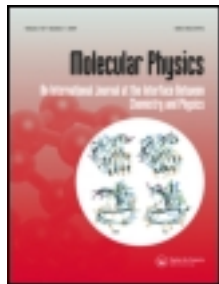


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## Molecular Physics: An International Journal at the Interface Between Chemistry and Physics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/tmph20>

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O. N. Ulenikov <sup>a</sup>, E. S. Bekhtereva <sup>a</sup>, M. R. Konova <sup>a</sup>, Yu V. Krivchikova <sup>a</sup> & V. -M. Horneman <sup>b</sup>

<sup>a</sup> Laboratory of Molecular Spectroscopy, Physics Department, National Research Tomsk State University, Tomsk, 634050, Russia

<sup>b</sup> Department of Physics, University of Oulu, P. O. Box 3000, FIN-90014 University of Oulu, Finland

Accepted author version posted online: 23 Apr 2013. Published online: 29 May 2013.

To cite this article: O. N. Ulenikov, E. S. Bekhtereva, M. R. Konova, Yu V. Krivchikova & V. -M. Horneman (2013): On the improvement of the rotational structure analysis of  $^{13}\text{CH}_3\text{D}$  ground vibrational state, *Molecular Physics: An International Journal at the Interface Between Chemistry and Physics*, DOI:10.1080/00268976.2013.798437

To link to this article: <http://dx.doi.org/10.1080/00268976.2013.798437>

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## On the improvement of the rotational structure analysis of $^{13}\text{CH}_3\text{D}$ ground vibrational state

O.N. Ulenikov<sup>a,\*</sup>, E.S. Bekhtereva<sup>a</sup>, M.R. Konova<sup>a</sup>, Yu.V. Krivchikova<sup>a</sup> and V.-M. Horneman<sup>b</sup>

<sup>a</sup>Laboratory of Molecular Spectroscopy, Physics Department, National Research Tomsk State University, Tomsk 634050, Russia;

<sup>b</sup>Department of Physics, University of Oulu, P. O. Box 3000, FIN-90014 University of Oulu, Finland

(Received 26 February 2013; final version received 3 April 2013)

The main goal of the present study was to improve the already published rotational structure analysis of the ground vibrational state of the  $^{13}\text{CH}_3\text{D}$  molecule. To realise that, we recorded high-resolution spectra of a set of the strongly interacting vibrational bands,  $2\nu_3(A_1)$ ,  $2\nu_6(A_1)$ ,  $2\nu_6(E)$ ,  $\nu_2(A_1)$ ,  $\nu_5 + \nu_6(A_1)$ ,  $\nu_5 + \nu_6(A_2)$ ,  $\nu_5 + \nu_6(E)$  and  $\nu_3 + \nu_6(E)$ . From the analysis of the experimental data, more than 1900 ground state combination differences (GSCD) were determined with  $J^{\max} = 18$ ,  $\Delta J^{\max} = 2$  and  $K^{\max} = 15$ . The  $a_1/a_2$  splittings of the states with quantum number  $K = 3$  were taken into account. The presence of numerous forbidden transitions allowed us to determine with high accuracy GSCD not only with  $\Delta K = 0$ , but with  $\Delta K = \pm 1$ ,  $\pm 2$  and  $\pm 3$ , as well. Spectroscopic parameters of the ground vibrational state were determined from the joint fit of the obtained GSCD (they are reproduced with  $d_{\text{rms}} = 0.00014 \text{ cm}^{-1}$ ). The 21 highly accurate THz-region transitions which were also used as input data, are reproduced with  $d_{\text{rms}} = 47 \text{ kHz}$ .

