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High sensitive measurements of $^{12}\text{CH}_3\text{D}$ pure rotational lines within ground and excited vibrational states in the subTHz region

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Abstract

The pure rotational transitions of $^{12}\text{CH}_3\text{D}$ having intensity down to $7.9 \cdot 10^{-28}$ cm/molec were studied by high sensitive spectrometer with radio-acoustic detection of absorption. Among the 14 measured spectral lines, 11 correspond to the rotational transitions within first three excited states of $^{12}\text{CH}_3\text{D}$. A theoretical description was carried out by effective polyad model expressed in irreducible tensor form including the Triad of interacting bands. An accurate set of ground state rotational and centrifugal distortion constants was determined using a simultaneous weighted fit of experimental transitions available in literature together with the new subTHz measurements. Pressure broadening and shifting parameters of the $J_K=1_0-0_0$ ground state rotational line were accurately measured and allowed estimating possible systematic errors in some previous studies.

Keywords: Methane, $^{12}\text{CH}_3\text{D}$, THz region, pure rotational lines, ground state parameters, GSCD

1. Introduction

Deuterated chemical compounds are of significant interest for astronomical applications. A determination of the D/H ratio by spectral analyses is the subject of numerous works since this permits

36 to test models of Galactic chemical evolution. Very contrasting D/H ratios in different parts of the
37 Universe have been obtained that stimulated challenging cosmochemical studies ([Owen 2015,
38 Lindskey2006] and reference therein).

39 Methane (CH_4) is one of the most abundant gas in planetary atmospheres. CH_4 and its
40 monodeuterated isotopologue CH_3D have been observed on the majority of the planets of the solar
41 system and most of the larger moons, in particular, in Jupiter, Titan, Saturn, Uranus, and Neptune
42 (see [Encrenaz1999, Penteado2005, Fletcher2009, Irwin2012, Irwin2014] and references therein).
43 Methane on Mars attracts much interest since it might be a sign of the microbial life or organic matter
44 by analogy with the biological origin of methane in the Earth's atmosphere. Although the pure
45 rotational transitions in CH_4 are forbidden by symmetry in a rigid rotor approximation, a very weak
46 absorption can be detected due to centrifugal distortions [Boudon2010]. Induced by isotopic
47 substitution permanent electric dipole moment of CH_3D is much larger than rotationally induced in
48 CH_4 but is still quite small (~ 0.006 D) [Ozier1969, Wofsy1970]. Therefore, investigation of CH_3D
49 spectra in THz region is a difficult/challenging task requiring a high sensitivity of the spectrometer.

50 First low resolution spectrum of $^{12}\text{CH}_3\text{D}$ (hereafter CH_3D) was recorded by Ozier et al.
51 [Ozier1969] in the $40\text{--}120\text{ cm}^{-1}$ ($1.2\text{--}3.6\text{ THz}$) frequency range using grating spectrometer. Ten
52 rotational lines identified as $\text{R}(5)$ to $\text{R}(14)$ transitions were observed. Despite no K-structure was
53 observed, the values of the dipole moment and the spectroscopic molecular constants were
54 determined. Later, the high resolution recordings of the $J_K = 1_0\text{--}0_0$ line near 232.6 GHz were obtained
55 by Pickett et al. [Pickett1980] and by Womack et al. [Womac1996], who also measured two lines
56 $J_K = 2_0\text{--}1_0$ and $J_K = 2_1\text{--}1_1$ around 465.25 GHz to analyze the telescopic observation toward Orion-KL.
57 Lattanzi et al. [Lattanzi2008] reported twelve new rotational transitions in the range of $697\text{--}1162$
58 GHz which correspond to the next series with $3_K\text{--}2_K$, $4_K\text{--}3_K$, and $5_K\text{--}4_K$. The spectral range was further
59 extended in work of Drouin et al. [Drouin2009] where the $7_K\text{--}6_K$ series has been recorded. In
60 [Drouin2009] the $5_K\text{--}4_K$ series was also re-measured with 100 kHz uncertainty because of small
61 inconsistency with the data of Lattanzi et al. In the recent work of Bray et al. [Bray2016], the
62 photomixing CW-THz spectrometer provided a relatively broad spectral coverage from $7_K\text{--}6_K$ to 11_K--
63 10_K series. As a result of these studies, line positions are known for 70 lines with the relative
64 uncertainty of 10^{-7} and an accurate set of ground state molecular spectroscopic constants was obtained
65 from the global fit analysis [Bray2016]. Intensities of 51 transitions were measured in the work
66 [Bray2016] with the estimated accuracy of 25% providing a set of the dipole moment components.
67 Almost all the lines studied have intensity of about 10^{-25} cm/molec or higher. However, many weaker
68 lines of hot band transitions located in the range of the rotational spectra can validate the theory
69 completeness and accuracy.

