A_1 - A_2 Splitting of CH_3D

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Sub-Doppler resolution spectroscopy of CH_3D has been carried out from 88.6 to 93.1 THz. Thirty transitions of the ν_1 and ν_4 bands from the low- J and $K = 3$ levels are observed, and the A_1 - A_2 splitting is resolved for twenty-three of the thirty transitions. The absolute frequencies are determined with a typical uncertainty of 4 kHz. The effective A_1 - A_2 splitting constant of the $K = 3$ levels is $2h_{3,\nu=0} = (1.5641 \pm 0.0026)$ Hz for the ground vibrational state, and those of the $K = 3$ levels for the $\nu_1 = 1$ state and of the ($K = 2, l = -1$) and ($K = 4, l = +1$) levels for the $\nu_4 = 1$ state are also determined.

Keywords: Isotope methane, A_1 - A_2 splitting, Mid-infrared, Sub-Doppler resolution, Optical frequency comb, Difference frequency generation

1. INTRODUCTION

A singly deuterium-substituted methane, CH_3D , belongs to the point group of C_{3v} , which gives rise to the A_1 - A_2 splitting of the otherwise degenerate levels of the same angular momentum quantum number K , where $K = 3n$ ($n = 1, 2, 3, \dots$) in the ground vibrational state. However, no radio-frequency spectroscopy between the A_1 and A_2 sublevels has been reported, as far as we know, because of the small permanent dipole moment of 5.6 mDebye [1]. Sub-millimeter-wave spectroscopy of pure rotational transitions was carried out for the $R(J \leq 6, K = 3)$ transitions in a Doppler-limited resolution [2, 3], in which the A_1 - A_2 splitting

was not resolved either even though the magnitude of the A_1 - A_2 splitting increases as J . Therefore, the A_1 - A_2 splitting of CH_3D has been investigated only by infrared spectroscopy so far. Because the energy separations between the A_1 and A_2 sublevels of the excited vibrational states are usually larger than those of the ground vibrational state, they are resolved for the high- J levels even in a Doppler-limited resolution. Ulenikov and his coworkers carried out FTIR spectroscopy of the ν_3 , ν_5 , and ν_6 bands with a resolution of 0.003 cm^{-1} . They derived the energy separation between the A_1 and A_2 sublevels in the ground vibrational state from the *super-combination difference* [4], they referred as. However, those of the low- J levels have not been reported because of the low resolution. The C-H stretching vibrational modes of CH_3D have intense fundamental ν_1 and ν_4 bands in the $3.3\text{-}\mu\text{m}$ wavelength region. These bands were also recorded with FTIR in a Doppler-limited resolution [5, 6], which did not provide any information on the A_1 - A_2 splitting of the low- J levels.

In this paper, we have applied a comb-referenced difference-frequency-generation (DFG) spectrometer to sub-Doppler resolution spectroscopy of the A_1 - A_2 splitting on the ν_1 and ν_4 bands of CH_3D . The spectrometer was applied to sub-Doppler resolution spectroscopy of CH_4 [7, 8], CH_3I [9, 10], and HCl [11] with a spectral resolution of 250 kHz and a frequency uncertainty of about 5 kHz. Subsequently, the observed Lamb dip was narrowed below 80 kHz (HWHM) by employing a new enhanced-cavity absorption cell (ECAC) coupled with a wide beam [12] and a new optical frequency comb (OFC) with servo control of the carrier-envelope offset frequency. The improved resolution has enabled us to resolve the A_1 - A_2 splitting of twenty-three transitions from the low- J and $K = 3$ levels and to determine the absolute transition frequency. The A_1 - A_2 coupling constants are derived for the ground and excited vibrational states.

2. A_1 - A_2 INTERACTION

Molecules of the C_{3v} symmetry such as CH_3D are symmetric tops. The K -degeneracy is lifted for the vibration-rotation levels with $K - l = \pm 3n$ ($n = 1, 2, 3, \dots$) into those labeled as A_1 and A_2 irreducible representations. Here l is the vibration-induced angular momentum quantum number, which is zero for the ground vibrational state and the $\nu_1 = 1$ state and takes the values of ± 1 for the $\nu_4 = 1$ state.

