



# Fourier Transform Infrared spectrum of the OCD bending mode in methanol-D<sub>1</sub>



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## HIGHLIGHTS

- The Infrared spectrum of CH<sub>2</sub>DOH for COD bending band has been analyzed.
- Assignments are confirmed by closed combination loops.
- As atlas of about 500 assigned lines have been presented.
- Anomalous intensity pattern has been observed and reason has been described.
- Optically Pumped Far Infrared Laser lines have been assigned.

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## ABSTRACT

The infrared (IR) spectra corresponding to OCD bending vibration of asymmetrically deuterated methanol species CH<sub>2</sub>DOH have been recorded with a Fourier Transform Spectrometer. The spectrum shows a typical structure of a parallel *a*-type band. This is expected because the bending vibration mainly executed parallel to the symmetry axis. The Q-branch lines are grouped closely around 896 cm<sup>-1</sup> and the P- and R-branches show complex structure. Nonetheless it was possible to assign *a*-type P- and R-branch lines up to *K* value of 8 and *J* value up to about 20 in most cases. The Q-branch lines for higher *K* values can be followed to about *J* = 15, the presence of which confirmed the assignments. The observations suggest that in the OCD bend some energy levels are highly interacted by highly excited torsional state from the ground torsional state. A full catalogue is presented along with the effective molecular parameters. An intensity anomaly was also observed in the transitions. So far it has been possible to assign only transitions between *e*<sub>0</sub> ← *e*<sub>0</sub> states. Plausible explanations of intensity anomaly are presented. Lastly, a number of optically pumped far infrared (FIR) laser lines have been assigned either to exact or tentative quantum states. These assignments should prove valuable for production of new FIR laser lines.

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## 1. Introduction

The singly deuterated asymmetric methanol (CH<sub>2</sub>DOH) species exhibits complex spectra from microwave to the IR regions of the electromagnetic spectrum. The presence of the off-axis deuterium introduces asymmetry in the three fold internal rotation in the molecule in addition to increasing the general asymmetry in the molecule. The torsional asymmetry mixes the symmetry species to relax the selection rules allowing strong transitions between different symmetry species, which are strictly forbidden in the symmetric parent species. These complexities discouraged the detailed high resolution spectroscopy in this molecular species. Albeit these difficulties some progress have been made in the past mainly by Quade and coworkers [1–6]. Some spectral analyses in

the millimeter wave (MMW) and FIR regions for this species and the doubly deuterated species have been communicated recently [7,8].

The Fourier Transform Infrared (FTIR) Spectral technique is an indispensable tool for the characterization of internal energy levels of complex molecules. In recent years there have been a renewed interest in the spectral studies of methanol and its isotopic variants in the IR regions not only because of the ability of these molecules to emit Far Infrared (FIR) laser lines when optically pumped by the 10 micron CO<sub>2</sub> lasers [9–12] but also for identification of these species in the interstellar space by “Radio Astronomy” [13–16].

The FTIR spectroscopy is an attractive tool in this process not only because of large range of coverage of the spectra but also the high precision of the frequencies of spectral lines obtained by using a large path length in the absorption process. The repeatability and stability of the commercial FTIR instruments allow addition

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of a large number of scans to improve the signal to noise (S/N) ratio and to measure weak features in the spectra. The ability of lowering the temperature of the gas sample also simplifies the spectra by increasing the population of lower lying states.

In this work spectra were recorded in the range 800–950  $\text{cm}^{-1}$  at the University of British Columbia at a resolution of 0.004  $\text{cm}^{-1}$  using a BOMEM FTIR spectrometer. The spectrum shows a typical structure of a parallel a-type band. This is expected because the bending vibration mainly executed parallel to the symmetry axis. The Q-branch lines are grouped closely around 896  $\text{cm}^{-1}$  and the P- and R-branches show complex structure. Nonetheless it was possible to assign a-type P- and R-branch lines up to  $K$  value of 8 and  $J$  value up to about 20 in most cases. The Q-branch lines for higher  $K$  values can be followed to about  $J = 15$ , the presence of which confirmed the assignments. The availability of the ground state a-type transitions [17] proved a valuable tool for forming closed combination loops thereby confirming the assignments. The closed combination loop technique is essentially independent of the molecular Hamiltonian models.

More recently the same spectrum has been recorded at a higher resolution of 0.002  $\text{cm}^{-1}$  at two different temperatures and pressures using the Bruker FTIR spectrometer at the University of Giessen in Germany. The analysis of the new spectrum is yet to be performed and the present report is expected to provide the starting point and new spectra with better signal to noise ratio will uncover many finer details of the torsion–rotation–vibration in the molecule. We also propose to record the spectra using a synchrotron radiation source at the Canadian Light Source Center in Saskatchewan at the highest resolution of 0.001  $\text{cm}^{-1}$ . The present paper is based on the 0.004  $\text{cm}^{-1}$  spectrum and should be considered as a preliminary report.

## 2. Theoretical aspects

The Zeroth order Hamiltonian of the asymmetrically deuterated methanol can be written as:

$$H = H_R + H_T + \Delta H \quad (1)$$

where  $H_R$  is the pure rotational Hamiltonian,  $H_T$  is the torsional Hamiltonian and  $\Delta H$  is torsion–rotation–vibration interaction terms. The higher order terms include effects of asymmetry and non-rigidity not included in the zeroth Hamiltonian.

The details of the Hamiltonian and Energy values can be found in Ref. [6]. Here we briefly discuss the effect of the asymmetry in the Barrier height on the energy level mixing and in turn the relaxation of the selection rules.

