-Rotation Analysis for the CH$_3$OD Isotopomer of Methanol

M. S. Walsh,* Li-Hong Xu,† R. M. Lees,* I. Mukhopadhyay,‡ G. Moruzzi,§ B. P. Winnewisser,¶ S. Albert,|| Rebecca A. H. Butler,||| and F. C. DeLucia||

*Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3; †Department of Physical Sciences, University of New Brunswick, Saint John, New Brunswick, Canada E2L 4L5; ‡Laser Programme, Centre for Advanced Technology, Indore 452 013, India; §Dipartimento di Fisica dell’Università di Pisa and INFN, Via Filippo Buonarroti 2, I-56127 Pisa, Italy; ¶Physikalisch Chemisches Institut, Justus Liebig Universität, Heinrich Buff Ring 58, D-35392 Giessen, Germany; and ||Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210

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New millimeter-wave and microwave measurements for CH$_3$OD have been combined with previous literature data and with an extended body of Fourier transform far-infrared observations in a full global analysis of the first two torsional states ($J = 0$ and 1) of the ground vibrational state. The fitted CH$_3$OD data set contained 564 microwave and millimeter-wave lines and 4664 far-infrared lines, representing the most recent available information in the quantum number ranges $J \leq 20$ and $K \leq 15$. A 53-parameter converged global fit was achieved with an overall weighted standard deviation of 1.060, essentially within the assigned measurement uncertainties of $\pm 100$ kHz for almost all of the microwave and millimeter-wave lines and $\pm 6$ MHz for the far-infrared lines. The new parameters for CH$_3$OD are compared to previous results obtained for the $^{12}$CH$_3$OH, $^{13}$CH$_3$OH, and CD$_3$OH isotopomers over the same quantum number ranges using the identical fitting program. Strong asymmetry-induced coupling between the accidentally near-degenerate 0E and $-1E \nu = 0$ substates is successfully modeled by the fit. © 2000 Academic Press

Key Words: methanol; CH$_3$OD; torsion; millimeter-wave spectra; far-infrared spectrum; global fitting.

I. INTRODUCTION

This analysis of the ground state spectrum of the CH$_3$OD species of methanol is the fourth in a series of global fitting studies of the microwave (MW), millimeter-wave (MMW), and far-infrared (FIR) spectra of methanol and its isotopomers (1–4). The data sets have all been chosen to cover closely similar ranges of quantum number to permit consistent intercomparison of the results. Each of the global fits reproduces the data to within experimental accuracy, using a computer program (5) based on the formalism of Herbst et al. (6). Here, we will give brief introductory remarks relating to CH$_3$OD and refer the reader to the previous literature (1–7) for details of the computer program, the Hamiltonian model used, and the background to the notation for the torsion–rotation quantum numbers and transition labeling.

There have been a number of studies of the MW and MMW spectra of CH$_3$OD (8–13), originally aimed at the structural determination of methanol via isotopic substitution, and later with astrophysical applications in view. CH$_3$OD was also included in Woods’ far-infrared (FIR) study of four methanol isotopomers (14), whose ground state spectra were subsequently analyzed by Kwan and Dennison (15) in order to better define the torsional potential and Hamiltonian parameters. Recently, the high-resolution Fourier transform far-infrared (FT-FIR) spectrum has been investigated for the ground vibrational state, and several fits to model Hamiltonians of differing orders have been reported (16–19) for a variety of subsets of the FTFIR data. Further ground state information is also available in the form of IR combination differences from the spectrum of the CO–stretching fundamental band (20) and from exploration by laser Stark spectroscopy of torsion–rotation transitions in the vicinity of the HCN laser lines (21).

The present paper reports new MMW measurements for CH$_3$OD in the ranges from 126–147 and 482–499 GHz, plus a number of further measurements in the MW region, which have yielded about 160 new line assignments. These have been combined with previous data in a global fit of a total of 5228 assigned MW, MMW, and FTFIR ground state transitions of CH$_3$OD involving levels of the first two torsional states ($\nu = 0$ and 1) up to a maximum rotational quantum number $J$ of 20. The one-dimensional torsion–rotation model is implemented in a well-tested computer program (5) previously applied successfully for the $^{12}$CH$_3$OH (1, 2), $^{13}$CH$_3$OH (3), and CD$_3$OH (4) isotopomers of methanol and also for acetaldehyde, CH$_3$CHO (7).

