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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 Lindsy2006] and reference therein).

39 Methane (CH<sub>4</sub>) is one of the most abundant gas in planetary atmospheres. CH<sub>4</sub> and its  
40 monodeuterated isotopologue CH<sub>3</sub>D 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<sub>4</sub> 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<sub>3</sub>D is much larger than rotationally induced in  
48 CH<sub>4</sub> but is still quite small (~ 0.006 D) [Ozier1969, Wofsy1970]. Therefore, investigation of CH<sub>3</sub>D  
49 spectra in THz region is a difficult/challenging task requiring a high sensitivity of the spectrometer.

50 First low resolution spectrum of <sup>12</sup>CH<sub>3</sub>D (hereafter CH<sub>3</sub>D) was recorded by Ozier et al.  
51 [Ozier1969] in the 40-120 cm<sup>-1</sup> (1.2-3.6 THz) frequency range using grating spectrometer. Ten  
52 rotational lines identified as R(5) to 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  $J_K = 1_0-0_0$  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  $J_K = 2_0-1_0$  and  $J_K = 2_1-1_1$  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 697–1162  
58 GHz which correspond to the next series with  $3_K-2_K$ ,  $4_K-3_K$ , and  $5_K-4_K$ . The spectral range was further  
59 extended in work of Drouin et al. [Drouin2009] where the  $7_K-6_K$  series has been recorded. In  
60 [Drouin2009] the  $5_K-4_K$  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  $7_K-6_K$  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<sup>-7</sup> 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<sup>-25</sup> 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.

70 Note that the data sets for the ground state rotational transitions of CH<sub>3</sub>D in HITRAN  
71 [[Gordon2017](#)], GEISA [[Jacquinet2016](#)], JPL [[Pearson2010](#)] and Cologne databases [[Christian2016](#)]  
72 are quite different, whereas information concerning CH<sub>3</sub>D transitions in this range is not available in  
73 TDS [[Tyuterev1994](#)] or MeCaSDa [[Ba2013](#)] compilations. To our knowledge, the CH<sub>3</sub>D transitions  
74 in the subTHz region within excited vibrational states have not been included in existing databases.

75 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  $\nu_6$ ,  $\nu_3$ , and  
76  $\nu_5$  excited states of CH<sub>3</sub>D. Lines were recorded in the frequency range up to 0.5 THz using a  
77 spectrometer with radio-acoustic detection of absorption (RAD spectrometer) [[Tretyakov2008](#),  
78 [Koshelev2017](#), [Golubyatnikov\\_unpub](#)]. The intensity of the studied lines varied from  $10^{-26}$  to  $10^{-29}$   
79 cm/molec. A new accurate set of rotational parameters of effective Hamiltonian expressed in  
80 irreducible tensors was determined by combining all measured in THz region transitions with those  
81 calculated by so called ground state combination differences (GSCD) method. Pressure broadening  
82 and shifting of the  $1_0-0_0$  ground state rotational line were accurately measured and allowed estimating  
83 possible systematic errors in some previous studies.  
84