**Keywords:** monodeuterated methane; ground state rotational structure; spectroscopic parameters

### 1. Introduction

The study of high-resolution spectra of monodeuteromethane is of interest for a number of reasons. It is obviously the most abundant deuterio isotopomer in natural environments allowing for its detection in the Earth's atmosphere and also in other astrophysical systems. In particular, monodeuteromethane has been detected spectroscopically in the atmospheres of Jupiter [1,2], Saturn [3,4], Titan [5–8], Uranus [9,10] and Neptune [11]. Any highly accurate spectroscopic information about spectra of monodeuteromethane has also a fundamental importance in the context of accurate multidimensional calculations of vibrational dynamics [12–16], and, as a consequence, in our understanding of the structure of potential hypersurfaces [17–20], unimolecular reaction rate theory [21] and fundamental bimolecular reaction dynamics [22–25]. All what is stated above can be repeated in relation to the  $^{13}\text{C}$  species of monodeuteromethane, e.g.  $^{13}\text{CH}_3\text{D}$  was detected in Titan's stratosphere from Cassini/CIRS infrared spectra [26].

There are some studies of the  $^{13}\text{CH}_3\text{D}$  high-resolution spectra in the literature [27–30]. In Ref. [27], GSCD obtained from assigned transitions of the  $\nu_2$  band were used for the determination of the ground state spectroscopic parameters. The values of the ground state parameters were improved in Ref. [28] on the basis of experimental ro-vibrational transitions of the  $\nu_3$ ,  $\nu_5$  and  $\nu_6$  bands. In this case, 'experimental' values of the  $a_1/a_2$  splittings in the

$K = 3$  states have been determined and analysed. Later the high-resolution spectra of  $^{13}\text{CH}_3\text{D}$  were considered in Refs. [29] and [30]. Three THz transitions were recorded in Ref. [29]. In Ref. [30], 21 THz transitions were recorded and some of the ground state spectroscopic parameters were improved. Unfortunately, only transitions between states with the same value of the quantum number  $K$  were recorded and assigned in all the above mentioned studies of the  $^{13}\text{CH}_3\text{D}$  high-resolution spectra. On that reason, the values of the parameters  $A_K^{gr}$ ,  $D_K^{gr}$ , etc., presented in any of the above studies, can be improved by taking into account transitions with  $\Delta K$  not equal to zero.

As our analysis of a set of the bands,  $2\nu_3(A_1)$ ,  $2\nu_6(A_1)$ ,  $2\nu_6(E)$ ,  $\nu_2(A_1)$ ,  $\nu_5 + \nu_6(A_1)$ ,  $\nu_5 + \nu_6(A_2)$ ,  $\nu_5 + \nu_6(E)$  and  $\nu_3 + \nu_6(E)$  has shown, the presence of strong resonance interactions between all the bands leads to the appearance of numerous 'forbidden' transitions. It allows to construct GSCD with values of  $\Delta K$  different from zero. As a consequence, one can expect that the values of the ground state parameters can be suitably improved. The present paper is devoted to a re-analysis of the rotational structure of the ground vibrational state of  $^{13}\text{CH}_3\text{D}$  on the basis of all experimental data known at the moment. Section 2 presents experimental conditions of our FTIR experiment. In Section 3, we briefly discuss general aspects and details of the rotational Hamiltonian of the  $^{13}\text{CH}_3\text{D}$  molecule. Analysis, results of the fit and a discussion are presented in Section 4.