Note that the data sets for the ground state rotational transitions of CH₃D in HITRAN [Gordon2017], GEISA [Jacquinet2016], JPL [Pearson2010] and Cologne databases [Christian2016] are quite different, whereas information concerning CH₃D transitions in this range is not available in TDS [Tyuterev1994] or MeCaSDa [Ba2013] compilations. To our knowledge, the CH₃D transitions in the subTHz region within excited vibrational states have not been included in existing databases.

In this work, we present the revised accurate measurements of the ground state transitions (1_0-0_0 , 2_0-1_0 , and 2_1-1_1) and the first measurements of the pure rotational transitions within ν_6 , ν_3 , and ν_5 excited states of CH₃D. Lines were recorded in the frequency range up to 0.5 THz using a spectrometer with radio-acoustic detection of absorption (RAD spectrometer) [Tretyakov2008, Koshelev2017, Golubyatnikov_unpub]. The intensity of the studied lines varied from 10^{-26} to 10^{-29} cm/molec. A new accurate set of rotational parameters of effective Hamiltonian expressed in irreducible tensors was determined by combining all measured in THz region transitions with those calculated by so called ground state combination differences (GSCD) method. Pressure broadening and shifting of the 1_0-0_0 ground state rotational line were accurately measured and allowed estimating possible systematic errors in some previous studies.

2. Experimental details

A spectrometer with radio-acoustic detection of absorption (RAD spectrometer) was used for recording the weak CH₃D lines. A detailed description of the spectrometer can be found elsewhere [Tretyakov2008, Koshelev2017, Golubyatnikov_unpub]. Briefly, the method is based on registering a pressure variations induced in a gas due to molecular absorption of radiation modulated by frequency or amplitude. A significant improvement of the spectrometer sensitivity can be achieved by an increase of the radiation power. In this study, the spectrometer was equipped with two types of continuous wave radiation sources. The first one is a series of three backward wave oscillators (BWOs) covering a frequency range 179-535 GHz which output power varies from a few milliwatts to about 50 mW (see [Korolev2001] and references therein). The second source is a gyrotron operating in a narrow frequency interval of about 1 GHz around 263.5 GHz with the maximum power of 1 kW [Glyavin2015]. Both sources were frequency stabilized by the PLL system against a harmonic of a high stable signal of microwave synthesizer (Anritsu MG3692C) providing relative frequency stability of about 10^{-10} and narrow spectrum bandwidth down to 1 Hz or less [Fokin2018]. Use of GPS Time and Frequency System (SR FS740) as a reference oscillator provided frequency setting accuracy and long term stability. Modulation of the radiation frequency by square-wave signal followed by demodulation at a synchronous detector was used for reducing the baseline effect when recording the weak lines. For this purpose, an arbitrary waveform generator (Tektronix AFG3101 and

105 Rohde & Schwarz HFM2550), which permits modulating the radiation frequency with a preset
106 modulation index, was employed in the PLL as the source of a reference signal for the phase detector.
107 Synchronous detection of the absorption signal was carried out both at the first (for BWO) and the
108 second (for gyrotron) harmonics of the modulation frequency.

109 A single pass cell of 10 cm length and 2 cm diameter connected with a microphone was used.
110 The cell was equipped with the conical HDPE windows of 2 mm thickness. All spectra were recorded
111 at room temperature 297 ± 1 K. For the line frequency measurements, the pressure of CH₃D in the
112 cell was about 0.4-0.5 Torr which seems to be the optimal compromise from the point of view of the
113 RAD spectrometer sensitivity, line width and the baseline influence on the line shape. Gas pressure
114 was measured using MKS Baratron (Type 626B) gauge having a declared accuracy of 0.25% of
115 reading. A commercial methane gas, enriched with at least 90% of the ¹²CH₃D isotopologue was used
116 in the study.