As described previously (4), the principal goals in our program of global analyses of ground state spectra for methanol isotopomers are as follows.

(i) To achieve fits of all observed transitions to within experimental accuracy over quantum number ranges sufficient for rigorous testing of the model. So far, our CH$_3$OH,
$^{13}$CH$_3$OH, and CD$_3$OH analyses have proven that the one-dimensional Hamiltonian model is very successful in describing $v_t = 0$ and 1 methanol energy levels below and immediately above the torsional barrier.

(ii) To obtain molecular parameters for different methanol isotopomers in as consistent a way as possible by using the same computer program to analyze data sets covering the same quantum number ranges. This should then permit meaningful intercomparison in order to explore the physical interpretation of the parameters.

II. NEW MMW AND MW SPECTRA

The majority of the new measurements in this work were obtained in two runs on the automated FASSST rapid-scan MMW spectrometer at Ohio State University (22). The first scan covered the region from 126.4 to 146.9 GHz, generating a peak list of 567 lines, and the second from 482.5 to 499.0 GHz with a peak list of 253 lines. We found that even with the short scanning times of the FASSST technique, rapid D $\leftrightarrow$ H chemical exchange in the absorption cell was a problem, as a significant number of known CH$_3$OH lines from the recent microwave review (23) turned up in the peak lists of the CH$_3$OD spectra. In addition to the new MMW observations, a number of additional lines have been measured in the MW region at the University of New Brunswick (24), using a conventional Stark-modulated spectrometer with klystron sources.

We have been able to assign torsion–rotation quantum numbers to a substantial number of the new lines. These transitions with their frequencies are included in the complete tables of assigned CH$_3$OD MW and MMW lines which are discussed below in Section III.3. As well, we have deposited the FASSST MMW peak lists, giving the line frequencies and relative intensities and marking the suspected CH$_3$OH features, as supplementary data with the JMS archive accessible through the JMS home page at www.idealibrary.com.

III. GLOBAL FIT

1. The $v_t = 0$ and 1 Data Set

Our fitted data set for CH$_3$OD included a total of 5228 MW, MMW, and FIR lines covering quantum number ranges $v_t \leq 1$ and $J \leq 20$ for both $A$ and $E$ torsional symmetries and all available $K$ states. The 564 MW and MMW frequencies were obtained from the NIST MW data center compilation (25), previous literature (8–13), private files (26), and the new measurements discussed above from Ohio State and UNB (24). The 4664 fitted FT FIR data were derived from analysis, with the aid of the Ritz program (27), of spectra recorded in the Giessen laboratory (16, 17). For the Fourier transform measurements, the long integration times again meant that chemical exchange between D and H was a significant problem, and strong CH$_3$OH lines can be seen in published segments of the FIR spectra (16, 18).

The present FT FIR dataset is about twice as large as has previously been analyzed, with a more complete range of $K$ values, particularly for torsionally excited $E$ transitions. Earlier reported fits (17, 19) were to a transition subset with $J \leq 20$ and $K \leq 6$, but included only $K$ states from $-3$ to $-6$ for $E$ subbands involving $v_t = 1$ levels. This previous data set, which was stated to contain 2348 lines in the 20–350 cm$^{-1}$ region, was archived as supplementary information and made available through both the British Library Document Supply Centre (17) and the JMS archive (19). (We note in passing, however, that the list from the former contains only 2306 entries, while the latter has 2348 transitions but includes around 50 wavenumbers below 20 cm$^{-1}$ which are duplicates of MW and MMW lines already in the fit. Also, the $A^\pm$ labeling is somewhat erratic in the archived data when the $K$-doubling is unresolved, and transitions are listed which formally are forbidden by the selection rules. With the $A^\pm$ splittings unresolved, of course, the forbidden and allowed transition wavenumbers are identical so that only the statistics of the fit are affected, with a single measured line being included up to four times. Nevertheless, one needs to be careful in reading $A^\pm$ transition labels from the archived data.)