\*Corresponding author. Email: ulenikov@phys.tsu.ru

## 2. Experimental details

The region from 2200 to 2800  $\text{cm}^{-1}$  was covered with three separate measurements. Radiation power to the indium antimony (InSb) detector was limited in these registrations with different optical filters: with a band pass from 1800 to 2400  $\text{cm}^{-1}$ , from 2300 to 2800  $\text{cm}^{-1}$  and from 2600 to 3300  $\text{cm}^{-1}$ . A glowbar was the radiation source and a germanium film between two potassium bromide (KBr) plates was used as a beamsplitter in a Bruker IFS-120 HR Fourier transform spectrometer on which the measurements were performed in the infrared laboratory at the University of Oulu. In every measurement the  $^{13}\text{CH}_3\text{D}$  sample, made by Prof. Suhei Ono of the Massachusetts Institute of Technology, was filled into a white type absorption cell optimised for the used spectrometer [31]. The cell was provided with two KBr windows. In the lowest region the sample pressure was 15.9 Pa and the absorption path length (APL) was 3.2 m. In the middle and highest regions the pressure was the same, but APL was longer, 41.6 m. The instrumental resolution was optimised according to the Doppler broadening: the resolution due to maximum optical path difference being 0.0033 or 0.0042  $\text{cm}^{-1}$  in the lowest and highest wavenumber region, respectively. The registration times were 16.6, 19.0 and 21.3 hours giving a signal to noise ratio (S/N) of about 3000 in the spectrum of the lowest and highest region. In the middle region, the transmission of the optical filter was reduced and that is why the S/N-ratio was lower, however better than 1300. The S/N value here are for peaks with 100% absorption and peak to peak amplitude noise. The calibration of the spectra in the lowest and middle regions were based on carbonyl sulphide (OCS) peaks [32], in the region from 2000 to 2100  $\text{cm}^{-1}$ . The lowest spectrum was first calibrated with OCS peaks and then the calibration was transferred to good carbon dioxide ( $\text{CO}_2$ ) and sample peaks in the overlapping region of the spectra. The middle spectrum was then calibrated with these peaks. The spectrum in the highest region was calibrated with good OCS peaks [32], in the region from 2850 to 3100  $\text{cm}^{-1}$ . Peak positions were calculated with an optimised centre of gravity method discussed in Ref. [33]. This method gives the position accuracy for well-separated peaks with 50 % absorption better than  $3 \times 10^{-6} \text{ cm}^{-1}$  in the whole region, if one takes into account the reached S/N-ratio and peak widths.

## 3. General properties and Hamiltonian of the ground vibrational state of $^{13}\text{CH}_3\text{D}$

The  $^{13}\text{CH}_3\text{D}$  molecule is a symmetric top of  $\text{C}_{3v}$  symmetry. Therefore its nine vibrational modes possess the following symmetry:  $q_\lambda \in A_1$  for  $\lambda = 1, 2, 3$  and  $q_\mu(q_{\mu_1}, q_{\mu_2}) \in E(E_1, E_2)$  for  $\mu = 4, 5, 6$ . As a consequence, two types of bands are allowed in absorption: parallel (or  $A_1$ ) type bands that correspond to the vibrational transitions  $(v_{A_1}) \leftarrow (v_{gr.})$

and perpendicular (or  $E$ ) type bands that correspond to the vibrational transitions  $(v_E) \leftarrow (v_{gr.})$ . In this case, the selection rules for ‘allowed’ transitions in the parallel bands are

$$\Delta J = 0, \pm 1; \Delta K = 0,$$

with the additional restriction that  $\Delta J \neq 0$ , if  $K = 0$ . Here the small letters  $a_1, a_2$ , and  $e$  describe the symmetries of the vibration–rotation states. The selection rules for the ‘allowed’ transitions in the perpendicular bands are

$$\Delta J = 0, \pm 1; \Delta K = \pm 1.$$

Besides ‘allowed’ transitions, weak ‘forbidden’ ones are allowed both in the parallel and perpendicular bands. In this case, the selection rules have the following form in both type of bands:

$$\Delta J = 0, \pm 1; e \rightarrow e, a_1 \leftrightarrow a_2.$$

It is known (see, e.g. Ref. [34]) that the Hamiltonian of  $\text{XYZ}_3$  type molecules for the ground vibrational state can be written in the following form:

$$\begin{aligned} H = & E + B(J_x^2 + J_y^2) + AJ_z^2 - D_J J^4 - D_{JK} J^2 J_z^2 \\ & - D_K J_z^4 + H_J J^6 + H_{JK} J^4 J_z^2 + H_{KJ} J^2 J_z^4 + H_K J_z^6 \\ & + L_J J^8 + \dots + \left\{ \left[ \left( \frac{1}{2} \epsilon + \frac{1}{2} \epsilon_J J^2 + \epsilon_K J_z^2 + \dots \right), \right. \right. \\ & (J_+^3 - J_-^3) \Big]_+ + [(\epsilon' J_z + \epsilon'_J J_z J^2 + \epsilon'_K J_z^3 + \dots), \\ & \left. \left. (J_+^3 + J_-^3) \right]_+ + h(J_+^6 + J_-^6) + \dots \right\}. \end{aligned} \quad (1)$$

