Catalogue of Very High Resolution Spectra of Asymmetrically Mono Deuterated Methanol (CH_2DOH) in the Ground Torsional Vibrational States

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Abstract: In this report a complete atlas of 4279 assigned has been presented for all possible transitions in the first three torsional vibrational states of Methanol-D$_1$ (CH_2DOH). The compete spectrum from 20-120 cm^{-1} has been presented. This is the first time such a catalogue has been reported in the literature. This atlas would be indispensable for astrophysical discovery of the deuterated species which in turn will yield D/H ratio in cold interstellar clouds especially in the star forming regions. A brief description of quantum number nomenclature has been presented.

Keywords: Astrophysics, Synchrotron Radiation, Spectroscopy, Interstellar Space, Methanol.

I. INTRODUCTION

Synchrotron Radiation (SR) sources are now available in handful of facilities around the world. These provide intense and highly collimated source in the far infrared (FIR) and infrared (IR) region of the electromagnetic spectrum. These makes the SR sources very attractive for Fourier transform (FT) spectroscopy. The conventional FT spectrometers use thermal sources e.g. globar and Hg discharge source operating at high pressure, which are rather weak in brightness and divergent. Most facilities use the commercial FT spectrometer or home built spectrometer coupled with FIR beamline in an electron storage ring or even linear accelerations using defectors or wigglers. These offer very high resolution and excellent signal/noise (S/N) ratio. Thus the uses of SR source based FT spectrometers are suitable for spectroscopy of highly crowded region of a spectrum and for very weak lines.

In the FIR region very high resolution spectroscopy is possible using the SR sources where spectroscopy with conventional sources with rather low brightness is particularly difficult. Spectrometers used at IR beamlines are virtually always Fourier transform instruments, for conventional high spectral resolution facilities. For the gaseous sample the sharp spectral lines impose coherence on the IR continuum radiation from the synchrotron. The optimum resolution obtained in the transformed spectra is limited the approximate instrumental line shape achieved by an apodization function applied in the time domain. In the FIR region the low line width (Doppler) provides its own apodization and hence sub Doppler spectra can be achieved.

In the field of astrophysics a large variety of molecules have been discovered in cold interstellar clouds especially near the star forming regions, out of these molecules methanol and its isotopic derivatives are present almost everywhere. Hence, methanol has become known as an interstellar ‘‘weed’’ in the radio astrophysical landscape. Recent advancements in a number of facilities, e.g., the Heterodyne Instrument for the Far-Infrared (HIFI) with extended spectral coverage, extreme sensitivity and resolution in the FIR region on board the Herschel Space Observatory [1-2], the ALMA (Atacama Large Millimeter Array) [3] and the SOFIA (Stratospheric Observatory for Infrared Astronomy) [4] have created substantial demand for accurate laboratory databases for the methanol and its isotopic derivatives. The present paper provides a catalog of the most accurate wavenumbers for the asymmetrically deuterated species known so far using the synchrotron based FT spectrometer at the Canadian Light Source [5]. This will make it well suited for development of extensive FIR and IR spectral atlases for astrophysical discovery.

The deuterated methanol species have been observed in most interstellar sources where the parent species (CH_3OH) has been detected [6]. These observations are a powerful diagnostic of evolution of chemistry in those clouds using the ratio of D/H abundances. The deuterated species have lower zero-point vibrational energy compared to the parent species makes the D/H ratio quite higher than the average cosmic value. It is noteworthy that the deuterated species are present in cometary tails and star forming regions.

In fundamental spectroscopy the symmetrically deuterated methanol species poses a challenge to theoretical scientists because of the complex asymmetry interactions with various degrees of freedom. These complexities have been outlined in our previous papers [7-8]. Nevertheless, a complete mapping of the ground vibrational state (in the three lowest torsional sub-states) allowed us to have a global analysis of the energy levels. The complete atlas is for about 4279 assigned transition with an accuracy reaching microwave accuracies are presented. This atlas can be obtained from the author vis e-mail. Transitions measured using microwave (MW) and millimeter wave (MMW) spectroscopy are also included. The spectrum in the range 50-120 cm^{-1} is presented here. A brief description is given for the quantum numbers and notational aspects. The theoretical aspects are well documented in the literature [7-21] and hence are not duplicated here. The readers are referred to the bibliography presented.

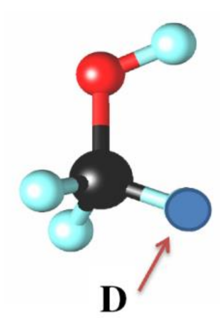
II. Notations and Selection Rules

When deuterium is substituted for one of the hydrogen atoms in the methyl top, the 3-fold symmetry of the molecule is broken. The torsional potential barrier of the molecule must then be extended to include the terms $\frac{1}{2}V_1(1-\cos\gamma)$ and $\frac{1}{2}V_2(1-\cos2\gamma)$ in addition to the 3-fold term $\frac{1}{2}V_3(1-\cos3\gamma)$, where g is the torsional angle. The effect of the V_1 and V_2 term is to lift the degeneracy of the σ=-1 and +1 levels and strongly mix the σ=0 and ±1 levels. The molecules are localized in the symmetric 'trans' and asymmetric 'gauche' configuration for the relative orientation of the -OH and the CH2D- groups (see Fig. 1). Hence the first three torsional vibrational states in increasing order in energy are then given by the symmetry species (σ) e_0, e_1 and o_1. These correspond to the ground torsional state for the parent methanol species CH_3OH. $1/\lambda = \nu/c$ (in cm^{-1}) the wavenumber of transitions. J is the overall rotational angular momentum quantum numbers, K is the components of J along the quasi-symmetric axis. The asymmetry mixing of the states due to ΔK=±2 and ±1 matrix elements causes the levels to split into the "+" and "–" components.