In our data set, all of the transition information was critically evaluated for reliability and internal consistency prior to fitting; this step had proven decisive in the earlier analyses in removing contamination from poorly measured or misassigned lines and thereby achieving convergence and stable fits. All 564 MW and MMW lines were assigned an uncertainty of $\pm 100$ kHz in the fit, except for a few unresolved $K$-doublet transitions which were given uncertainties of $\pm 200$ kHz. The 4664 FT FIR lines were assigned a uniform uncertainty of $\pm 0.0002$ cm$^{-1}$ (\pm 6 MHz). Here, use of the line-fitting routine developed for the Ritz program (28) was important in resolving blended features and enhancing the accuracy of the wavenumbers. A further group of assigned MW and MMW lines were excluded from the fit because the $(v_{obs} - v_{calc})$ residuals were unreasonably high or because they were blended and had multiple assignments. A number of FT FIR lines were omitted as well for the latter reason. In view of the large size and broad quantum number range of the overall fitted dataset, we do not believe that the omission of these doubtful lines would substantially affect the values of the fitted parameters.

We also chose at this stage not to incorporate $v_t = 2$ $a$-type MMW lines, which had been included in one of the previous studies (19), in order to maintain consistency and comparability with the earlier global fits in our series (1–4). To treat $v_t = 2$ data properly in a true $v_t = 0$–2 fit, one would look for $\Delta K = \pm 1$ $b$-type transitions more sensitive to the torsional potential and seek to include data covering a substantial range of $J$ and $K$ quantum numbers. Such $v_t = 2$ data have so far only been treated in a single-$v_t$-state fit (18). In the present work, as discussed below in Section II.3, we did calculate the

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\( v_t = 2 \) \( a \)-type transition frequencies utilizing our \( v_t = 0 + 1 \) parameter set to explore how well these parameters would account for that \( v_t = 2 \).

2. Overall Fit Results and Parameters

In the global fit to the CH\(_3\)OD data, we achieved convergence with an overall unitless weighted standard deviation of 1.060 using 53 adjusted parameters. The MW and MMW lines were fitted with weighted rms errors of 1.149 for the 424 \( v_t = 0 \) transitions and 1.816 for the 140 \( v_t = 1 \) transitions. The FTFIR lines were fitted with a weighted rms error of 1.011. Table 1 presents the parameters from the fit arranged according to increasing order of torsion–rotation operator. The overall order is \( n = l + m \), where \( l \) is the order of the torsional factor, and \( m \) is the order of the rotational factor (6). For comparison, the results from the previous corresponding fits for CH\(_3\)OH, \(^{13}\)CH\(_3\)OH, and CD\(_3\)OD (2–4) are included in Table 1 as well.

In general, the four sets of molecular constants show good consistency, with comparable values for the larger parameters allowing for changes with mass, and no obvious discrepancies in the lower order terms. As found for CD\(_3\)OD (4), the “\( a \)"-type parameters with a \( P^2 \) factor in their matrix elements decrease significantly with deuteration, but now the “\( b \)"-type terms with \( P_a \)-dependence such as \( k_1 \) or \( k_2 \) also change substantially, indicating that centrifugal distortion with axial \( K \)-rotation tends to be dominated by the light OH rotor.

In Table 1, we did not attempt to compare our parameters with those of other workers, due to a problem with contemporary detailed analyses of methanol spectra that the specific Hamiltonians used in the various studies almost all differ in some important aspect, with significant effects on the parameters. One of the major differences arises through the definition of the molecular axes. The torsional angular momentum \( P_t \), in the commonly used IAM internal axis method (9, 15) corresponds in our rho-axis system (7) to the operator \( (P_3 + \rho P_\varphi) \), which leads to major changes in the expectation values of terms of the type \( P^2 \), and sizeable deviations between superficially identical Hamiltonian parameters. Thus, one must exercise great care in comparing the parameters from the different models. Recent discussion (29) of the possible reasons for large discrepancies between the \( k_1 \), \( k_2 \), and \( k_3 \) values in \(^{13}\)CH\(_3\)OH global fits, for example, should be revised because the differences between the two axis systems and Hamiltonians were not taken into account. If one transforms appropriately between the two axis systems, the parameters turn out to be closely similar.