Here the expression  $[\dots, \dots]_+$  denotes an anticommutator. The  $B, A, D_J, D_{JK}, D_K, H_J, H_{JK}, H_{KJ}, H_K, L_J, \dots$  are the rotational and centrifugal distortion parameters. Operators  $(J_+^3 + J_-^3)$  connect rotational states  $|JK\rangle$  and  $|JK'\rangle$  with different values of the quantum numbers  $K$ , namely  $\Delta K = K - K' = \pm 3$ . They account, in particular, for the  $a_1/a_2$  splitting of  $K=3$  levels. Parameters  $\epsilon_J/\epsilon'_J$  and  $\epsilon_K/\epsilon'_K$  describe the  $J$  and  $K$  dependency of the main  $\epsilon/\epsilon'$  parameter. Operators  $(J_+^6 + J_-^6)$ , on the one hand, connect rotational states with  $\Delta K = K - K' = \pm 6$  and, on the other hand, contribute to the  $a_1/a_2$  splitting of the  $K=3$  levels. As was discussed in Refs. [35] and [36] for a symmetric top molecule, which is not very close to a spherical top, parameters  $\epsilon'$  and  $h$  are strongly correlated and cannot be determined separately from a fit of experimental data. On that reason the parameter  $\epsilon'$  was estimated numerically in our case in accordance with the formula [37]

$$\epsilon' = \sum_{\lambda} \frac{1}{\omega_{\lambda}^2} (B_x^e)^3 B_z^e a_{\lambda_1}^{xx} a_{\lambda_1}^{xz} \left( \frac{4\pi c}{\hbar} \right), \quad (2)$$

where

$$a_{\lambda_1}^{\alpha\alpha} = 2 \sum_N m_N^{1/2} (l_{N\beta\lambda_1} r_{N\beta}^e + l_{N\gamma\lambda_1} r_{N\gamma}^e), \quad (3)$$

$$a_{\lambda_1}^{\alpha\beta} = -2 \sum_N m_N^{1/2} l_{N\alpha\lambda_1} r_{N\beta}^e, \quad \alpha \neq \beta, \quad (4)$$

and  $l_{N\beta\lambda_1}$  are the transformation coefficients known in the rotational-vibrational theory (see e.g. Refs. [38,39]). From formula (2), the value of  $\epsilon'$  can be estimated as  $0.32 \times 10^{-5} \text{ cm}^{-1}$ .

#### 4. Ground state combination differences and determination of the ground state spectroscopic parameters

In the analysis of the high-resolution FTIR spectra of the set of strongly interacting bands,  $2\nu_3(A_1)$ ,  $2\nu_6(A_1)$ ,  $2\nu_6(E)$ ,  $\nu_2(A_1)$ ,  $\nu_5 + \nu_6(A_1)$ ,  $\nu_5 + \nu_6(A_2)$ ,  $\nu_5 + \nu_6(E)$  and  $\nu_3 + \nu_6(E)$ , we assigned without doubt a large number of ‘forbidden’ transitions in all three ( $P$ ,  $Q$  and  $R$ ) branches allowed in absorption. That gave us the possibility to construct more than 200 GSCD with the difference  $\Delta K$  not only equal to zero, but also  $\Delta K = \pm 1$ ,  $\pm 2$  and  $\pm 3$ . In this case, it was found that the obtained ‘experimental’ GSCD considerably differ from the corresponding ones calculated with any set of the ground state spectroscopic parameters from the literature [27–30]. This will be clear if one remembers that any set of parameters have been obtained from the fit of experimental data with the  $\Delta K = 0$  GSCD only. As an illustration, Figure 1 presents three plots of the dependency of the differences  $\Delta_{J'K'\gamma}^{JK\gamma} = {}^{(\text{exp})}\delta_{J'K'\gamma}^{JK\gamma} - {}^{(\text{calc})}\delta_{J'K'\gamma}^{JK\gamma}$  (here  $\delta_{J'K'\gamma}^{JK\gamma} = E_{JK\gamma} - E_{J'K'\gamma}$ ;  $\gamma$  is the symmetry of ro-vibrational state) between experimental and calculated (with the parameters from Ref. [28]) values of ground state combination differences on the value of the quantum number  $J$ . The curves Ia, IIa and IIIa correspond to the values  $J' = J - 2$  and  $K' = K - 3 = 1$  (curve Ia),  $J' = J - 1$  and  $K' = K + 3 = 3$  (curve IIa) and  $J' = J$  and  $K' = K - 1 = 1$  (curve IIIa), respectively. As one can see from Figure 1, the differences,  $\Delta_{J'K'\gamma}^{JK\gamma}$  can achieve the value of  $65 \times 10^{-4} \text{ cm}^{-1}$ . At the same time, the accuracy of our experiment in the region of 2200–2800  $\text{cm}^{-1}$  is about 60 times better. This means that the rotational structure of the ground vibrational state of  $^{13}\text{CH}_3\text{D}$  can be improved.

