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Improved measurements and analysis of the far-infrared spectrum of methanol-D_1 (CH_2DOH) arising from trans- (e_0) to gauche- (e_1 & o_1) states

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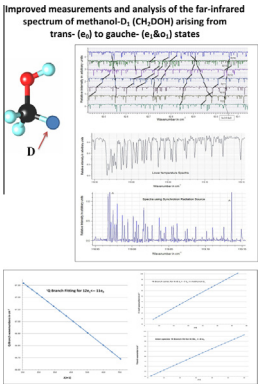
HIGHLIGHTS

- Improved spectra have been recorded and used to determine the transition wavenumbers.
- Synchrotron Radiation Source spectrum has been measured at 0.001 cm^{-1} resolution.
- Assignments are confirmed by combination loops in situ using Q and R branch lines.
- The results will be useful for Astronomical and laser discovery.
- Corroborate previous spectral study.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work the millimeter-wave (MMW) and far infrared (FIR) absorption spectrum for the asymmetrically deuterated Methanol (CH_2DOH) species measured recently at a temperature of −60 °C with better accuracy and signal/noise (S/N) ratio than known before has been assigned for transitions originating at the lowest lying trans- to gauche-states. The entire spectrum for 50–1200 cm^{-1} has been re-recorded recently using the Synchrotron Radiation Source coupled with the Bruker Fourier Transform Infrared (FTIR) spectrometer with a resolution of about 0.001 cm^{-1} or better. Complete spectrum has not been exploited a great deal but it helped to entangle overlapping lines in the present work. This also fills the gap remaining in the usual FTIR in the range 400–500 cm^{-1}. Hence it is expected to help the interacting partner for the Coriolis interaction encountered earlier. The assigned transitions mostly for the axial rotational angular momentum quantum number $K + 1 \leftarrow K$, both for R- and Q-sub bands for wide range of rotational angular momentum quantum number. The MMW spectrum has been recalibrated and assigned for a number of Q-branches. The assignments are confirmed rigorously using closed loop residual technique. The assigned ^rR and ^rQ lines have been analyzed in terms of polynomial expansion parameters. The new assignments are presented for about 750 transitions and a grand atlas of more than 1000 lines has been prepared which will be made available through the open source server at "research gate". The present work should be useful in the area of astrophysical detection and further understanding of the energy relaxation pathways in the molecule.

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1. Introduction

Methanol is one of the simple complicated molecules or the most complex of the simple polyatomic molecules. The complication arises because this molecule has an internal degree of freedom, in which a part of the molecule (the methyl top) can rotate relative to the rest of the molecule. The three equivalent hydrogen atoms in the top makes this internal rotation undergoes a threefold hindering potential humps. In addition the presence of the hydrogen atom in the hydroxyl group makes the C–O bond to little off axis from the symmetry axis of the methyl top, introducing a slight asymmetry in the molecule. This asymmetry introduces cross terms in the Hamiltonian representing additional effects in the rotational–torsional interaction terms making the energy level structure quite complicated. Furthermore, the substitution of one of the hydrogen atom by deuterium makes the hindering potential departing from the 3-fold symmetry of internal rotation. This torsional asymmetry had dramatic effects on the energy level structure. First, every principal torsional vibrational state already split into three sub-levels due to finite barrier height (the classical tunneling effect) as in the case of the parent symmetrical methanol. Secondly, these levels now become highly mixed and making transitions between the sub-levels allowed. Hence the selection rules re relaxed and the spectrum become many fold more complex than that for the parent species. The details are discussed in our previous paper [1].

In this work, the transitions originating from the e_0 state to e_1 and o_1 are considered. Transitions with similar $K+1 \leftarrow K$ values differ approximately about 3.4 cm^{-1} and helped the identification of the transition series. Once an ^rR branch is identified the corresponding ^rQ branch approximately $2B_{eff}(K+1)$ toward to lower side in the wavenumber scale (where $B_{eff} \approx \frac{1}{2}(B+C)$). The details of the assignment procedure are discussed in later in this paper.

This molecule along with its isotopic derivatives has been found in the interstellar space especially in the star forming region [2,3]. The laboratory spectrum is a necessary tool for identification of these species. Often this molecule is found in an abundant numbers and elimination these lines are sought in order to identify other molecular species. Secondly this molecule has strong absorption bands in the 10 μm region where the powerful CO_2 lasers operate. Thus these molecules have been used [4–7] to generate long wavelength laser emission lines, where the available monochromatic sources are limited. Lastly there remains a scarcity of wavenumber standard in the FIR region and the spectra of these molecular species can be used as a secondary standard [8]. Furthermore the strong absorption in the FIR region makes it an attractive medium to test the working of a fabricated spectrometer.