3. CH\(_3\)OD MW and MMW Transitions

To partially display the range and quality of the global fit, we list all \( v_t = 0 \) \( \leftrightarrow \) 0 and \( 1 \) \( \leftrightarrow \) 1 MW and MMW transitions that were considered in this work in Tables 2 and 3 for \( A \) and \( E \) torsional symmetries, respectively. The data are arranged by \( K' \) \( \leftrightarrow \) \( K'' \) subband, together with the (\( v_{obs} - v_{calc} \)) residuals and

the original literature references. About 160 of the lines are the new CH\(_3\)OD measurements from the FASSST spectrometer at Ohio State University (22) or the Stark spectrometer at UNB. The literature lines marked with an asterisk in the tables were not included in the fit because they violated closed-loop combination relations, had unreasonably large \((O - C)\) residuals, or were blended with multiple assignments.

For the quantum number ranges covered in this work, the accuracies of line predictions based on the final parameter set of Table 1 will be either \( \sim 100 \) kHz or \( \sim 6 \) MHz depending on whether frequency-measured or Fourier transform FIR data were fitted in the original data set. Thus, the ranges of the MW and MMW data in Tables 2 and 3 also serve as guides as to whether a given calculated transition may be expected to have the higher 100 kHz level of accuracy. The uncertainties in calculated frequencies increase sharply above the fit upper limit of \( J = 20 \).

To explore whether \( v_t = 2 \) \( a \)-type data were predictable from our \( v_t = 0 + 1 \) parameter set or whether they contained significant new information that would require further higher order parameters, we calculated frequencies for the known \( v_t = 2 \) MW lines. The results are presented in Table 4 and show that our parameters do a reasonably good job of accounting for the \( v_t = 2 \) data. However, the \((O - C)\) errors are relatively systematic and increase fairly linearly with \( J' \) to typically about 6 MHz at \( J' = 10 \), suggesting that refinements or additions to the \( J \)-dependent terms in the Hamiltonian would indeed improve the agreement. The very large residuals obtained for the \( K = -4 \) \( E \) transitions indicate a possible misassignment of that series in the literature.

4. Coupling between the \( K = 0 \) and \(-1 \) \( E \) States

One of the notable features of the energy level structure of CH\(_3\)OD is an accidental near-degeneracy between the \( K = 0 \) and \( K = -1 \) \( E \) levels for \( v_t = 0 \), leading to particularly strong asymmetry-induced coupling and mixing among the low-\( K \) \( E \) levels. Due to partial cancellation of torsional and rotational energies, the \( K = -1 \) \( E \) levels lie only about 0.6 cm\(^{-1} \) above the \( K = 0 \) \( E \) levels at low \( J \). Furthermore, the large CH\(_3\)OD value for the product of inertia term, \( D_{ab} \), gives a large \( \Delta K = 1 \) asymmetry matrix element coupling the \( K = 0 \) and \(-1 \) levels. Thus, when the \( \Delta K = 2 \) asymmetry matrix elements connecting to the \( K = 1 \) and \( K = \pm 2 \) \( E \) levels not far above are brought in as well, strong mixing occurs throughout the whole 5 \( \times \) 5 \( K = 0 - \pm 2 \) sublevel complex with significant perturbations to transition frequencies and intensities. With the resulting difficulties in assignment, the energies for these \( v_t = 0 \) \( E \) substates have been determined from the FTFIR spectrum so far only up to \( J = 18 \) for \( K = 0 \) and \(-1 \), \( J = 17 \) for \( K = 1 \) and \( 2 \), and \( J = 14 \) for \( K = -2 \). In Fig. 1a, we show the pattern of the experimental energies in \( J \)-reduced form, obtained by subtracting \( BJ(J + 1) \) from the term values using a mean effective \( B \) value of 0.7576 cm\(^{-1} \). The close approach
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**TABLE 1**
Torsion-Rotation Parameters (in cm⁻¹) for Global Fits of Transitions Involving v₁ = 0 and v₂ = 0 Torsional States of CH₃OH, 13CH₃OH, CD₃OH, and CH₃OD.
TABLE 2

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<th>( J' ) P'</th>
<th>( J'' ) P''</th>
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<th>Unc (kHz)</th>
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<th>Ref</th>
<th>( J' ) P'</th>
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Note: Refs.: A, (9); B, (10); C, (11); D, (12); E, (13); W, (24); O, new Ohio State FASSST measurements.
and strong downward shifts of the $K = 0$ and $-1$ levels at high $J$ are quite striking.