85

## 86 2. Experimental details

87

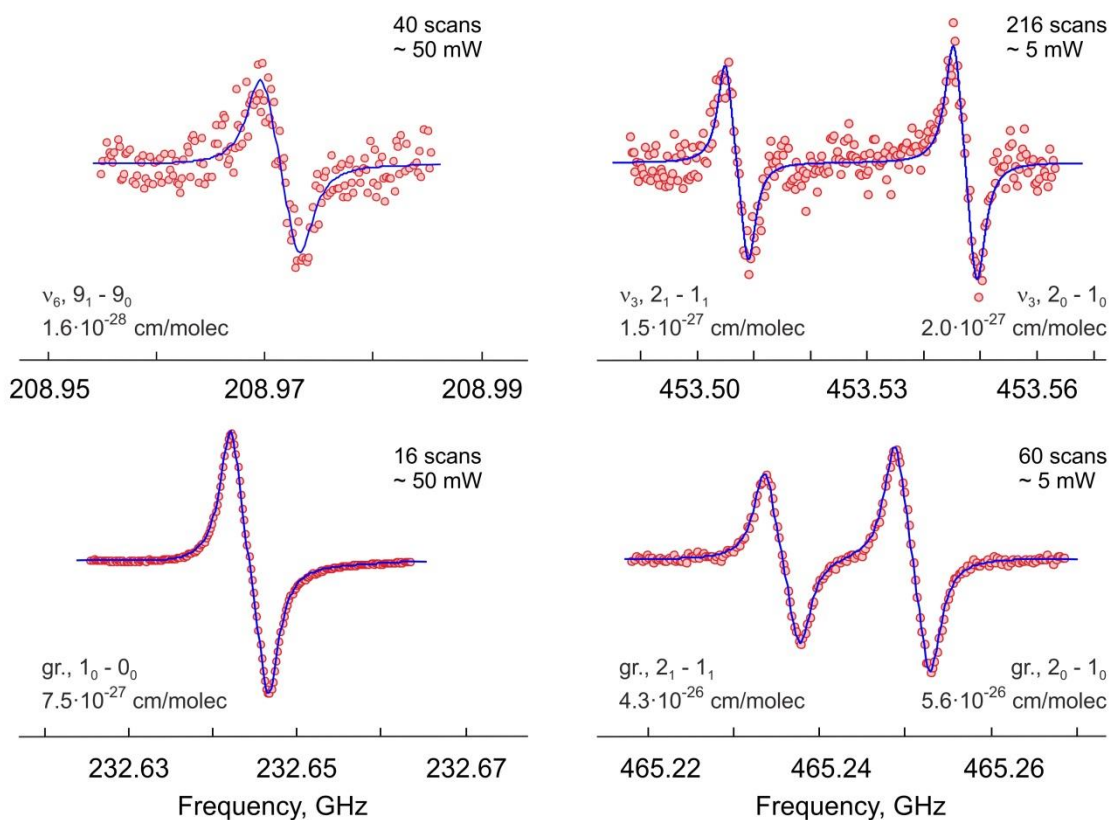
88 A spectrometer with radio-acoustic detection of absorption (RAD spectrometer) was used for  
89 recording the weak CH<sub>3</sub>D lines. A detailed description of the spectrometer can be found elsewhere  
90 [[Tretyakov2008](#), [Koshelev2017](#), [Golubyatnikov\\_unpub](#)]. Briefly, the method is based on registering  
91 a pressure variations induced in a gas due to molecular absorption of radiation modulated by  
92 frequency or amplitude. A significant improvement of the spectrometer sensitivity can be achieved  
93 by an increase of the radiation power. In this study, the spectrometer was equipped with two types of  
94 continuous wave radiation sources. The first one is a series of three backward wave oscillators  
95 (BWOs) covering a frequency range 179-535 GHz which output power varies from a few milliwatts  
96 to about 50 mW (see [[Korolev2001](#)] and references therein). The second source is a gyrotron  
97 operating in a narrow frequency interval of about 1 GHz around 263.5 GHz with the maximum power  
98 of 1 kW [[Glyavin2015](#)]. Both sources were frequency stabilized by the PLL system against a  
99 harmonic of a high stable signal of microwave synthesizer (Anritsu MG3692C) providing relative  
100 frequency stability of about  $10^{-10}$  and narrow spectrum bandwidth down to 1 Hz or less [[Fokin2018](#)].  
101 Use of GPS Time and Frequency System (SR FS740) as a reference oscillator provided frequency  
102 setting accuracy and long term stability. Modulation of the radiation frequency by square-wave signal  
103 followed by demodulation at a synchronous detector was used for reducing the baseline effect when  
104 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.

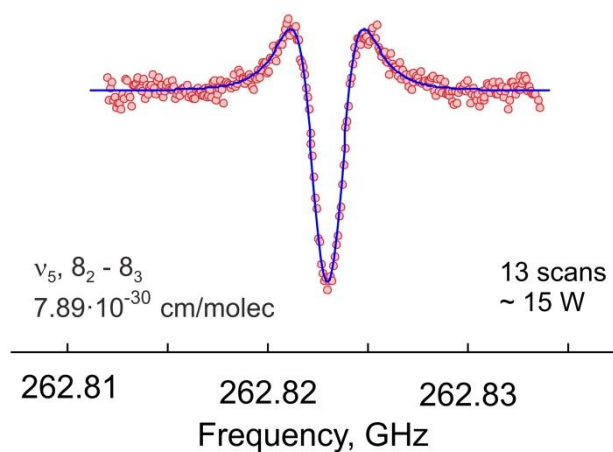
109 A single pass cell of 10 cm length and 2 cm diameter connected with a microphone was used.  
110 The cell was equipped with the conical HDPE windows of 2 mm thickness. All spectra were recorded  
111 at room temperature  $297 \pm 1$  K. For the line frequency measurements, the pressure of CH<sub>3</sub>D 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 <sup>12</sup>CH<sub>3</sub>D 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 CH<sub>3</sub>D 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 CH<sub>3</sub>D 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 CH<sub>3</sub>D 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 CH<sub>3</sub>D 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 CH<sub>3</sub>D 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.