117 High stability of the experimental conditions (parameters of laboratory air, radiation and gas
118 sample) allowed averaging a large number (up to 216) of repeated single scans without noticeable
119 distortions in the observed spectra. The obtained signal-to-noise ratio (SNR) was sufficient (at least
120 10) for accurate determining the central frequencies of the weak CH₃D lines. Acquisition parameters
121 of the single scan were the following: 200 frequency points for a single line and 250 points for
122 doublets, lock in time constant was 0.5 s. Thus, the accumulation time was up to 7.5 hours. Examples
123 of experimental spectra of CH₃D obtained using RAD spectrometer are shown in Fig. 1 for the BWO
124 and in Fig. 2 for the gyrotron.

125

Fig. 1. Experimental spectra of CH₃D obtained using RAD spectrometer with BWO are shown by red circles. Acquisition details (number of scans and approximate radiation power) and observed line parameters (approximate position and intensity) are presented near each spectrum. Solid lines are fitted model functions.

Fig. 2. Experimental spectra of CH₃D obtained using RAD spectrometer with the gyrotron are shown by red circles. Line parameters (approximate position and intensity) and acquisition details (number of scans and approximate radiation power) are presented in the insets. Solid line is fitted model function.

127 3. Spectra analysis

128

129 A model function based on the Voigt profile was fitted to the experimental spectra and the line
130 shape parameters were derived. Measured central frequencies are presented in Table 1 along with the
131 experimental details (number of averaged recordings and SNR) and spectroscopic information
132 (calculated intensities and assignment) on the studied lines.

133 Self-broadening and self-shifting parameters of the rotational spectrum lines of CH₃D were
134 estimated on example of our best quality (in terms of SNR) ground state line $J_K = 1_0-0_0$ near
135 232.644 GHz. For this, the line recordings were obtained at six pressures in a range 0.26 – 1.04 Torr.
136 For each recording the modulation depth was preset approximately equal to the line half width at half
137 maximum (HWHM) and this value was fixed in the model function. Both multispectra (Fig. 3) and
138 single-spectra fitting procedures were applied and demonstrated similar results for the line shape
139 parameters. SNR for the line recordings was 110–440. Pressure dependence of the line width and
140 center position obtained from the single-spectra fitting is shown in Fig. 4.

141 Self-broadening and shifting parameters determined by both fitting procedures are
142 3.285(30) MHz/Torr and 0.085(25) MHz/Torr, respectively. Errors are threefold uncertainties
143 obtained from the spectra fitting which seems to be reasonable estimate taking into account possible
144 sources of inaccuracies (finite SNR, pressure and temperature measurement, gas impurities and
145 others). Our measured self-broadening coefficient is about 4.5% less than the value tabulated in
146 HITRAN [HITRAN] with 2-5% uncertainty on the base of IR measurements [M_Devi2002]. The
147 only previous measurement of the self-broadening of the THz lines of CH₃D was performed by Bray
148 et al [Bray2016] for the ^QR(7) multiplet. Experimental values obtained with total uncertainty of 25%
149 for six *K*-structure lines are scattered in the interval 0.079-0.09 cm⁻¹/atm (3.11 - 3.55 MHz/Torr) and
150 no *K*-dependence was observed. Our accurate value of self-broadening coefficient confirms the
151 results of Bray et al [Bray2016] demonstrating as well good general agreement with the IR
152 measurements in several excited vibrational band (see, e.g., Fig. 5 in [Bray2016] and references
153 therein).

154 To the best of our knowledge, self-shifting has never been studied for the pure rotational lines
155 of CH₃D as opposed to the lines of the excited vibrational states, e.g., for ν_5 [M_Devi2002_v5], ν_6
156 [M_Devi2002_v6], ν_3 [M_Devi2002_v3], ν_2 [Predoi-Cross2005_v2] bands. Both positive and
157 negative shifts were observed with values varying from line to line from -0.014 to 0.004 cm⁻¹/atm (-
158 0.55 to 0.2 MHz/Torr). Our self-broadening parameter is within this interval thus confirming its
159 validity.