The potential energy of the molecule due to torsion has a significant contribution to the level classification of energy levels and is described in brief in the following. The asymmetric barrier potential can be represented by the terms  $\frac{1}{2}V_1(1 - \cos\gamma)$  and  $\frac{1}{2}V_2(1 - \cos 2\gamma)$  in addition to the regular 3-fold term  $\frac{1}{2}V_3(1 - \cos 3\gamma)$ , where  $\gamma$  is the OH-torsional angle relative to a plane which includes the symmetry axis almost parallel to the C–O bond and the OH bond. The effect of the  $V_1$  term is to remove the degeneracy between the  $\sigma = +1$  and  $-1$  levels and strongly mix the  $\sigma = 0$  and  $\pm 1$  levels (where,  $\sigma$  represents the three energy states in a given torsional vibrational states due to the finite barrier height. The mixed symmetry species are designated by  $\sigma' = 0$ , '+', and '-'. In the ground torsional vibrational state, the  $\sigma' = 0$  and '+' states have eigenfunctions even in the torsional angle  $\gamma$  and are denoted by  $e_0$  and  $e_1$ , respectively. In the torsional ground state  $\sigma' = '-'$  state that has odd parity in  $\gamma$  and is denoted by  $o_1$ . In general, states with even parity are designated by  $e_n$  (with  $n = 1, 2, 3, 4, \dots$ ) and similarly those with odd parity by  $o_n$ , in increasing order. The first three sub-states viz.  $e_0$ ,  $o_1$  and  $e_1$  correspond to the ground torsional state in

the nomenclature of symmetric methanol molecule, with  $e_0$  being the lowest trans-state.

## 3. Analysis and interpretation

Since the spectra show a-type behavior, in this work the normal method of arranging the spectral chunks separated approximately by  $2B_{\text{eff}}$  (where  $B_{\text{eff}}$  is the effective rotational constant  $(B + C)/2$  which equals about 1.5  $\text{cm}^{-1}$  vertically above each other in increasing or decreasing order of wavenumbers as shown in Figs. 1 and 2, for the P- and R-branch regions, respectively. Traditionally this kind of spectral arrangement is known as “Loomis Wood” diagram. (Note that for clarity these figures show the spectra from the higher resolution runs). The lines belonging to definite  $K$  (here  $K$  stands for the  $K$  value for a prolate top and the usual notation of + and – are employed to designate the asymmetry splitting of the levels) form identifiable semi-vertical lines. The lines for various R- and P-branches for were grouped together. The use of EXCEL spread sheets employing second order polynomials provided quick and easy method for the grouping. A given R-branch series was matched with a P-branch series so that the difference between  $R(J) - P(J + 2)$  are equal to the ground state energy difference  $E(J + 2) - E(J)$  for all  $J$ -values which have been calculated precisely from MMW studies. The intensity of the matched series also provided additional clue. Lastly for higher  $K$  values the Q-Branch lines were quite strong and provided final confirmation of the assignments. The first member of the Q-branch line is the strongest in a given series and its approximate location differs from the first member of the R- and P-branch are  $R(J = K) - Q(J = K) = 2(K + 1)B_{\text{eff}}$ ,  $P(J = K + 1) - Q(J = K) = 2(K + 1)B_{\text{eff}}$ , since the effective  $B$ -value of the upper state is not too different from that of the ground state.

Asymmetry splitting has been observed for low  $K$  values and is maximum for  $K = 1$ . The asymmetry splitting often makes the spectrum complicated but it also serves as a confirmatory tool for the correctness of quantum number assignments. Here some examples involving  $K = 0$   $e_0$  sub-states are provided. The asymmetry splitting for  $K = 1$  is given by  $\Delta_1(J) = S_1 J(J + 1)$  and is therefore highly dependent on  $J$ . For the ground state  $S_1$  has been found from MMW studies [8] to be about 0.02266  $\text{cm}^{-1}$ . The asymmetry splitting for the mode this value turns out to be 0.02757  $\text{cm}^{-1}$ . This is expected because the OCD bending mode is a major contributor of potential energy asymmetry in the molecule as discussed later in this report. A few combination loops can be considered using  $K = 1/+/-$  states as follows:

$$K = 1 + e_0 \\ \delta_1 = R(5) - P(7) - [v(7 \leftarrow 6) + v(6 \leftarrow 5)]^{\text{gs}} = 900.31241 - 881.23428 - 19.078052 = 0.0001 \text{ cm}^{-1}.$$

$$K = 1 - e_0 \\ \delta_2 = R(5) - P(7) - [v(7 \leftarrow 6) + v(6 \leftarrow 5)]^{\text{gs}} = 900.79051 - 881.12927 - 19.661238 = 0.00001 \text{ cm}^{-1}$$

where  $[v(7 \leftarrow 6) + v(6 \leftarrow 5)]^{\text{gs}}$  is known within an accuracy of  $\pm 100$  kHz.

The low loop defects  $\delta_1$  and  $\delta_2$  prove the correctness of the assignments beyond doubt. It is needless to say that most of the assignments passed this rigorous test. One particular sub-band for  $K = 4$   $e_0$  demands some discussion. It was found that the q-branch for this sub-band is pushed upwards from the other group of q-branches. A closer look at the energy states for the ground vibrational state reveals that the energies of the  $K = 4$  levels for the  $o_6$  corresponding to  $\nu = 12$  torsional vibrational state lie very close to the  $K = 4$   $e_0$  state for OCD bend state. Hence they interact via Fermi interaction and mix these two sets of levels. As a result two sets of transitions for  $K = 4$  was found with sufficient

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