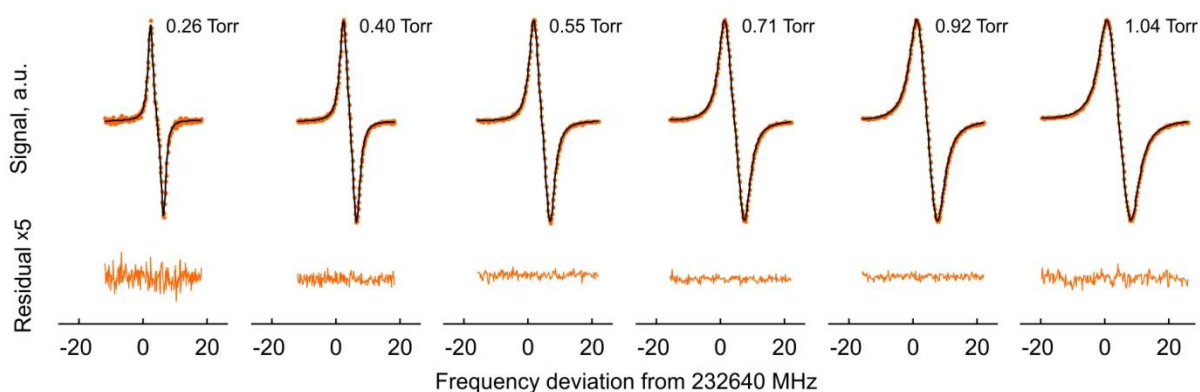
141 Self-broadening and shifting parameters determined by both fitting procedures are  
142 3.285(30) MHz/Torr and 0.085(25) MHz/Torr, respectively. Errors are threefold uncertainties  
143 obtained from the spectra fitting which seems to be reasonable estimate taking into account possible  
144 sources 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 CH<sub>3</sub>D was performed by Bray  
148 et al [Bray2016] for the <sup>Q</sup>R(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<sup>-1</sup>/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 CH<sub>3</sub>D as opposed to the lines of the excited vibrational states, e.g., for  $\nu_5$  [M\_Devi2002\_v5],  $\nu_6$   
156 [M\_Devi2002\_v6],  $\nu_3$  [M\_Devi2002\_v3],  $\nu_2$  [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<sup>-1</sup>/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

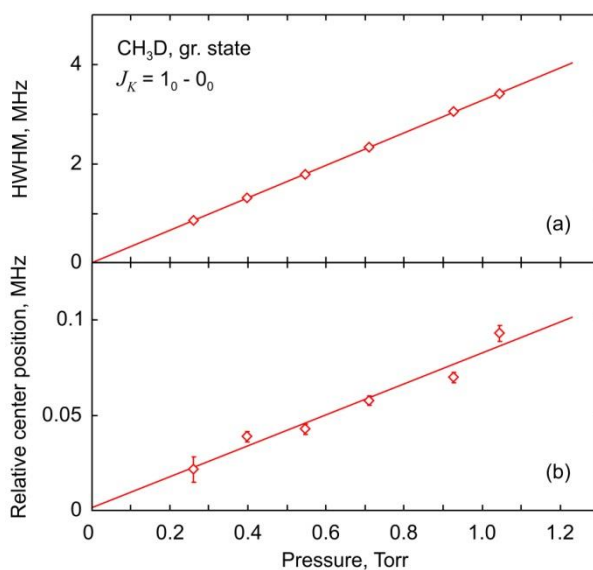
162 not taken into account in all previous experimental studies [Pickett1980, Womac1996, Lattanzi2008,  
 163 Drouin2009, Bray2016], the problem of corresponding systematic error seems to be common. As an  
 164 estimate, operating pressures were 0.05 Torr in [Womac1996], 0.28 Torr in [Lattanzi2008]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

