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High resolution synchrotron radiation Fourier transform infrared spectrum of the COH-bending mode in methanol-D_1 (CH_2DOH)

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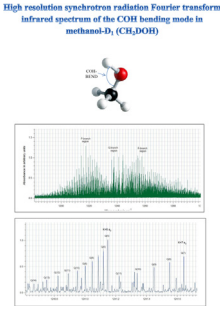
HIGHLIGHTS

- High Resolution IR Spectra of CH_2DOH of OH bending mode is being reported for the first time.
- Assignments are confirmed by closed combination loops.
- Results are in agreement with MMW ground state measurements.
- Asymmetry splitting in the excited state are very small.
- Perturbation and Energy level structure in the excited state are characterized.
- A catalogue of about 450 assigned lines are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work the high resolution synchrotron radiation Fourier transform spectrum in the range 1180–1300 cm^{-1} corresponding to the COH-bending vibrational mode has been recorded and analyzed. The spectrum shows a structure analogous to a parallel band. Since the COH bending motion is one of the main contributors to the asymmetry in the torsional hindering potential barrier, the torsional barrier height in the excited state is expected to be quite different from that of the ground state. This makes the spectrum to spread over a wide region. Although the spectrum corresponding to the P- and R-branch looks very complicated, the Q-branches are well resolved and can be identified without much difficulty. It was possible to assign the spectra for K = 0 to 10 for the trans- (e_0) species. The interesting feature of the spectra is the absence of the lines for two other lower lying gauche symmetry species e_1 and o_1. The spectra due to any perpendicular transitions were absent as well. However some weak ***c***-type transitions from gauche states (o_1 and e_1) in the ground state to the trans-species (e_0) in the COD bending mode for low K-values $\Delta K = 0$ have been seen to be present in the spectra. These along with similar transitions for the OCD vibrational band are under investigation and the results will be communicated elsewhere. In the present work, analysis of the spectrum has been carried out to obtain precise term values and molecular parameters in the excited COH-bending state for the trans-species. The results will be shown valuable to assign similar spectra for the methanol-D_2. This work represents the first reported high resolution study of this illusive vibrational mode in methanol-D_1.

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1. Introduction

The advent of intense infrared and far infrared radiation source using synchrotron radiation extracted from highly energetic electron beams opened a new vista to unlock the details of inner structure of energy levels in complex but important molecular species. In the conventional Fourier transform infrared (FTIR) spectroscopy the source of radiation used almost always the hot filament (Globar) type and has poor intensity distribution in the far infrared (FIR) region. The FIR radiation extracted from the synchrotron storage ring on the other hand is significantly brighter than the thermal sources. This has provided excellent signal to noise (S/N) ratio even for the weaker absorption lines (including forbidden lines) in the spectra, providing valuable information about the energy level structure in the absorbing molecular system.

The advantage of using synchrotron radiation source becomes evident while studying molecules with many degrees of freedom and the modes have delicate interactions between them, exhibiting complex spectral structure. Because of the high intensity and superior S/N weak transitions become clearly visible in the spectrum. These often include transitions which are normally forbidden according to the selection rules but acquire sufficient strength through intensity borrowing effect and become visible in the spectra. These weak transitions are normally buried under noise or overlap with strong lines in conventional thermal source based spectroscopy. When the thermal IR source is used, often to rescue even the stronger features in the spectrum hundreds of co-adding of the signals were necessary with identical scanning parameters requiring a tedious process. On the contrary the use of synchrotron radiation based Fourier transform spectroscopic method allows one to record such weak features routinely owing to the high S/N ratio in the system. Therefore, the synchrotron radiation based studies are opening up new vistas in understanding the internal energy structure of complex molecules.