Hamiltonians of the ground and vibrational excited states consist of various terms caused by the vibration and rotation energies and the vibration-rotation interactions. Molecular constants associated with these terms are determined from a global data set containing a large number of transition frequencies. In this work, however, we have observed only thirty ν_1 - and ν_4 -band transitions from the low- J and $K = 3$ levels. Therefore, we concentrate ourselves to determine the energy separation and the effective splitting constants between the A_1 and A_2 components in the ground vibrational state and the $\nu_1 = 1$ and the $\nu_4 = 1$ states.

The A_1 - A_2 splitting is induced by higher-order vibration rotational interactions, which are usually regarded as small perturbations. This is, however, remarkably prominent when the perturbation is the first-order for the effective Hamiltonian [13]. For example, the otherwise degenerate $K = 3$ levels in the ground vibrational state are separated by the vibration-rotation interaction connecting between the $\Delta k = \pm 6$ levels, where $k = \pm K$. However, the same levels are also connected by the $\Delta k = \pm 3$ -type interaction as the second-order perturbation. Hence, the coupling constants of the $\Delta k = \pm 6$ and ± 3 -type interactions are strongly correlated. They can be determined only when the global data are available for near-spherical-top molecules. In this work, therefore, we determine the effective A_1 - A_2 splitting constants as follows.

For $l = 0$ such as in the ground vibrational state and the $\nu_1 = 1$ state, the energy separation between the A_1 and A_2 sublevels for the $K = 3$ level is given by

$$\delta\nu_3^{(v)} = 2h_{3,v}J(J+1)[J(J+1)-2][J(J+1)-6] , \quad (1)$$

where v indicates the vibrational state, and $h_{3,v}$ is the effective splitting constant [14]. Here, the first subscript of h represents K . For $l = \pm 1$ in the $v_4 = 1$ state, the energy separation between the A_1 and A_2 sublevels for the $(K = 2, l = -1)$ level is given by

$$\delta\nu_2^{(v)} = 2h_{2,v}J(J+1)[J(J+1)-2] , \quad (2)$$

and that for the $(K = 4, l = +1)$ level is presented as

$$\delta\nu_4^{(v)} = 2h_{4,v}J(J+1)[J(J+1)-2][J(J+1)-6][J(J+1)-12] , \quad (3)$$

where $h_{2,v}$ and $h_{4,v}$ are the effective splitting constants.

3. EXPERIMENTAL DETAILS

Figure 1 presents a schematic diagram of the spectrometer, which is similar to that of the previous work [7]. Briefly, the pump and signal sources for DFG are a 1.064- μm Nd:YAG laser and a 1.5- μm extended-cavity laser diode (ECLD). The signal wave is phase-modulated at 10.7 MHz (RF1) using an electro-optic modulator (EOM) for the Pound-Drever-Hall (PDH) technique [15] and then amplified using a C- or L-band fiber amplifier. The pump and amplified signal waves are introduced into a periodically-poled lithium niobate (PPLN) module to generate an idler wave. Two PPLN modules are used to cover the frequency range of 88.6 to 93.1 THz. The idler wave enters an ECAC [11] coupled with a Gauss beam of 1.9-mm beam radius at the beam waist. The finesse of the empty ECAC is 770, the idler power incident to the ECAC is typically 200 μW , and the ECAC is filled with 0.01 to 0.4 Pa of CH_3D . The transmitted idler wave is detected with a liquid-nitrogen cooled InSb detector (D4). Part of the idler wave reflected from the ECAC is extracted using a combination of a quarter-wave plate and a Brewster plate, and then detected using a fast liquid-nitrogen-cooled

InSb photodiode (D1). The detected signal is converted to an error signal, which is fed back to the PZT of the ECAC to implement the PDH technique.