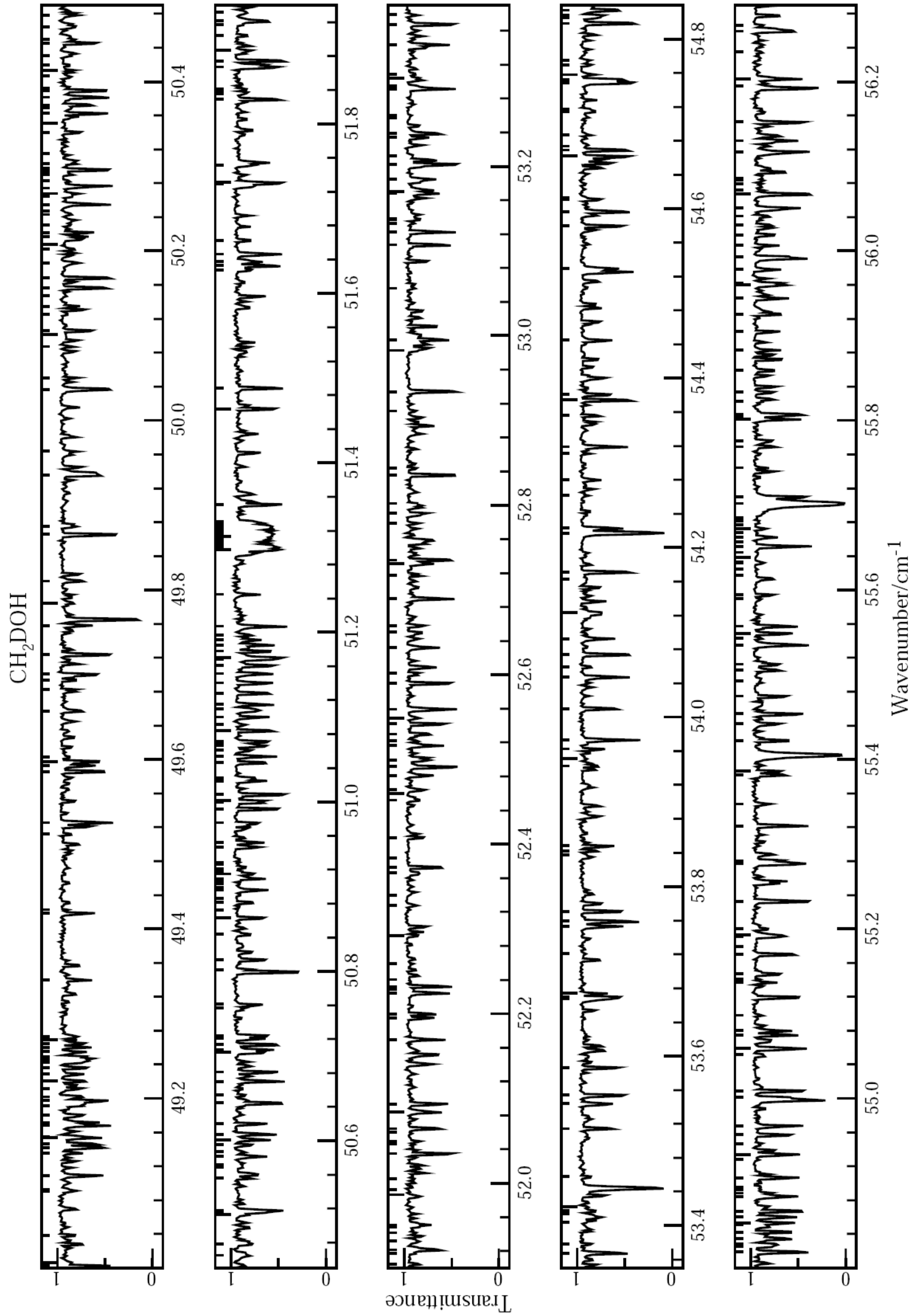
III. Absorption Selection Rules:

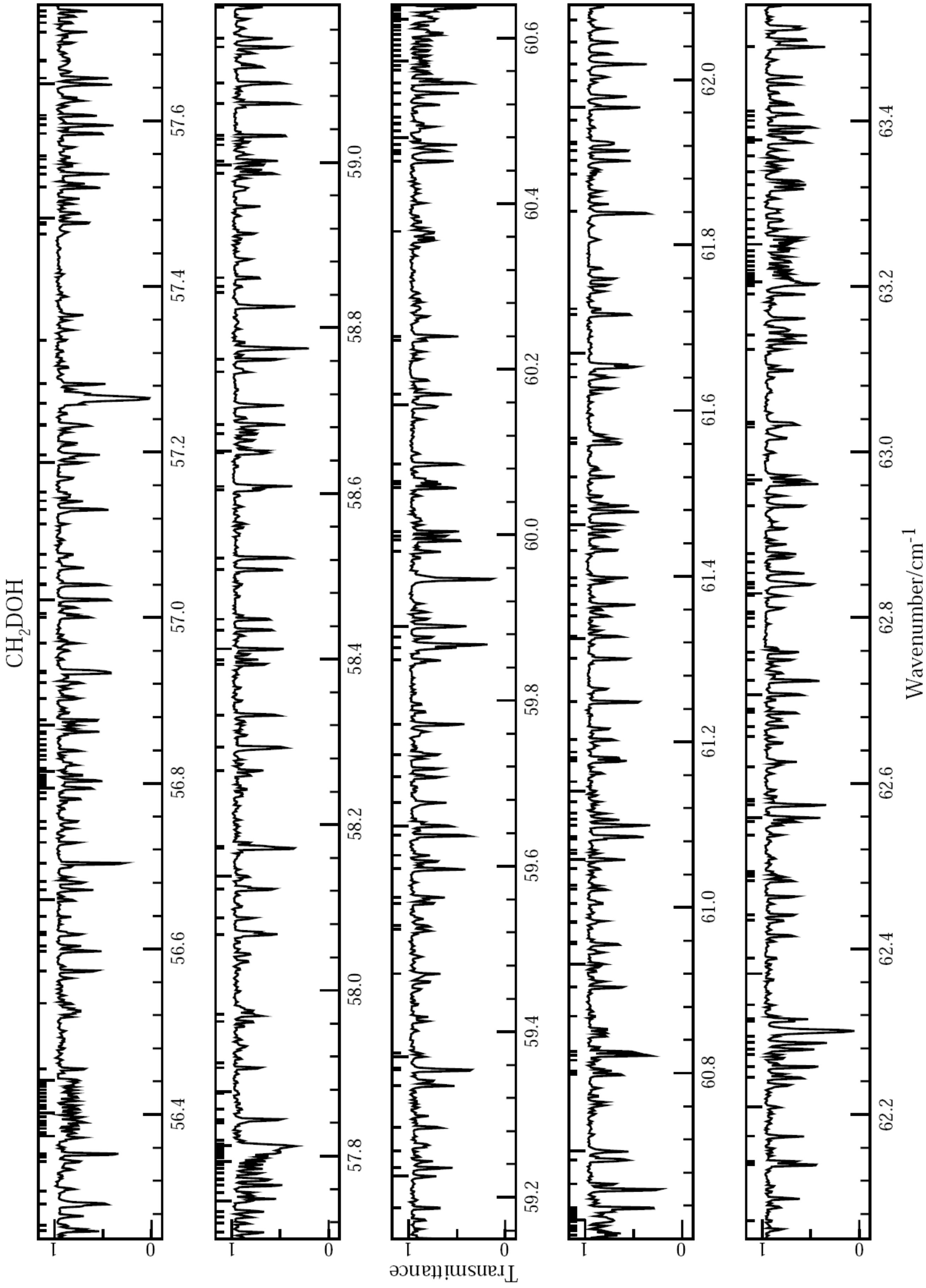
a-type transitions ΔK = 0, ΔJ = +1, Δσ = 0, "+ ↔ +", "- ↔ -",
b-type transitions ΔK = ±1, ΔJ = 0, +1, σ [even ↔ even, and odd ↔ odd, "+ ↔ +", "- ↔ -", for ΔJ = 1 (R/P branch)
"+ ↔ -", "- ↔ +", for ΔJ = 0 (Q-branch),
c-type transitions ΔK = ±1, ΔJ = 0, +1, σ [even ↔ odd, and odd ↔ even, "+ ↔ +", "- ↔ -", for ΔJ = 1 (R/P branch) , "+ ↔ -", "- ↔ +", for ΔJ = 0 (Q-branch) .