160 Pressure shifting if not taken into account causes systematic uncertainty in the line center
161 determining. The higher the operating pressure the larger the error. Since the pressure shifting was

not taken into account in all previous experimental studies [Pickett1980, Womac1996, Lattanzi2008, Drouin2009, Bray2016], the problem of corresponding systematic error seems to be common. As an estimate, operating pressures were 0.05 Torr in [Womac1996], 0.28 Torr in [Lattanzi2008] and 0.75 Torr in [Bray2016] that give center shifting as 4, 24 and 64 kHz, respectively, if our measured shift coefficient is used. Corresponding uncertainties should be taken into account in the error budget by its summing with the statistical one, because both positive and negative shifts are equally probable. In our measurements we estimate the maximum value of the systematic error as 35 kHz, which is comparable with the statistical uncertainty.

Fig. 3. Experimental line recordings of the ground state rotational transition $J_K = 1_0 - 0_0$ obtained at different pressures and the result of the multispectra fitting. Pressure values are presented for each recording. Magnified (x5) residuals are demonstrated in the lower part.

Fig. 4. Pressure dependence of the line shape parameters of the ground state rotational transition $J_K = 1_0-0_0$: (a) HWHM and (b) relative center position shifted by the value 232644.26 MHz. Error bars are statistical uncertainties obtained from the spectra fitting.

4. Fitting of the center positions and comparison with previous works

As can be seen from Table 1, three measured frequencies of the ground state transitions of Womack et al [Womack1996] and Pickett et al [Pickett1980] agree with our results within the combined experimental uncertainties. However, the present values are more accurate. Weak lines of a series of the Q -branch pure rotational transitions with J ranging from 1 to 11 and $\Delta K = +1$ belonging to the collisionally excited first vibrational state ν_6 (1161 cm^{-1}) were also recorded. In the second vibrational state ν_3 (1306 cm^{-1}) of A_1 symmetry, three weak rotational transitions of the R branch were observed as well as one Q -branch rotational line within the third excited state ν_5 (1472 cm^{-1}) of E symmetry.

To determine the parameters of the ground state, THz transitions from Table 1 were included into the fit together with those measured previously by [Pickett1980], [Womack1996] [Lattanzi2008], [Drouin2009], [Bray2016] and collected in Table 1 of [Bray2016]. The pure rotational transitions in first three excited states were also fitted by our effective polyad model constructed for the ground state and Triad interacting bands. The effective Hamiltonian was expressed in terms of irreducible tensor operators adapted to symmetric top C_{3v} molecules. This approach implemented in MIRS package [Nikitin2003, Nikitin2012] was previously applied for CH_3D [Nikitin1997] [Nikitin2000] [Nikitin2002] [Nikitin2013CH3D], PH_3 [Nikitin2017PH3], and recently for NF_3 [Rodina2019] [Egorov2019]. The initial values of the effective Hamiltonian parameters were obtained by the contact transformation method [Tyuterev1980, Tyuterev2013] from the molecular potential energy surface [Nikitin2011] similarly to the procedure previously applied for CH_4 spectra analyses. The line intensities predicted [Rey2014, Rey2016] from the *ab initio* dipole moment surfaces [Nikitin2013CH4, Nikitin2017CH4] using variational method [Rey2013] were employed for the line searching and transition assignments.

Table 1. Measured pure rotational transition of CH_3D in the ground and excited vibrational states. Errors are 1- σ fitting uncertainty. Intensities are presented for 100% of $^{12}\text{CH}_3\text{D}$.

Wavenumber in MHz	Δ^c	Intensity in 10^{-28} cm/molec	Number of averages	SNR ^e	Assignment ^d		
					$\nu' - \nu''$	$J' K' \Gamma'$	$-J'' K'' \Gamma''$
196367.89(24)	265	0.715	50	12	1 – 1	11 1 E	– 11 0 E