High resolution spectroscopy is proven to be a valuable tool to aid the above applications. In addition to low temperature conventional FTIR and MMW spectroscopic methods the Synchrotron Radiation Source at the "Canadian Light Source" in Saskatchewan has been used to record the best possible spectrum in the range 30–1190 cm^{-1} with a resolution of 0.001 cm^{-1}. This spectrum represents the best possible spectral map of this molecule till today. Although the synchrotron spectrum has been used sparingly in this work, the complete analysis is in progress. The spectrum fills a gap in the previous spectra in the range 400–500 cm^{-1} where many of the highly interacting torsional lines are present. The results of the studies will be communicated elsewhere.

2. Theoretical aspects

The basic understanding energy level structure has been developed by successive studies of Quade and his coworkers [9–11]. They used an internal axis method in which the methyl top and the rest of the molecule (the framework which is the hydroxyl group) internally rotate in opposite directions so that overall internal angular momentum is zero. The model has been extended later to include higher axial rotational quantum number and highly excited torsional vibrational states [11]. This work has been found valuable to know the approximate locations and strength of the torsional–rotational transitions. The detailed discussions about the model have been discussed earlier [1,12]. Here we briefly discuss the quantum number nomenclature, selection rules and the overall asymmetry effects.

Since methanol is a near prolate top the prolate top K-value (K_p or K_{-1}) the prolate top K is used in this work. The rotational energy is proportional to K^2 to a first approximation but and hence the $-K$ and $+K$ levels are degenerate. However, the off diagonal $\langle K|H|K \pm 2\rangle$ elements in the Hamiltonian due to asymmetry of the molecule, can couple mixes the $|-K\rangle$ and $|+K\rangle$ states and thereby remove the degeneracy to give asymmetry doublets. The overlap integral $\langle K|H|K \pm 2\rangle$ can be shown to be

$$\langle K|H|K \pm 2\rangle = 1/4(B-C)[J(J+1) - K(K \pm 1)]^{1/2}[J(J+1) - (K \pm 1)(K \pm 2)]^{1/2} \quad \langle K|K \pm 2\rangle \tag{1}$$

It follows that $H_{K,K\pm2} = H_{K\pm2,K} = H_{-K,-(K\pm2)} = H_{-(K\pm2),-K}$

First of all, the $|K\rangle$ states are mixed due to the asymmetry only with $|K \pm 2\rangle$, $|K \pm 4\rangle$, $|K \pm 6\rangle$, and so on. Therefore, the $|K\rangle$ can be conveniently denoted by E or O, for even or odd K. Secondly, because $\pm K$ degeneracy is removed as above, a more appropriate basis states as follows become convenient.

$$|\pm K\rangle = \sqrt{(1/2)}\{|+K\rangle \pm |-K\rangle\} \tag{2}$$

where $K > 0$ with $|O+\rangle = |K = 0\rangle$ as a special case.

This further sub classifies the basis states into four classes, viz. E^+, E^-, O^+ and O^- with $|K = 0\rangle$ taken as E^+. The transformation to the new basis states can be performed by the Wang Transformation.

$S = X|K\rangle$ is the new basis sets. Where $X = X^{-1}$ is the Wang symmetrizing matrix [19] and S represents the new basis states. It can be shown that

$$X|K\rangle = \sqrt{(1/2)}\{|+K\rangle + |-K\rangle\} = |K+\rangle \tag{3}$$

$$X|K\rangle = \sqrt{(1/2)}\{|+K\rangle - |-K\rangle\} = |K-\rangle \tag{4}$$

$$X|K=0\rangle = |K0+\rangle \tag{5}$$

The transformed Hamiltonian $H' = X^{-1}\,H\,X$. As long as only the Hamiltonian $\Delta K = \pm 2$ overlap matrix elements considered, the Hamiltonian can be factored into four blocks with the non-mixing basis $|K+\rangle$ and $K-\rangle$, i.e., $\langle K+|H|K'-\rangle \cong 0$. It can be shown that the asymmetry splitting is maximum for $K = 1$ and is given by $\Delta E(1) = 1/2(B-C)J(J+1)\langle K = -1|K = \pm 1\rangle$. It is needless to say the $\langle K|H|K \pm 1\rangle$ elements also couples all K values but the effect is small.

In general, the asymmetry splitting for a given K can be shown to have a form:

$$\Delta(K,J) = S(K)(J+K)!/(J-K)! \tag{6}$$

For $K = 1$ the "−" level is above the K=+. If the $K = 2$ level is above the $K = 0$ level the +/− levels will be opposite to that of $K = 1$. Therefore the +/− ordering alternates with increasing K. It is worth noting that for excited torsional states the energy levels $K = 0+$ states may be pushed up by perturbation and can lie above $K = 2$ states. The interaction between $K = 0$ and $K = 2$ the $K = 0+$ level pushes the 2+ level downwards and thus in that case the + levels are always downwards, and there is no alternation. Without the knowledge of this the assignments might be misleading for these unusual cases, in addition, proper combination loop closure check may not be possible for the assignments because of the +/− selection rules.