The signal and pump frequencies are offset-locked to the individual adjacent modes of the OFC, which replaces that used in the previous work [7]. The repetition rate is 97 MHz, and the carrier-envelope-offset frequency is servo-controlled with a wide bandwidth of about 400 kHz, which reduces the linewidth of the OFC to about 20 kHz from 100 kHz in the previous work [7]. The repetition rate of the OFC is swept to record the spectrum. Accordingly, the frequencies of the pump and signal waves follow those of the corresponding OFC modes, and the idler frequency is eventually swept. The resonant frequency of the ECAC immediately follows the idler frequency through the PDH technique, as well. The transmitted intensity signal from D4 and the repetition frequency of the OFC are stored with a PC. The frequency scale of the recorded spectrum is calibrated with a Rb atomic clock linked with International Atomic Time (TAI) through the Global Positioning System (GPS). The detected signal is averaged over 16 sweeps without any frequency drift.

4. RESULTS

Figure 2 depicts the recorded spectra of the ν_1 band $^qQ(3, 3)$ transition of $^{12}\text{CH}_3\text{D}$. The A_1 and A_2 components are barely resolved. The background level varies because the injection current of the Nd:YAG laser changes so that the pump frequency follows the nearest comb mode and inevitably alters the output power level at the same time. The horizontal axis is scaled in absolute frequency [10]. Figures 3 and 4 depict sub-Doppler resolution spectra of the ν_4 band $^pP(J, 3)$ transitions and the ν_4 band $^rQ(J, 3)$ transitions. The observed spectra are fitted to the Lorentz profile and an inclined background (Appendix A). The nonlinear fitting program in Mathematica [16] is used to determine the parameters and the uncertainties. In Fig. 2, red dots are acquired data, and a fitting curve is drawn in blue. The spectral lines are

60 to 100 kHz wide from the fitting; these are narrower than 250 kHz in the previous works [8, 10]. This contributes to the small uncertainty in the frequency determination.

Tables 1, 2, and 3 list the determined transition frequencies of a total of fifty-five spectral lines for the ν_1 band, the ν_4 $l = -1$ sub-band, and the ν_4 $l = +1$ sub-band together with the assignments, the uncertainties, the transition frequencies from the HITRAN2012 database [17] calculated from the FTIR works [5, 6], and the discrepancies. Each spectrum was recorded twice on different days. The determined frequencies in Tables 1, 2, and 3 are the weighted average of the two frequencies (Appendix B). The total uncertainty of the determined frequency, which is represented in parentheses in the unit of the last digit, is given by

$$\sigma_{\text{tot}} = \sqrt{\sigma_{\text{stat}}^2 + \sigma_{\text{Rb}}^2}, \quad (4)$$

where σ_{stat} is the statistical uncertainty given in Appendix B, and σ_{Rb} is the frequency uncertainty of 2.7 kHz relative to 89 THz caused by the frequency stability of 3×10^{-11} /s of a Rb atomic clock. The total uncertainty is typically a few kHz, and the relative uncertainty is an order of magnitude of 10^{-11} .

The A_1 and A_2 components of the ${}^rQ(J, 3)$ and ${}^rR(J, 3)$ transitions in the ν_4 band are not resolved up to $J = 6$. However, the ${}^rQ(6, 3)$ transition, as seen in Fig. 4, is wider than the other transitions and has a flattened top. The ${}^rR(6, 3)$ transition has similar characteristics. Indeed, they are not fitted to a one-line model but to a two-line model in Appendix A, and the transition frequencies are determined with random residuals and reasonably small uncertainties. Therefore, Table 3 includes the transition frequencies of the unresolved A_1 and A_2 components of the ${}^rQ(6, 3)$ and ${}^rR(6, 3)$ transitions.

4. ANALYSIS

Table 4 lists the frequency differences between the A_1 and A_2 components calculated from the determined transition frequencies of Tables 1, 2, and 3 together with the uncertainties in the parentheses in the unit of the last digit. Transitions sharing an identical upper level are listed in the same row. The frequency separation between the A_1 and A_2 components of the ${}^qQ(3, 3)$ transition in Fig. 2 is 121 kHz in Table 4, which is the smallest among the A_1 - A_2 resolved transitions in this work. The A_1 - A_2 splitting is resolved except for seven transitions of the ν_4 $l = +1$ sub-band. However, Table 4 includes the frequency differences of 88 and 98 kHz for the unresolved ${}^rQ(6, 3)$ and ${}^rR(6, 3)$ transitions because the transition frequencies are reasonably determined by the line-fitting described above.