170



**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.

171



**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.

172

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

174

175 As can be seen from Table 1, three measured frequencies of the ground state transitions of  
 176 Womack et al [Womack1996] and Pickett et al [Pickett1980] agree with our results within the  
 177 combined experimental uncertainties. However, the present values are more accurate. Weak lines of  
 178 a series of the  $Q$ -branch pure rotational transitions with  $J$  ranging from 1 to 11 and  $\Delta K = +1$  belonging  
 179 to the collisionally excited first vibrational state  $\nu_6$  ( $1161\text{ cm}^{-1}$ ) were also recorded. In the second  
 180 vibrational state  $\nu_3$  ( $1306\text{ cm}^{-1}$ ) of  $A_1$  symmetry, three weak rotational transitions of the  $R$  branch  
 181 were observed as well as one  $Q$ -branch rotational line within the third excited state  $\nu_5$  ( $1472\text{ cm}^{-1}$ ) of  
 182  $E$  symmetry.

183 To determine the parameters of the ground state, THz transitions from Table 1 were included  
 184 into the fit together with those measured previously by [Pickett1980], [Womack1996] [Lattanzi2008],  
 185 [Drouin2009], [Bray2016] and collected in Table 1 of [Bray2016]. The pure rotational transitions in  
 186 first three excited states were also fitted by our effective polyad model constructed for the ground  
 187 state and Triad interacting bands. The effective Hamiltonian was expressed in terms of irreducible  
 188 tensor operators adapted to symmetric top  $C_{3v}$  molecules. This approach implemented in MIRS  
 189 package [Nikitin2003, Nikitin2012] was previously applied for  $\text{CH}_3\text{D}$  [Nikitin1997] [Nikitin2000]  
 190 [Nikitin2002] [Nikitin2013CH3D],  $\text{PH}_3$  [Nikitin2017PH3], and recently for  $\text{NF}_3$  [Rodina2019]  
 191 [Egorov2019]. The initial values of the effective Hamiltonian parameters were obtained by the  
 192 contact transformation method [Tyuterev1980, Tyuterev2013] from the molecular potential energy  
 193 surface [Nikitin2011] similarly to the procedure previously applied for  $\text{CH}_4$  spectra analyses. The line  
 194 intensities predicted [Rey2014, Rey2016] from the *ab initio* dipole moment surfaces  
 195 [Nikitin2013CH4, Nikitin2017CH4] using variational method [Rey2013] were employed for the line  
 196 searching and transition assignments.

197

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

Wavenumber in MHz	$\Delta^c$	Intensity in $10^{-28}\text{ cm/molec}$	Number of averages	SNR <sup>e</sup>	Assignment <sup>d</sup>		
					$\nu' - \nu''$	$J' K' \Gamma'$	$-J'' K'' \Gamma''$
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 E – 9 0 E
219282.532(48)	-14	2.978	40	13	1 – 1	7 1 E – 7 0 E
225694.315(52)	72	4.035	30	16	1 – 1	5 1 E – 5 0 E
226757.394(42)	120	2.725	50	22	2 – 2	1 0 A – 0 0 A
227493.903(57)	33	4.133	36	15	1 – 1	4 1 E – 4 0 E
228590.864(46)	-67	3.823	50	17	1 – 1	3 1 E – 3 0 E
229493.023(67)	29	2.018	100	14	1 – 1	1 1 E – 1 0 E
232644.260(10) <sup>f</sup>	-33	75.19	16	400	0 – 0	1 0 A – 0 0 A
232644.301(75) <sup>a</sup>	8					
232644.327(18) <sup>b</sup>	34					
262822.959(20)	-1	0.0789	13	35	3 – 3	8 2 E – 8 3 E
453506.92(11)	-65	15.36	216	16	2 – 2	2 1 E – 1 1 E
453547.12(10)	-94	20.51	216	19	2 – 2	2 0 A – 1 0 A
465235.540(75) <sup>a</sup>	-30	429.0	60	70	0 – 0	2 1 E – 1 1 E
465235.553(13)	-17					
465250.691(75) <sup>a</sup>	-25	560.0	60	95	0 – 0	2 0 A – 1 0 A
465250.725(10)	9					

200 <sup>a</sup> results of Womack et al [[Womac1996](#)].