208971.359(85)	-83	1.640	40	10	1 – 1	9 1 <i>E</i> – 9 0 <i>E</i>
219282.532(48)	-14	2.978	40	13	1 – 1	7 1 <i>E</i> – 7 0 <i>E</i>
225694.315(52)	72	4.035	30	16	1 – 1	5 1 <i>E</i> – 5 0 <i>E</i>
226757.394(42)	120	2.725	50	22	2 – 2	1 0 <i>A</i> – 0 0 <i>A</i>
227493.903(57)	33	4.133	36	15	1 – 1	4 1 <i>E</i> – 4 0 <i>E</i>
228590.864(46)	-67	3.823	50	17	1 – 1	3 1 <i>E</i> – 3 0 <i>E</i>
229493.023(67)	29	2.018	100	14	1 – 1	1 1 <i>E</i> – 1 0 <i>E</i>
232644.260(10) ^f	-33	75.19	16	400	0 – 0	1 0 <i>A</i> – 0 0 <i>A</i>
232644.301(75) ^a	8					
232644.327(18) ^b	34					
262822.959(20)	-1	0.0789	13	35	3 – 3	8 2 <i>E</i> – 8 3 <i>E</i>
453506.92(11)	-65	15.36	216	16	2 – 2	2 1 <i>E</i> – 1 1 <i>E</i>
453547.12(10)	-94	20.51	216	19	2 – 2	2 0 <i>A</i> – 1 0 <i>A</i>
465235.540(75) ^a	-30	429.0	60	70	0 – 0	2 1 <i>E</i> – 1 1 <i>E</i>
465235.553(13)	-17					
465250.691(75) ^a	-25	560.0	60	95	0 – 0	2 0 <i>A</i> – 1 0 <i>A</i>
465250.725(10)	9					

^a results of Womack et al [[Womack1996](#)].

^b result of Pickett et al [[Pickett1980](#)].

^c difference between the observed and calculated wavenumbers in kHz.

^d $\nu = 0, 1, 2$ and 3 corresponds to 000000(*A*₁), 000001(*E*), 001000(*A*₁), and 000010(*E*) vibrational states; *A* means no information on *A*₁–*A*₂ splitting.

^e SNR was determined as a ratio of peak-to-peak signal amplitude to the noise standard deviation.

^f Pressure shifting is taken into account.

Table 2. Ground State Effective Hamiltonian parameters of CH₃D (in MHz)

No	Parameter, Tensorial Nomenclature*	Value
1	<i>R</i> 2(0, 0 <i>A</i> ₁)	130021.9620(38)
2	<i>R</i> 2(2, 0 <i>A</i> ₁)	8387.2084(23)
3	<i>R</i> 4(0, 0 <i>A</i> ₁)	–2.368268(44)
4	<i>R</i> 4(2, 0 <i>A</i> ₁)	1.55723(16)×10 ^{–1}
5	<i>R</i> 4(4, 0 <i>A</i> ₁)	7.06776(61)×10 ^{–2}
6	<i>R</i> 4(4, 3 <i>A</i> ₁)	–2.35(28)×10 ^{–2}
7	<i>R</i> 6(0, 0 <i>A</i> ₁)	1.1961(19)×10 ^{–4}
8	<i>R</i> 6(2, 0 <i>A</i> ₁)	6.298(32)×10 ^{–6}
9	<i>R</i> 6(4, 0 <i>A</i> ₁)	3.168(18)×10 ^{–6}
10	<i>R</i> 6(6, 0 <i>A</i> ₁)	–1.445(49)×10 ^{–7}
11	<i>R</i> 8(0, 0 <i>A</i> ₁)	–1.009(40)×10 ^{–8}
12	<i>R</i> 8(2, 0 <i>A</i> ₁)	4.41(25)×10 ^{–10}
13	<i>R</i> 8(6, 6 <i>A</i> ₁)	–2.08(21)×10 ^{–10}

209 *see details in [Nikitin1997]

210

211 The rotational constants of the ground vibrational state corresponding to the K -dependence
 212 cannot be extracted from the pure rotational transitions due to $\Delta K = 0$ selection rule. Therefore, the
 213 GSCD method was applied to obtain pure rotational transitions from IR line positions of CH₃D
 214 analyzed previously in Triad [Nikitin2000], Nonad [Nikitin2002], and Enneadecad [Nikitin2006]
 215 [Nikitin2013CH3D] regions of interacting bands. Finally, we fitted more than 11900 rotational
 216 transitions including 77 known from THz measurements. Thirteen ground state parameters of the
 217 irreducible tensor operators were determined (Table 2) from the total number of 23 with the standard
 218 deviation of 5.70 MHz ($0.19 \times 10^{-3} \text{ cm}^{-1}$).