To explore qualitatively the effects of asymmetry mixing in producing this energy pattern, we used Matlab to set up and diagonalize a simple $5 \times 5$ Hamiltonian matrix for the $K = 0$ to $\pm 2$ levels of given $J$. We took the $J_{\text{K}} = \pm 1$ Ritz term values as the unperturbed diagonal elements and used molecular constants $D_{ab} = 840.8 \text{ MHz}$ and $(B - C) = 1483.2 \text{ MHz}$ derived from Table 1 to calculate the $D_{K = 56}^{1}$ and $D_{K = 56}^{2}$ off-diagonal asymmetry matrix elements. Figure 1b illustrates the resulting energy curves, showing the $K = 0$ and $-1$ levels slowly converging to a minimum separation at $J_{\text{K}} = 16$ and then gradually moving apart again at higher $J$. The experimental and calculated patterns are remarkably similar, showing that asymmetry coupling is certainly the dominant contributor to the energy perturbations. However, in quantitative detail the separation between $K = 0$ and $-1$ levels calculated from the simple $5 \times 5$ model is significantly larger than that implied by the experimental data.

\section*{Table 2—Continued}

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**TABLE 3**

CH$_3$OD MW and MMW $v_1 = 0 \rightarrow 0$ and $v_1 = 1 \rightarrow 1$ Transitions of $E$ Torsional Symmetry for $J \leq 20$, with $O - C$ Residuals from the Global Fit

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Note: Refs.: A, (9); B, (10); C, (11); D, (12); E, (13); W, (24); L, (26); O, new Ohio State FASSST measurements.

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observed, possibly reflecting the influence of higher order Hamiltonian terms or interaction with the $K = -3$ levels which would act to push the $K = -1$ levels further down.

The strong coupling and mixing among the substates indicated by Fig. 1 also created difficulties within the fitting program in assigning consistent $K$ labels to the Hamiltonian eigenvalues and correctly keeping track of each particular series of substate levels with increasing $J$ value. Originally, a number of FTFIR lines involving the levels with $J$. labeled as $K = 0$ or $K = 1$ $E$ had conspicuously large residuals so were removed from the fit. However, the magnitudes of the residuals were quite consistent at 0.172 and 0.165 cm$^{-1}$ for $J = 17$ and 18, respectively, and on inspection turned out to be precisely the separations between $K = 0$ and $2$ term values for those $J$ states. A plot of the computer-generated energies was virtually identical to Fig. 1a but had a “level crossing” between $J = 16$ and $J = 17$ due to interchange by the program of the $K = 0$ and $-1$ labeling for $J \geq 17$. Thus, simply switching the $K = 0$ and $-1$ assignments for $J \geq 17$ sufficed to solve the problem and bring the residuals back down to experimental accuracy. (Note that both the original and the reversed assignments are shown in the archived FTFIR data set, in order to highlight the $K$-labeling problem and to emphasize the successful modeling of these lines with the $K$-ordering reversed.)