201 <sup>b</sup> result of Picket et al [[Pickett1980](#)].

202 <sup>c</sup> difference between the observed and calculated wavenumbers in kHz.

203 <sup>d</sup>  $\nu = 0, 1, 2$  and  $3$  corresponds to  $000000(A_1)$ ,  $000001(E)$ ,  $001000(A_1)$ , and  $000010(E)$  vibrational states;  $A$   
204 means no information on  $A_1$ – $A_2$  splitting.

205 <sup>e</sup> SNR was determined as a ratio of peak-to-peak signal amplitude to the noise standard deviation.

206 <sup>f</sup> Pressure shifting is taken into account.

207

208 **Table 2.** Ground State Effective Hamiltonian parameters of CH<sub>3</sub>D (in MHz)

No	Parameter, Tensorial Nomenclature*	Value
1	$R2(0, 0A_1)$	130021.9620(38)
2	$R2(2, 0A_1)$	8387.2084(23)
3	$R4(0, 0A_1)$	-2.368268(44)
4	$R4(2, 0A_1)$	$1.55723(16)\times 10^{-1}$
5	$R4(4, 0A_1)$	$7.06776(61)\times 10^{-2}$
6	$R4(4, 3A_1)$	$-2.35(28)\times 10^{-2}$
7	$R6(0, 0A_1)$	$1.1961(19)\times 10^{-4}$
8	$R6(2, 0A_1)$	$6.298(32)\times 10^{-6}$
9	$R6(4, 0A_1)$	$3.168(18)\times 10^{-6}$
10	$R6(6, 0A_1)$	$-1.445(49)\times 10^{-7}$
11	$R8(0, 0A_1)$	$-1.009(40)\times 10^{-8}$
12	$R8(2, 0A_1)$	$4.41(25)\times 10^{-10}$
13	$R8(6, 6A_1)$	$-2.08(21)\times 10^{-10}$

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 CH<sub>3</sub>D  
 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 CH<sub>3</sub>D

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)
$\nu_6$	7 / 1575 / 290	TH / [Nikitin2002] / [Ulenikov2000]	20	14.69(0.49)
$\nu_3$	3 / 641 / 121	TH / [Nikitin2002] / [Ulenikov2000]	18	16.19(0.54)
$\nu_5$	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  $\nu_6$ ,  $\nu_3$ , and  $\nu_5$  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) <sup>a</sup>	-17	108	2 1 E – 1 1 E

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

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

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

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

239

240 The determined ground state parameters reproduce in most cases (in 61 out of 77) the  
 241 experimental THz transitions within their experimental uncertainty. Examples can be seen in Table 1  
 242 and Table 4 (a total list of the deviations is given in **supplementary material I; supplementary**  
 243 **material II** contains rotational energy levels up to  $J = 20$ ). The calculated rotational transitions within  
 244 three excited states  $\nu_6$ ,  $\nu_3$ , and  $\nu_5$  fall into experimental uncertainty in half of the cases. However the  
 245 number of the transitions is not so much to make the conclusion on the quality of the corresponding  
 246 parameters, taking into account the possible resonance interactions at higher  $J$  values.

247

#### 248 4. Conclusion

249

250 New high sensitive measurements of pure rotational transitions of CH<sub>3</sub>D by radio-acoustic  
 251 method are presented. Pressure broadening and shifting of the  $1_0$ - $0_0$  ground state rotational line were  
 252 accurately measured and allowed estimating the possible systematic errors in some previous studies.  
 253 Among the 14 measured transitions, 3 correspond to the ground vibrational state. Other 11 lines were  
 254 assigned to rotational transitions within first three excited vibrational states:  $\nu_6=1$ ,  $\nu_3=1$  and  $\nu_5=1$ .  
 255 Experimental frequencies of the ground state transitions agree with the previous experimental data  
 256 but the present results are more accurate. These transitions together with those published previously  
 257 were described in most cases within their experimental uncertainties using our effective Hamiltonian  
 258 expressed in irreducible tensor operators. For determining the rotational parameters of the  
 259 Hamiltonian, more than 11800 ground state combination differences were also calculated and  
 260 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 CH<sub>3</sub>D 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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