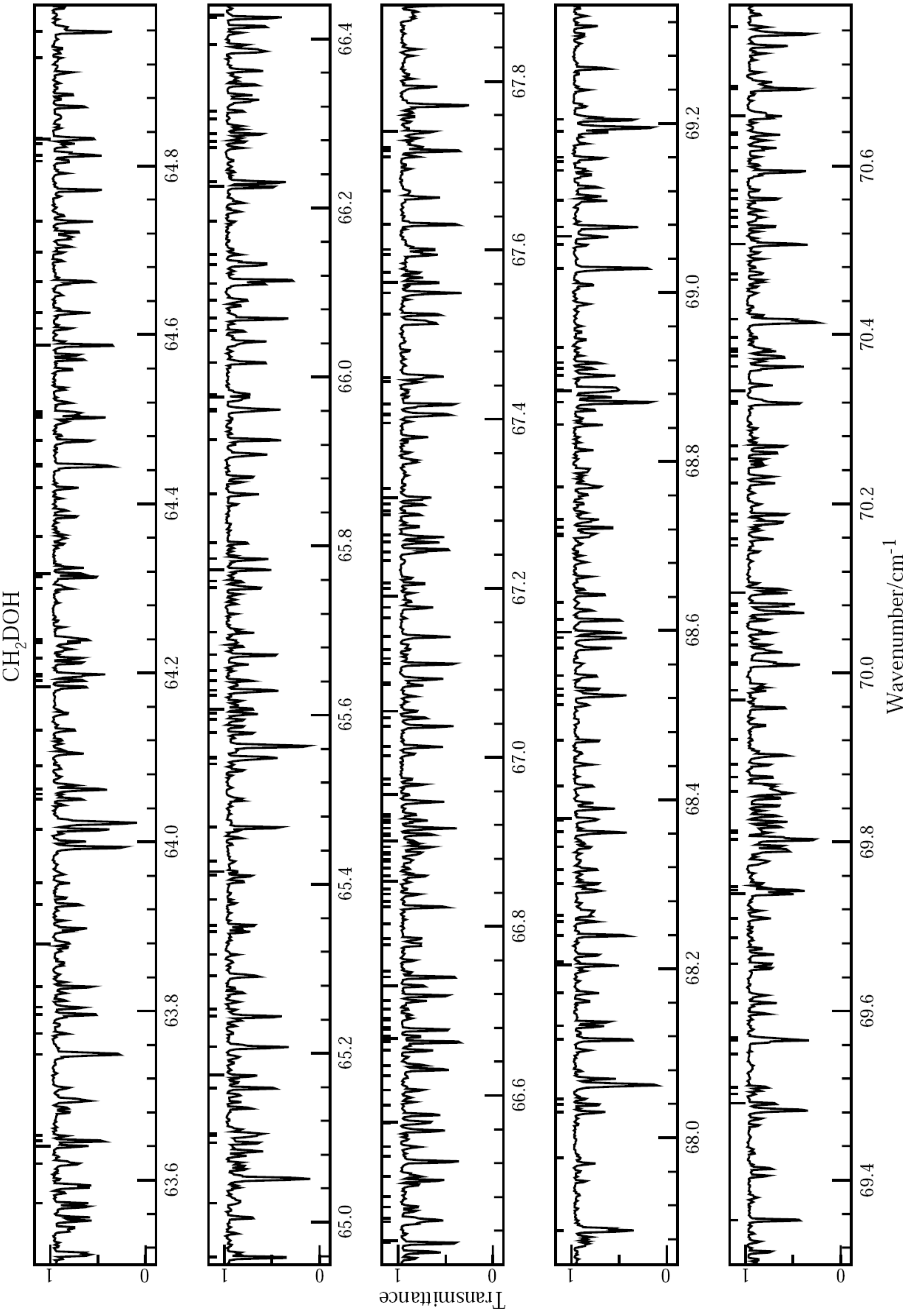
Fig .1 The structure of CH_2DOH

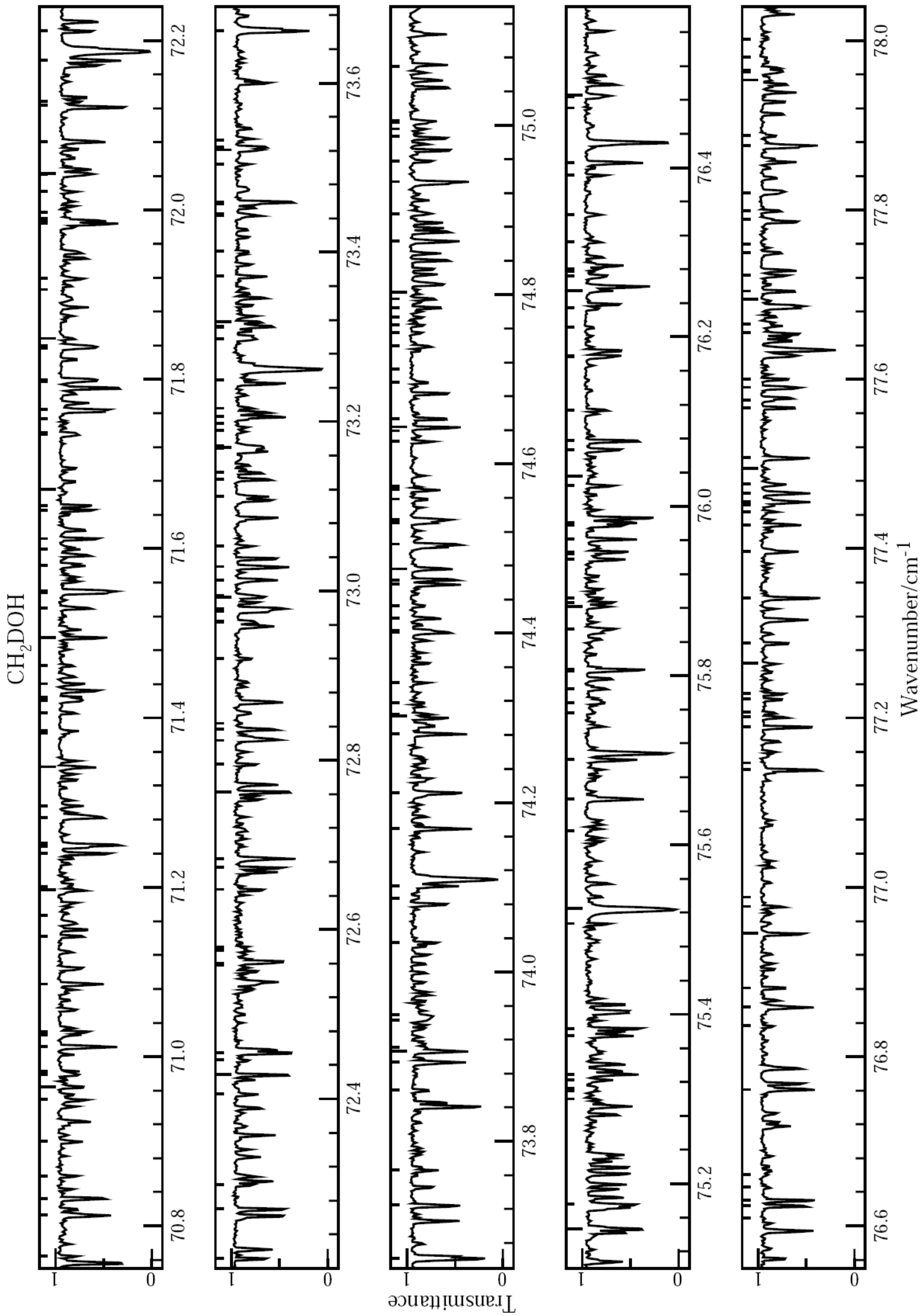


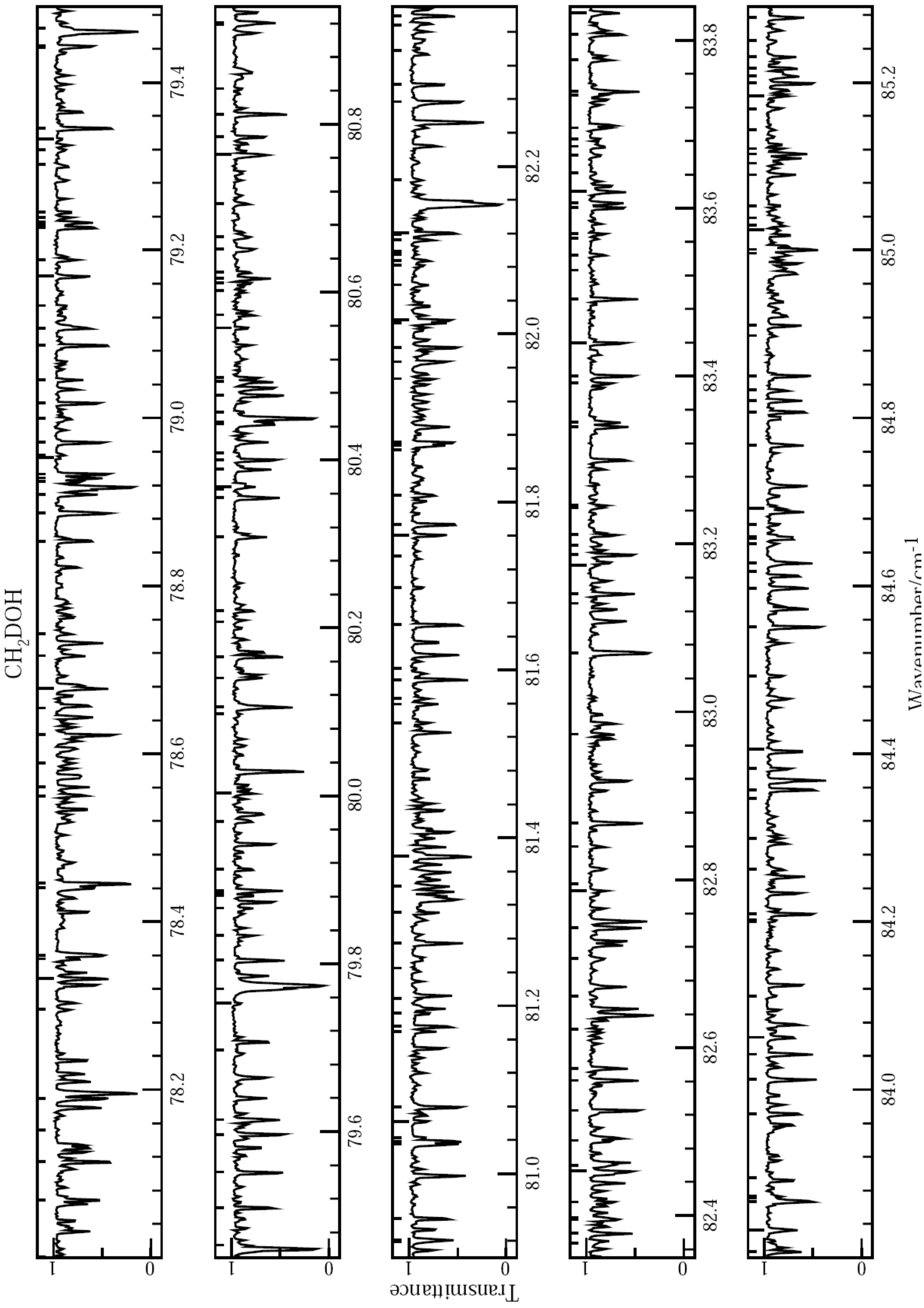