In our present analysis we used three sets of experimental data:

- (1) The 21 high accurate THz transitions from Ref. [30]. They are reproduced in column 2 of Table 1; values in parentheses are the experimental uncertainties.

Table 1. High accurate THz-region transitions of the  $^{13}\text{CH}_3\text{D}$  molecule.

Transition	Wavenumber <sup>a</sup> (MHz)	$\Delta^b$ (kHz)	$\Delta^c$ (kHz)
1	2	3	4
2 1 e ← 1 1 e	464838.762(050)	0	0
2 0 a <sub>1</sub> ← 1 0 a <sub>2</sub>	464854.085(050)	30	34
3 2 e ← 2 2 e	697095.120(050)	−8	−20
3 1 e ← 2 1 e	697163.887(050)	−7	−5
3 0 a <sub>2</sub> ← 2 0 a <sub>1</sub>	697186.811(050)	−1	7
4 3 a ← 3 3 a	929131.760(100)	−13	−50
4 2 e ← 3 2 e	929284.510(100)	58	51
4 1 e ← 3 1 e	929375.957(100)	−60	−54
4 0 a <sub>1</sub> ← 3 0 a <sub>2</sub>	929406.620(100)	87	99
5 4 e ← 4 4 e	1160865.964(100)	31	−19
5 3 a <sub>2</sub> ← 4 3 a <sub>1</sub>	1161132.774(100)	−41	−72
5 2 e ← 4 2 e	1161323.261(100)	−82	−83
5 1 e ← 4 1 e	1161437.684(100)	79	88
5 0 a <sub>2</sub> ← 4 0 a <sub>1</sub>	1161475.722(100)	38	50
7 6 a ← 6 6 a	1623098.742(100)	−27	−8
7 5 e ← 6 5 e	1623684.410(100)	22	50
7 4 e ← 6 4 e	1624163.088(100)	65	85
7 3 a <sub>2</sub> ← 6 3 a <sub>1</sub>	1624534.942(100)	34 <sup>d</sup>	30
7 3 a <sub>1</sub> ← 6 3 a <sub>2</sub>	1624534.942(100)	−101 <sup>d</sup>	30
7 2 e ← 6 2 e	1624800.411(100)	−74	−90
7 1 e ← 6 1 e	1624959.715(100)	−7	−37
7 0 a <sub>2</sub> ← 6 0 a <sub>1</sub>	1625012.817(100)	26	−8

<sup>a</sup>Experimental values reproduced from Ref. [30].

<sup>b</sup>Differences between values of experimental transitions and corresponding values calculated with the obtained set of spectroscopic parameters from column 2 of Table 2.

<sup>c</sup>Values of differences reproduced from Ref. [30].

<sup>d</sup>Doublet should be here in accordance with the theory. The lines were not experimentally resolved in Ref. [30].