219

220 **Table 3.** Statistical information of the fit of the parameters of the ground and Triad vibrational states
 221 of CH₃D

Vibrational state	Number of data: THz / IR / Levels	Sources*	J_{max}	SD
Ground	77 / 11828 / 0	[P] [W] [L] [D] [B] TH / GSCD	19	5.70(0.19)
ν_6	7 / 1575 / 290	TH / [Nikitin2002] / [Ulenikov2000]	20	14.69(0.49)
ν_3	3 / 641 / 121	TH / [Nikitin2002] / [Ulenikov2000]	18	16.19(0.54)
ν_5	1 / 1417 / 270	TH / [Nikitin2002] / [Ulenikov2000]	18	15.89(0.53)

222 *TH – this work results; GSCD – transitions were determined by ground state combination differences method
 223 (see details in the text); SD – standard deviation of the difference between experimental and calculated
 224 frequencies in MHz ($\times 10^{-3} \text{ cm}^{-1}$)

225

226 Eleven rotational transitions within the Triad vibrational states measured in this work (Table 1)
 227 were fitted with the IR transitions from [Nikitin2002] and experimental energy levels of Ulenikov et
 228 al. [Ulenikov2000]. For more than 3640 transitions and 680 levels, the achieved standard deviation
 229 of 15.59 MHz ($0.52 \times 10^{-3} \text{ cm}^{-1}$) corresponds to the accuracy of the majority of the experimental data
 230 from [Nikitin2002]. The detailed statistical information of the fit of the parameters of the ground and
 231 ν_6 , ν_3 , and ν_5 excited states is presented in Table 3.

232

233 **Table 4.** Examples of the experimental transitions (in MHz) fitted in this work

Exp.*	Exp.–Calc.(kHz)		Assignment*** $J' K' \Gamma' - J'' K'' \Gamma''$
	This work	Ulenikov et al.**	
465235.553(13) ^a	-17	108	2 1 E – 1 1 E

465250.725(10) ^a	9	111	2 0 A – 1 0 A
929926.571(50) ^b	28	255	4 3 A – 3 3 A
1162125.166(100) ^c	-10	210	5 3 A – 4 3 A
1394135.500(70) ^d	20	171	6 3 A – 5 3 A
1625919.9988(100) ^c	-155	9	7 3 A – 6 3 A
1625920.161(40) ^d	7	171	
1857442.241(70) ^d	193	63	8 3 A – 7 3 A
2088664.258(60) ^d	28	159	9 3 A – 8 3 A
2319550.084(90) ^d	-111	-645	10 3 A – 9 3 A
2550063.123(130) ^d	91	384	11 3 A – 10 3 A

*Experimental transitions fitted in this work; *a*, *b*, *c*, and *d* correspond to this work, Ref. [Lattanzi], Ref. [Drouin], and Ref. [Bray2016].

**Theoretical transitions were calculated on the basis of energy levels from Table 6 of Ulenikov et al. [Ulenikov1999].

***Information on A_1 – A_2 splitting is not presented in experimental works used in the fitting

The determined ground state parameters reproduce in most cases (in 61 out of 77) the experimental THz transitions within their experimental uncertainty. Examples can be seen in Table 1 and Table 4 (a total list of the deviations is given in **supplementary material I**; **supplementary material II** contains rotational energy levels up to $J = 20$). The calculated rotational transitions within three excited states ν_6 , ν_3 , and ν_5 fall into experimental uncertainty in half of the cases. However the number of the transitions is not so much to make the conclusion on the quality of the corresponding parameters, taking into account the possible resonance interactions at higher J values.

4. Conclusion

New high sensitive measurements of pure rotational transitions of CH₃D by radio-acoustic method are presented. Pressure broadening and shifting of the 1_0-0_0 ground state rotational line were accurately measured and allowed estimating the possible systematic errors in some previous studies. Among the 14 measured transitions, 3 correspond to the ground vibrational state. Other 11 lines were assigned to rotational transitions within first three excited vibrational states: $\nu_6=1$, $\nu_3=1$ and $\nu_5=1$. Experimental frequencies of the ground state transitions agree with the previous experimental data but the present results are more accurate. These transitions together with those published previously were described in most cases within their experimental uncertainties using our effective Hamiltonian expressed in irreducible tensor operators. For determining the rotational parameters of the Hamiltonian, more than 11800 ground state combination differences were also calculated and included into the fit. The obtained parameters will be used in our future works devoted to describing

261 experimental intensities of pure rotational lines of CH₃D measured by various experimental groups
262 including those measured in this work.

263

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265

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271

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