The A_1 - A_2 splitting for the ${}^pP(J, 3)$ transition is, as seen in Table 4, quite similar to that for the ${}^pQ(J-1, 3)$ transition. This indicates that the energy separation in the $\nu_4 = 1, l = -1$ state is considerably larger than that in the ground vibrational state. In contrast, that of the ${}^rQ(J, 3)$ is on the same order of magnitude as that of the ${}^rR(J, 3)$ transitions for relatively low J . This suggests that the energy separation in the ground vibrational state dominates over that in the $\nu_4 = 1, l = +1$ state.

Figure 5 illustrates the energy levels in the ground and $\nu_4 = 1$ states associated with the A_1 - A_2 splitting for even J . The labels of A_1 and A_2 exchange for odd J . Solid (dotted) lines of Fig. 5(a) illustrates the ${}^pP(J+1, 3)$ (${}^pQ(J, 3)$) transitions. The frequency difference between the A_1 and A_2 components of the ${}^pP(J+1, 3)$ transition is given by

$$\Delta_1 = \delta_2 + \delta_3, \quad (5)$$

and that of the ${}^pQ(J, 3)$ transitions is represented as

$$\Delta_2 = \delta_3 - \delta_1, \quad (6)$$

where δ_1 and δ_2 are the energy separations between the A_1 and A_2 sublevels of the J - and $(J+1)$ - levels of the ground vibrational state, and δ_3 is the energy separation between those sublevels of the $(J, K=2, l=-1)$ level of the $\nu_4 = 1$ state. Figure 5(b) illustrates the ${}^rQ(J+1,$

3) and ${}^rR(J, 3)$ transitions, where the energy separation of the A_1 and A_2 sublevels of the $(J + 1, K = 4, l = +1)$ level of the $v_4 = 1$ state is smaller than in the ground vibrational state. The frequency differences between the A_1 and A_2 components of the ${}^rQ(J + 1, 3)$ and ${}^rR(J, 3)$ transitions are

$$\Delta_1 = \delta_2 - \delta_3, \quad (7)$$

and

$$\Delta_2 = \delta_1 + \delta_3. \quad (8)$$

Therefore, the sum of the energy separation of the A_1 and A_2 sublevels for the neighboring rotational levels in the ground vibrational state, $\delta_1 + \delta_2$, is given by $D_1 - D_2$ for the ${}^pP(J + 1, 3)$ and ${}^pQ(J, 3)$ transitions and by $\Delta_1 + \Delta_2$ for the ${}^rQ(J + 1, 3)$ and ${}^rR(J, 3)$ transitions. These sums are listed as super-combination differences (SCD) [4] in Table 4. The SCD derived from the ${}^pP(7, 3)$ and ${}^pQ(6, 3)$ transitions agrees with that determined from the ${}^rQ(7, 3)$ and ${}^rR(6, 3)$ transitions within the measurement uncertainty.

Here we can obtain the energy separation between the A_1 and A_2 sublevels of the $K = 3$ levels in the ground vibrational state. According to equation (1), the SCDs are represented as

$$\begin{aligned} \delta_1 + \delta_2 = 2h_{3,v=0} \big\{ & J(J+1)[J(J+1)-2][J(J+1)-6] \\ & + (J+1)(J+2)[(J+1)(J+2)-2][(J+1)(J+2)-6] \big\}. \end{aligned} \quad (9)$$

Least-squares fitting of only the present measurements yields the effective splitting constant as

$$2h_{3,v=0} = (1.5641 \pm 0.0026) \text{ Hz}. \quad (10)$$

The residuals between the determined and calculated frequencies are indicated in the last column of Table 4. Table 5 gives the calculated energy separation between the A_1 and A_2 sublevels of the $K = 3$ levels in the ground vibrational state together with the expected uncertainties.