- (2) More than 1900 GSCD obtained from high-resolution infrared FTIR spectra [28,40]: the 850 ‘allowed’ ( $\Delta K = 0$ ) GSCD obtained from the bands  $\nu_3$ ,  $\nu_5$  and  $\nu_6$  [28]; more than 850 ‘allowed’ and more than 200 ‘forbidden’ ( $\Delta K \neq 0$ ) GSCD obtained from the bands  $2\nu_3(A_1)$ ,  $2\nu_6(A_1)$ ,  $2\nu_6(E)$ ,  $\nu_2(A_1)$ ,  $\nu_5 + \nu_6(A_1)$ ,  $\nu_5 + \nu_6(A_2)$ ,  $\nu_5 + \nu_6(E)$  and  $\nu_3 + \nu_6(E)$  (the list of transitions assigned in the recorded bands is presented as the Supplementary Materials to this paper). In the last case, the ground state combination differences,  ${}^{(\text{exp})}\delta_{J+\Delta JK+\Delta K\gamma}^{JK\gamma}$ , with the values  $J^{\text{max}} = 11$ ,  $K^{\text{max}} = 5$ ,  $\Delta J = 0, \pm 1, \pm 2$  and  $\Delta K = \pm 1, \pm 2, \pm 3$  were used as input data.
- (3) The 10 ground state supercombination differences (see Ref. [41]) of the  $^{12}\text{CH}_3\text{D}$  species from Ref. [36]. In this case we took into account that, as the analysis showed, there is practically no difference between the values of supercombination differences of the  $^{13}\text{CH}_3\text{D}$  and  $^{12}\text{CH}_3\text{D}$  species.

The Hamiltonian, Equation (1), was used in the fit procedure. We took into account that the  $^{12}\text{CH}_3\text{D}$  and  $^{13}\text{CH}_3\text{D}$

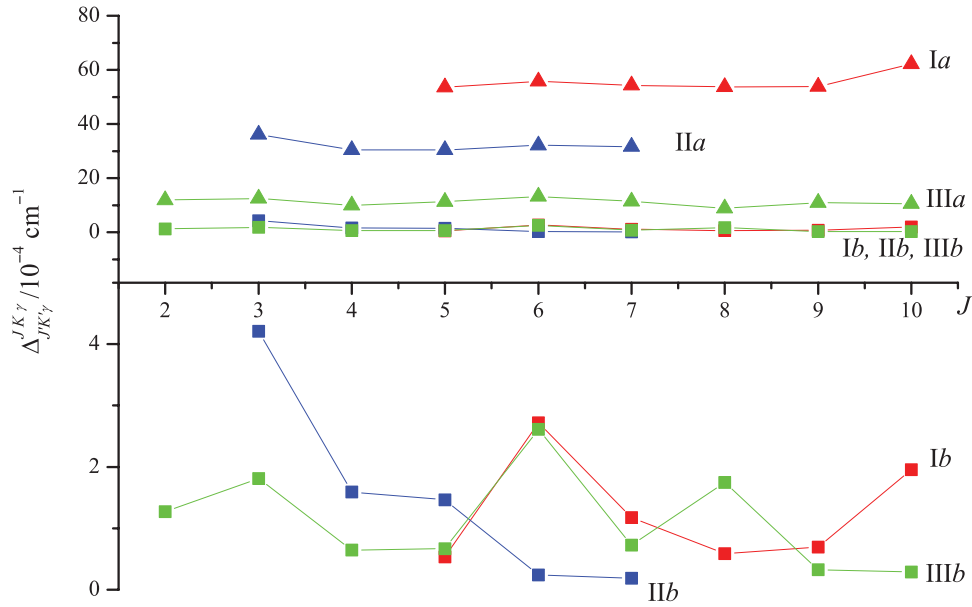


Figure 1. Plots of the dependency of the differences  $\Delta_{JK'\gamma}^{JK\gamma} = {}^{(\text{exp})}\delta_{J'K'\gamma}^{JK\gamma} - {}^{(\text{calc})}\delta_{J'K'\gamma}^{JK\gamma}$  (here  $\delta_{J'K'\gamma}^{JK\gamma} = E_{JK\gamma} - E_{J'K'\gamma}$ ) between experimental and calculated values of the ground state combination differences on quantum number  $J$ . The curves Ia, IIa and IIIa correspond to the values  $J' = J - 2$  and  $K' = K - 3 = 1$  (curve Ia),  $J' = J - 1$  and  $K' = K + 3 = 3$  (curve IIa) and  $J' = J$  and  $K'_a = K - 1 = 1$  (curve IIIa), respectively. Curves Ib, IIb and IIIb correspond to results obtained on the basis of our ground state parameters from column 2 of Table 2. For a better visibility, the same curves, Ib, IIb and IIIb, are reproduced in the bottom part of Figure 1.