IV. ATLAS OF HIGH RESOLUTION SPECTRA OF METHANOL-D1 IN THE RANGE 50-120 CM^{-1}

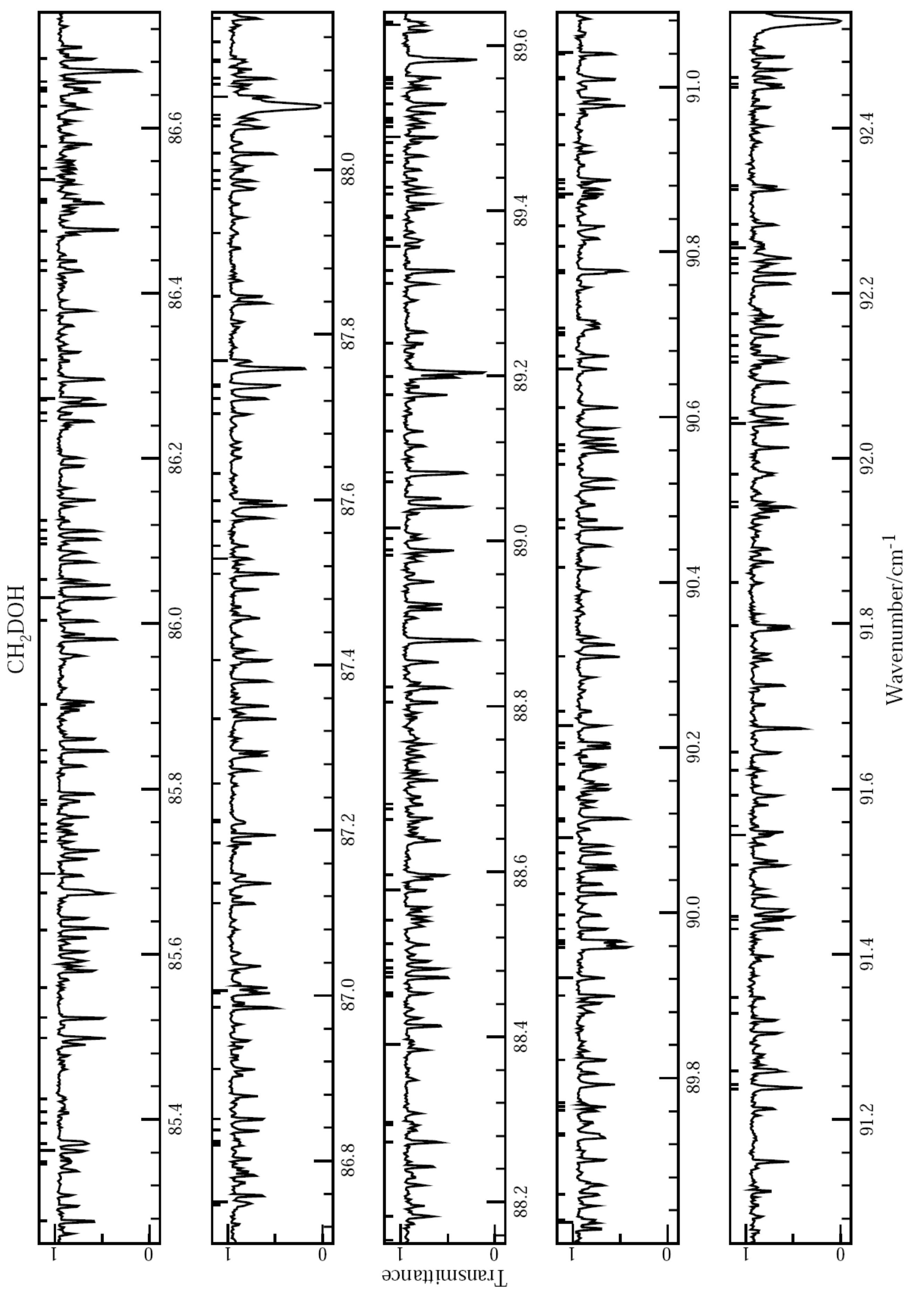


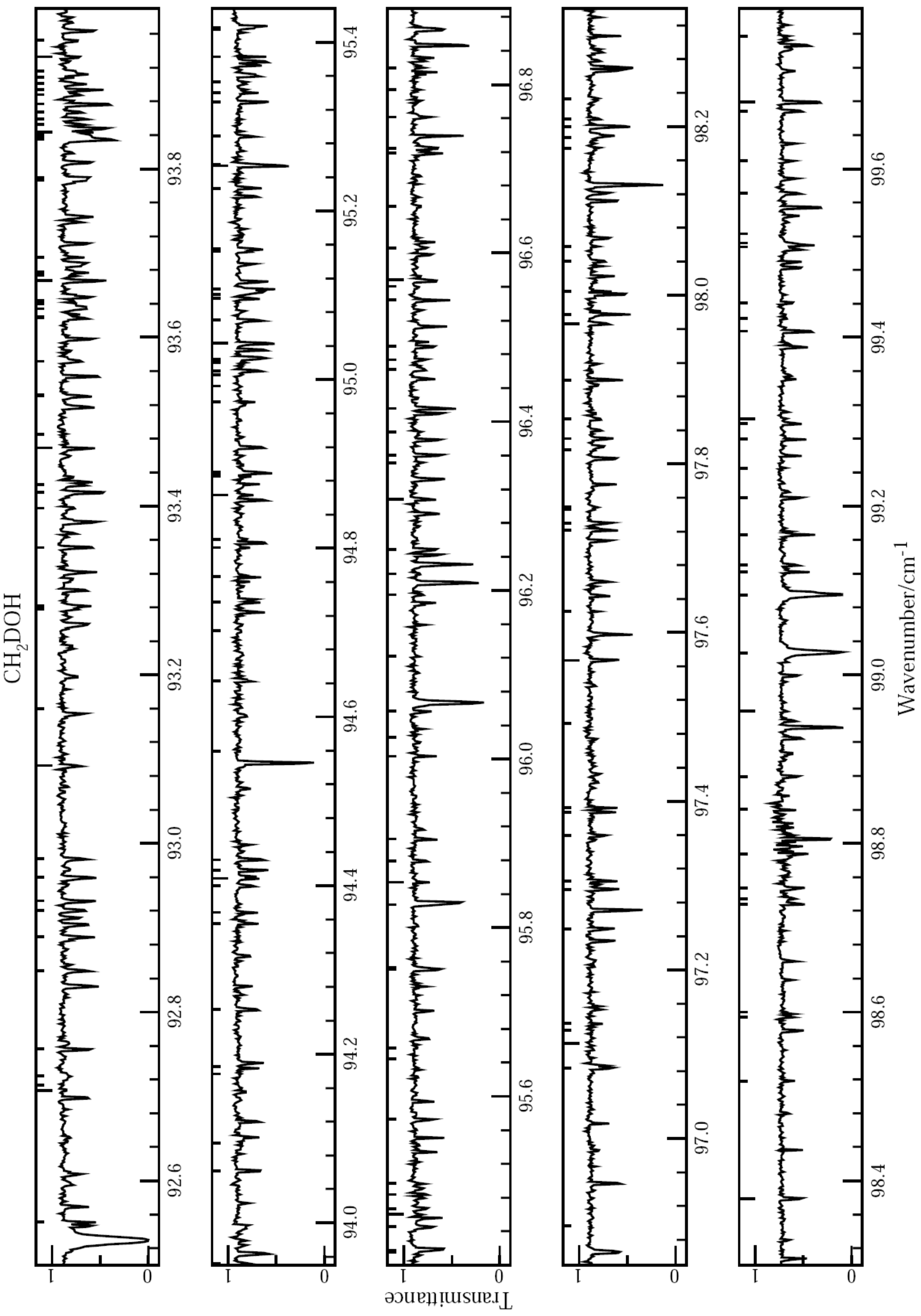

CH_2DOH
Transmittance
1
0
Wavenumber/cm^{-1}
56.4
56.6
56.8
57.0
57.2
57.4
57.6
57.8
58.0
58.2
58.4
58.6
58.8
59.0
59.2
59.4
59.6
59.8
60.0
60.2
60.4
60.6
60.8
61.0
61.2
61.4
61.6
61.8
62.0
62.2
62.4
62.6
62.8
63.0
63.2
63.4