In continuation of our study of very high resolution synchrotron radiation spectrum of the asymmetrically deuterated methanol species (CH_2DOH and CHD_2OH) [1], in the present study the infrared band originating from the COH-bending mode of methanol-D_1 (CH_2DOH) has been assigned and analyzed in detail. The COH bending mode has been studied at low resolution by Serrallach et al. [2] way back in 1974. The features at 1237 cm^{-1} were associated to this band. In this work the high resolution ($\sim$0.002 cm^{-1}) synchrotron radiation Fourier transform spectrum of singly deuterated asymmetric methanol (CH_2DOH) in the range 1180–1300 cm^{-1} has been recorded at the Canadian Light Source at Saskatoon. The vibrational band corresponding to the COH-bending motion shows a structure analogous to a parallel ***a***-type band as shown in Fig. 1, where the Q-branch region is almost exactly around $\sim$1237 cm^{-1}, confirming that this band was correctly identified in Ref. [2]. Since the COH-bending motion changes the molecular structure from asymmetric to more symmetric configuration, the molecular parameters and the torsional energy level structure in the excited state is expected to be quite different from that of the ground state. This makes the spectrum to spread over a wide region. It appears that in the upper vibrational state the wavefunction seems to be localized in the so called trans-(e_0) state and as a consequence the spectrum mainly consists of transitions between the trans- (e0) ground state to trans- (e0) excited state.

The energy level structure in the COD bending is quite different from that of the ground state as was the case for the OCD bending band communicated earlier [3]. The similarity is that no transitions originating from the gauche species in the ground state to the gauche states in the vibrational band have been observed to occur in the present band.

Although few tentative assignments for weak interspecies $\Delta K = 0$ transitions e.g. from the gauche- (e1 and o1) ground state to the same trans- (e0) state in the excited state have been made, no transitions belonging to gauche- (e_1 and o_1) to gauche- (e_1 and o_1) in the excited state have been observed. This was also the case for OCD bending mode [3]. This phenomenon is not yet well understood but preliminary understanding can be obtained by simple minded overlap integral calculations as discussed later in this report [4]. The P- and R-branch spectrum for the present band looks very complicated [see Fig. 2 for example]; however the Q-branches for various axial angular momentum quantum numbers (K) are well resolved and can be identified without much difficulty. The spread of the well resolved Q-branches indicate that the molecular parameters in the excited state to be quite different from that of the ground state as argued above. It was possible to assign the ***a***-type ($\Delta K = 0$) spectra (P, R and Q branches) for K = 0 to 10 for the trans- (e_0) species (see Table 1). Note that for K = 0 the Q-branch does not exist and for K = 1, lines were too weak to be followed confidently. The absence of the lines for two other lower lying symmetry species e_1 and o_1 and perpendicular transitions for any species indicate that COH-bending motion affects mainly the quasi symmetric axial component of the dipole

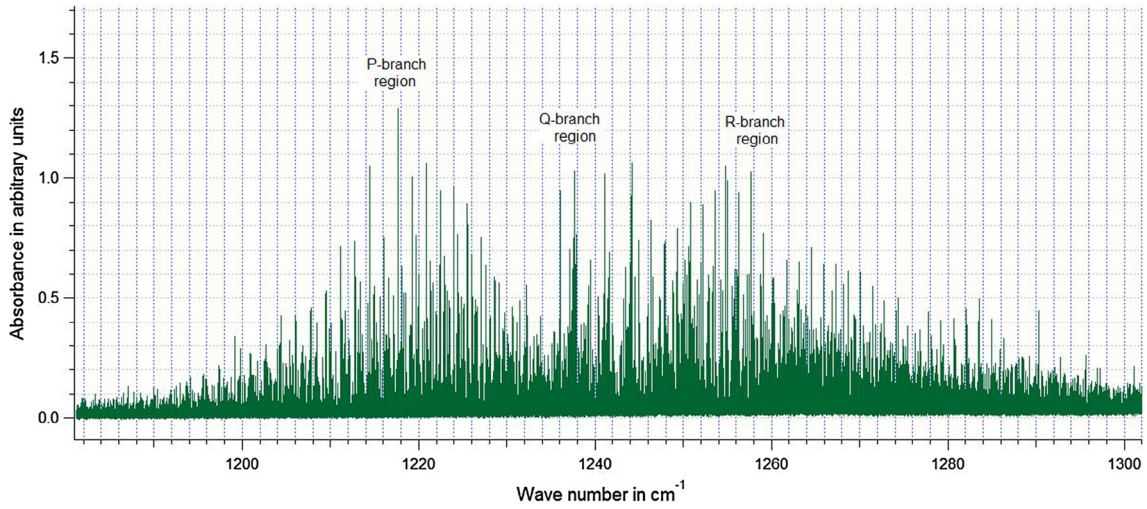

Fig. 1. The overall COH bending ban is shown in the diagram. The band is spread over a wide range of 1180–1300 cm^{-1} (120 cm^{-1}), suggesting that the barrier height in the COH state quite different from the ground state values.