Table 2. Ground state spectroscopic parameters (in  $\text{cm}^{-1}$ ) of  $^{13}\text{CH}_3\text{D}^a$ .

Parameter	This work	Ref. [28]
$B_0$	3.8768849720(856)	3.876884527
$A_0$	5.25117526(260)	5.25082109
$D_0^J \times 10^4$	0.5243717(244)	0.5243010
$D_0^{JK} \times 10^4$	1.276162(105)	1.276156
$D_0^K \times 10^4$	-0.7896593	-0.7896593
$H_0^J \times 10^8$	0.14543(233)	0.143479
$H_0^{JK} \times 10^8$	1.2045(141)	1.214490
$H_0^{KJ} \times 10^8$	-0.6613(296)	-0.67214
$H_0^K \times 10^8$	-0.16436	-0.16436
$L_0^{JK} \times 10^{12}$	-1.1836	-1.1836
$L_0^{KJ} \times 10^{12}$	1.490	1.490
$e' \times 10^5$	0.32	0.32
$h_3 \times 10^{10}$	0.32463(380)	0.32503

<sup>a</sup>Values in parentheses are one standard deviation given in units of the last digit. Values that are presented without standard deviation have been fixed to the values from Ref. [28].

species are very similar and, in a first approximation, the values of higher order spectroscopic parameters of the  $^{12}\text{CH}_3\text{D}$  species can be taken as the values of the corresponding parameters of the  $^{13}\text{CH}_3\text{D}$  species. The result of the final fit is presented in column 2 of Table 2. Values in parentheses are  $1\sigma$  statistical confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to the values of corresponding parameters of the

ground vibrational state of the  $^{12}\text{CH}_3\text{D}$  molecule from Ref. [36]. Column 3 of Table 2 shows, for comparison, values of the  $^{13}\text{CH}_3\text{D}$  ground state parameters from an earlier paper [28]. One can see the good agreement between the values of the parameters in both columns. At the same time, our new result gives the possibility to describe the known experimental data more correctly. As an illustration, in Figure 1 the new results of the present work (curves Ib, IIb and IIIb) are compared with the results of the previous work [28] (curves Ia, IIa and IIIa). One can see, the differences between experimental and calculated values of the GSCD become considerably better compared to earlier results. It should be mentioned also that the root mean square deviation of the initial infrared GSCD is  $d_{\text{rms}} = 0.00014 \text{ cm}^{-1}$ . Columns 3 and 4 of Table 1 present, for illustration, the differences between experimental and calculated values of THz-transitions (in kHz). Values of  $\Delta$  in column 4 are reproduced from Ref. [30]. Values of  $\Delta$  presented in column 3 were determined with the parameters obtained in the present paper (see column 2 of Table 2). One can see the good correlation between experimental and calculated values, with the exception of the transition  $(7\ 3\ a_1/a_2 \leftarrow 6\ 3\ a_2/a_1)$ . We believe that the reason is in fact that, in accordance with the supercombination differences model (see, Refs. [28,41]), the two lines corresponding of the transitions  $(7\ 3\ a_1 \leftarrow 6\ 3\ a_2)$  and  $(7\ 3\ a_2 \leftarrow 6\ 3\ a_1)$  should be resolved as a consequence of the value of the line splitting of 150 kHz. In the experiment of Ref. [30], the lines were

not resolved (as an confirmation, we take the presence of only one transition ( $7\ 3\ a \leftarrow 6\ 3\ a$ ) in the list of experimental lines in Ref. [30]). We should also mention that the other 20 high accurate THz-region transitions from Ref. [30] are reproduced with a  $d_{\text{rms}} = 47$  kHz. All the reasons given above can be considered as a confirmation of the fact that the obtained set of spectroscopic parameters improves the rotational structure of the ground vibrational state of the  $^{13}\text{CH}_3\text{D}$  molecule.

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