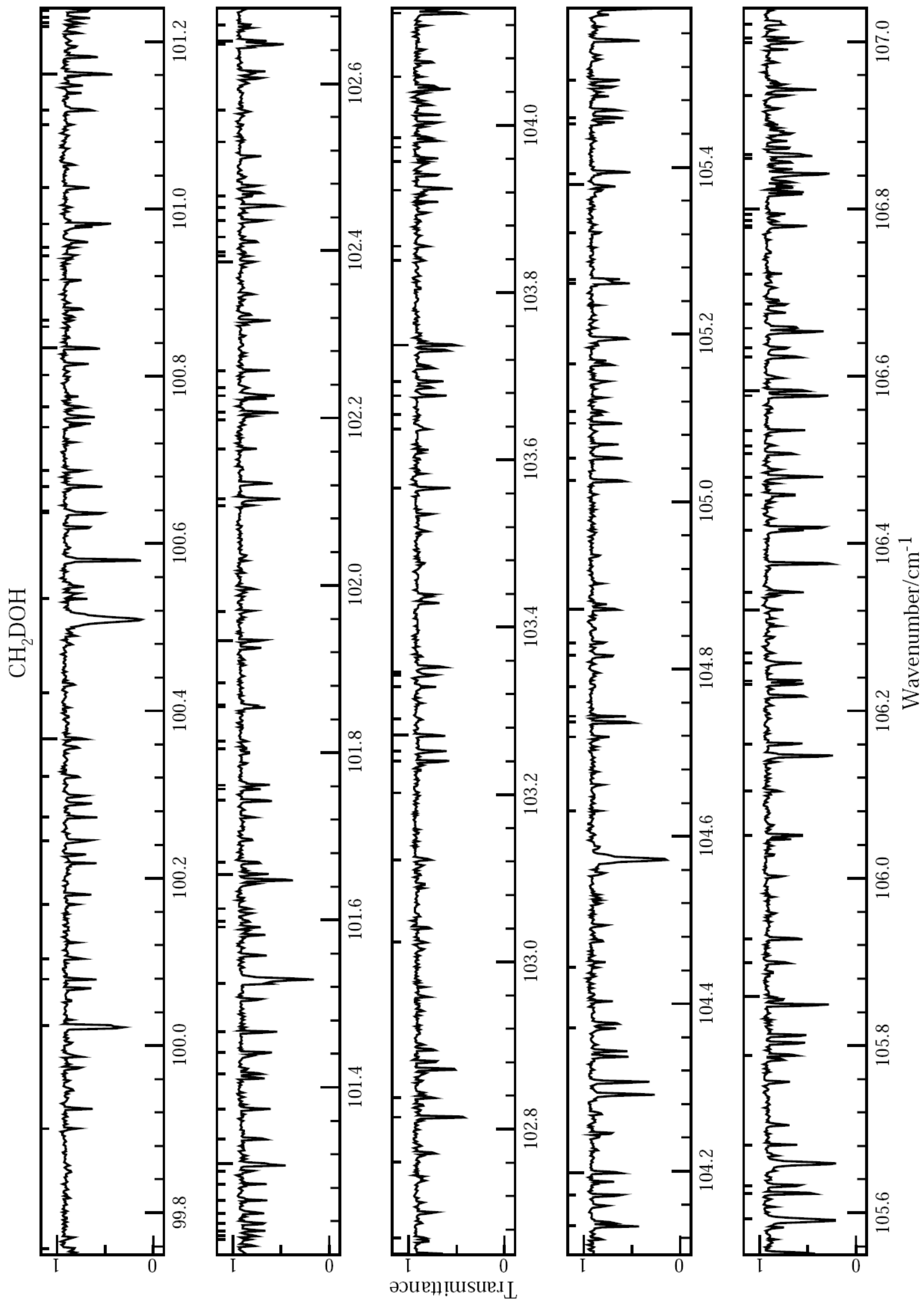

CH2DOH
Transmittance
Wavenumber/cm-1
63.6
63.8
64.0
64.2
64.4
64.6
64.8
65.0
65.2
65.4
65.6
65.8
66.0
66.2
66.4
66.6
66.8
67.0
67.2
67.4
67.6
67.8
68.0
68.2
68.4
68.6
68.8
69.0
69.2
69.4
69.6
69.8
70.0
70.2
70.4
70.6
1
0