The only other major discrepancies between observed and calculated wavenumbers in the fit occurred for the $(v_v, K, J) = (1, 0, 18) \leftrightarrow (0, 1, 17) E$ transition, with a residual of $0.14249$ cm$^{-1}$, and the $(1, -1, 13) \leftrightarrow (0, -2, 14)$ and $(1, -1, 14) \leftrightarrow (0, -2, 14) E$ transitions with residuals of $0.07329$ and $0.07297$ cm$^{-1}$, respectively, as seen in the archived data. Each of these lines was the last identified member of its particular series in the spectrum, suggesting that the literature assignments had gone off track at those points. We realized that we could explicitly check for this by using published IR wavenumbers for the CO–stretching band (20) to determine $K = 1$ and $-2 E v_v = 0$ ground state combination differences. These were then matched against the corresponding combination differences calculated with ground state term values obtained from analysis of the assigned FIR lines using the Ritz fitting program (27). We found that to reproduce the CO–stretching IR combination differences, the $(0, 1, 17)$ and $(0, -2, 14) E$ energies indeed needed to be adjusted by $0.1418$ and $0.0732$ cm$^{-1}$, as implied from the residuals in the fit, showing that the global analysis is correctly modeling these levels.

As implied above, the large asymmetry shifts and mixing of the five strongly coupled $K = 0$ to $-2 v_v = 0$ substates make detailed calculation of transitions involving their sublevels a rigorous test for the global fitting program. However, our current corrected ($v_v$ obs $- v_v$ calc) residuals for these transitions show no features unaccounted for, and the perturbed subbands are well reproduced. With respect to the question of whether the $K = 0$ and $-1 v_v = 0$ E levels start to slowly diverge again above $J = 18$ as our analysis predicts, an extrapolation of the $K = 0$ and $-1 E$ series using the IR ground state combination differences indicates that this is in fact the case, and that the energies are well modeled by the calculations based on the parameters of Table 1.

**TABLE 3—Continued**

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IV. DISCUSSION AND CONCLUSIONS

In this work on the \( v_t = 0 \) and 1 ground state spectrum of the CH\(_3\)OD isotopic species of methanol, new measurements and line assignments have been obtained in the MMW and MW spectral regions and have been incorporated into a large data set of 564 MW and MMW lines and 4664 FTFIR lines. Global analysis of this data set has been accomplished with an overall weighted standard deviation of 1.060, i.e., essentially to

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Note: Refs.: A, (9); E, (13); O, new Ohio State FASSST measurements.
within mean experimental uncertainty, using a torsion–rotation model with 53 adjustable parameters and including terms of up to sixth order in the torsion–rotation operators. The new MMW measurements, plus the results of the fit in the form of the full dataset together with the least-squares ($n_{obs}^2 - n_{calc}$) residuals, have been deposited as supplementary information in the JMS archive, accessible from the JMS home page at www.idealibrary.com.

There is good internal consistency among the parameter sets obtained here for CH$_3$OD and previously for $^{12}$CH$_3$OH (2), $^{13}$CH$_3$OH (3), and CD$_3$OH (4). This reinforces confidence in the fitting procedure, suggesting that the right minima are being found in the least-squares process and that the parameter reliability will permit meaningful intercomparison. Furthermore, recent ab initio calculations using the Gaussian program to explore structural relaxation when going from the bottom to the top of the torsional barrier (30) have shown promising agreement with the global fitting results for $^{12}$CH$_3$OH for those distortional terms having a ($1 - \cos 3 \gamma$) functional dependence.

Altogether, we have now achieved global fits for the $v_t = 0$ and 1 torsional states of CH$_3$OH, $^{13}$CH$_3$OH, CD$_3$OH, and CH$_3$OD for $J \leq 20$ over the full available $K$ value ranges. The parameter sets have been used to calculate reliable ground state energies which have proven to be extremely valuable for the assignment of IR vibrational bands through the use of ground state combination differences.

Planned extensions to the program of global fitting include a move upward in energy to torsional states with $v_t \geq 2$ in order to test the one-dimensional Hamiltonian model in the near free-rotor regime above the barrier. Once the lower levels of the ground state are firmly under control, we will be in a position to explore coupled-state analysis of the vibrational perturbations that enter the problem when high $v_t$ ground state levels interact with $v_t = 0$ and 1 states of the small-amplitude vibrations. We will also extend our global fitting to additional methanol isotopomers for which large spectroscopic data sets exist, in order to probe further the isotopic dependence of the parameters. At present, the encouraging convergence of experimental spectroscopy and theoretical ab initio techniques (30–32) holds promise for detailed understanding of the isotopic results and quantitative interpretation of many of the Hamiltonian parameters.

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