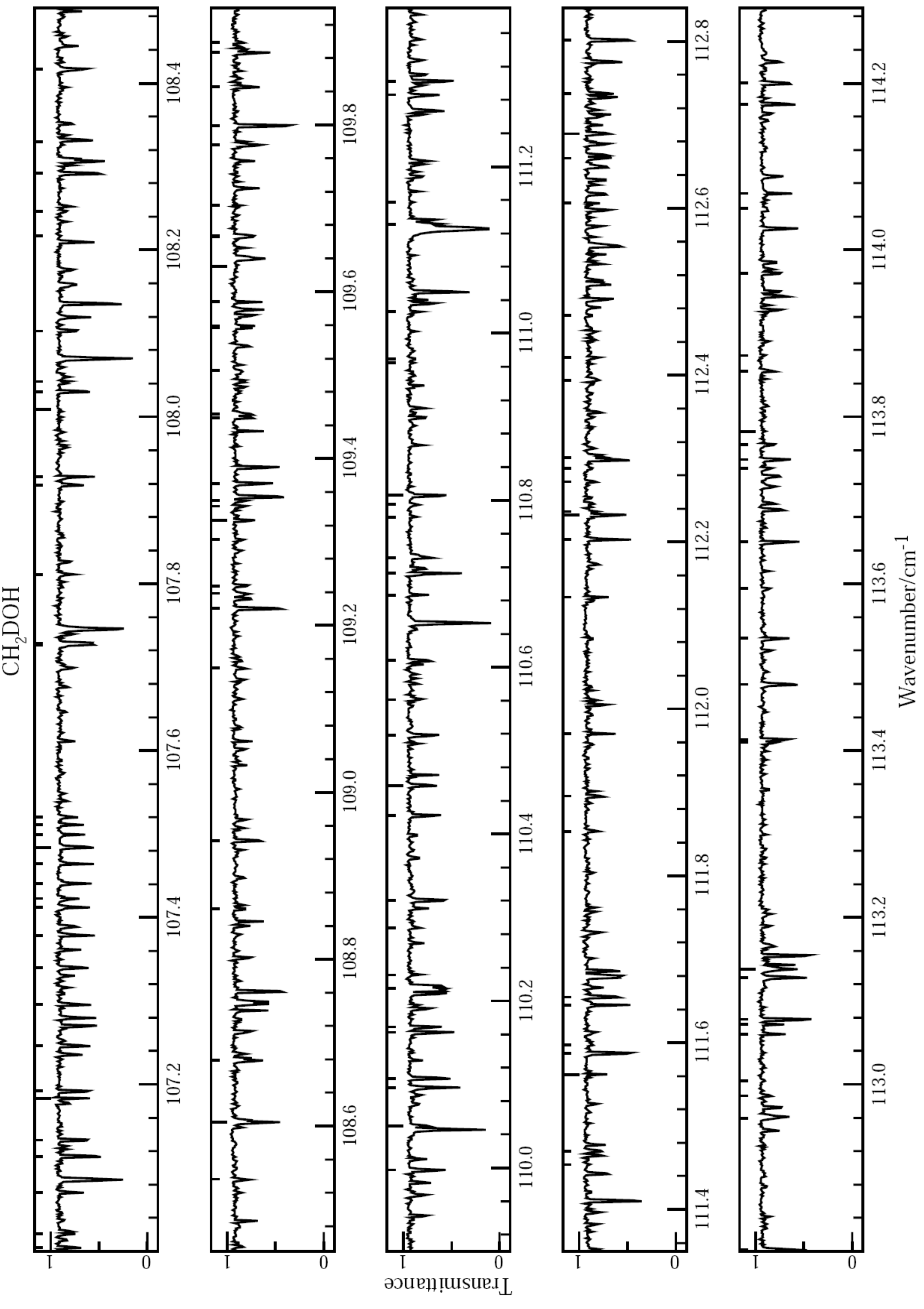

CH2DOH
Transmittance
Wavenumber/cm-1

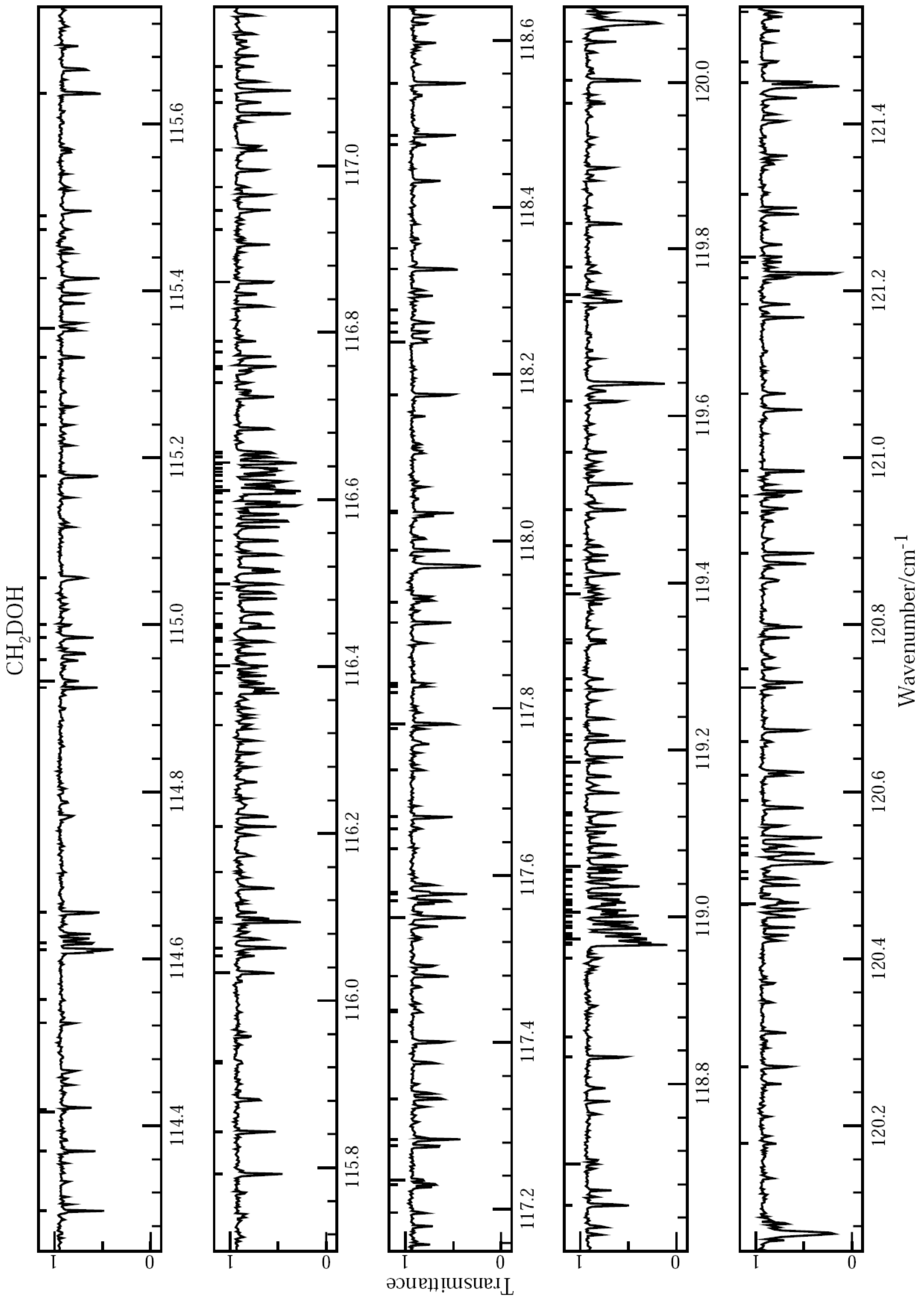

CH2DOH
Transmittance
Wavenumber/cm-1


CH_2DOH
Transmittance
Wavenumber/cm^{-1}


CH_2DOH
Transmittance
Wavenumber/cm^{-1}
1
0
92.6
92.8
93.0
93.2
93.4
93.6
93.8
94.0
94.2
94.4
94.6
94.8
95.0
95.2
95.4
95.6
95.8
96.0
96.2
96.4
96.6
96.8
97.0
97.2
97.4
97.6
97.8
98.0
98.2
98.4
98.6
98.8
99.0
99.2
99.4
99.6


CH2DOH
Transmittance
Wavenumber/cm-1
99.8
100.0
100.2
100.4
100.6
100.8
101.0
101.2
101.4
101.6
101.8
102.0
102.2
102.4
102.6
102.8
103.0
103.2
103.4
103.6
103.8
104.0
104.2
104.4
104.6
104.8
105.0
105.2
105.4
105.6
105.8
106.0
106.2
106.4
106.6
106.8
107.0
1
0


CH$_2$DOH
Transmittance
Wavenumber/cm^{-1}


CH2DOH
Transmittance
Wavenumber/cm-1
1
0
114.4
114.6
114.8
115.0
115.2
115.4
115.6
115.8
116.0
116.2
116.4
116.6
116.8
117.0
117.2
117.4
117.6
117.8
118.0
118.2
118.4
118.6
118.8
119.0
119.2
119.4
119.6
119.8
120.0
120.2
120.4
120.6
120.8
121.0
121.2
121.4

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Personal Profile of Dr. Indra Mukhopadhyay

Dr. Indra Mukhopadhyay received the M.Tech. degree in Electronics and Electrical Communication Engineering from the IIT, Kharagpur and received his Ph.D. degree in Physics at the University of New Brunswick. In 1990, he joined as a Senior Scientist at the Atomic Energy Department. He was involved in various projects including optically pumped molecular lasers, atomic and molecular physics and solid state electronics. In recent years his research interests included Stark Effect, high resolution MMW, FIR and IR Spectroscopy and Radio Astronomy.

Dr. Mukhopadhyay was involved with the detection of methanol in a distant Star forming region and the calculation of D/H ratio which has important significance to the "Big Bang" theory. He spent time in various laboratories in USA, Germany, and Canada and is a member of the Canadian Association of Physicists, Indian Laser Association and Laser and Spectroscopy Society of India. He is a member Physics and Astronomy Advisory Committee of the University System of Georgia.

Presently he is the Professor of Engineering and Physics at Albany State University, University System of Georgia, USA. He has been nominated for the "US professor of the year" and for the "Excellence in Teaching" award by the Georgia Board of Regents. Dr. Mukhopadhyay has published more than 150 papers in referred journals.