Ulenikov et al. investigated the ν_3 , ν_5 , and ν_6 bands of CH_3D with Doppler-limited resolution. They measured the A_1 - A_2 splitting of the transitions from the levels with J ranging from 10 to 21, and derived $2h_{3,v=0} = (1.471 \pm 0.011)$ Hz [4]. This value departs from that determined in the present work beyond the claimed uncertainty. The reason is that a rotation-dependent constant may be required for fitting the energy separations across the wide range of J .

Now we are able to determine the energy separations between the A_1 and A_2 sublevels of the excited vibrational states from the determined transition frequency differences in Table 4 and the calculated energy separations in the ground vibrational state in Table 5. Tables 6, 7, and 8 list these for the $\nu_1 = 1$, $K = 3$ levels, the $\nu_4 = 1$, $K = 2$, $l = -1$ levels, and the $\nu_4 = 1$, $K = 4$, $l = +1$ levels. The number in parentheses is the uncertainty in the unit of last digit. Tables 7 and 8 indicate excellent agreements of the 10-kHz level between the two energy separations derived from different transitions and thereby demonstrate the remarkable consistency of the frequency measurements.

Equations (1), (2), and (3) do not fit the determined energy separations of the vibrational excited states in Tables 6, 7, and 8 within the measurement uncertainty. Therefore, the centrifugal distortion of the primary effective splitting constants is considered as

$$h_{3,v1=1} = h_{3,v1=1}^{(0)} + h_{3,v1=1}^{(1)} J(J+1) + h_{3,v1=1}^{(2)} [J(J+1)]^2, \quad (11)$$

$$h_{2,v4=1} = h_{2,v4=1}^{(0)} + h_{2,v4=1}^{(1)} J(J+1) + h_{2,v4=1}^{(2)} [J(J+1)]^2, \quad (12)$$

and

$$h_{4,v4=1} = h_{4,v4=1}^{(0)} + h_{4,v4=1}^{(1)} J(J+1). \quad (13)$$

These effective coupling constants are determined using least square fitting as

$$2h_{3,v1=1}^{(0)} = (154 \pm 3) \text{ Hz},$$

$$2h_{3,v1=1}^{(1)} = (2.02 \pm 0.14) \text{ Hz},$$

$$2h_{3, v_1=1}^{(2)} = (-24.7 \pm 1.5) \text{ mHz},$$

$$2h_{2, v_4=1}^{(0)} = (99.32 \pm 0.09) \text{ kHz},$$

$$2h_{2, v_4=1}^{(1)} = (509 \pm 6) \text{ Hz},$$

$$2h_{2, v_4=1}^{(2)} = (4.22 \pm 0.08) \text{ Hz},$$

$$2h_{4, v_4=1}^{(0)} = (-3.0 \pm 0.3) \text{ mHz},$$

and

$$2h_{4, v_4=1}^{(1)} = (54.5 \pm 2.4) \text{ }\mu\text{Hz}. \quad (14)$$

These values are used to derive the calculated values and the discrepancies between the determined and calculated values in Tables 6, 7, and 8. The J -dependent terms in equations (11), (12), and (13) are required to reduce the discrepancies down to the same magnitude as the measurement uncertainty. The uncertainties of the constants are considerably smaller than the constant values.

5. SUMMARY

The A_1 - A_2 splitting of the v_1 and v_4 bands of CH_3D is resolved for twenty-three transitions in sub-Doppler resolution spectra with a resolution of 80 kHz, and the transition frequencies are determined with an uncertainty of 4 kHz. The A_1 - A_2 interaction in the ground vibrational, $v_1 = 1$ and $v_4 = 1$ states is analyzed, and the effective splitting constants are found to have significantly improved. They reproduce the measured frequencies within the measurement uncertainty.

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Appendix A: Fitting function

The model function of the fitting is explicitly given by

$$f_1(n) = a_0 n + b_0 + \frac{a_1}{(n - n_1)^2 + (Dn_1)^2} \quad (\text{A.1})$$

for a line isolated from the other lines and by

$$f_2(n) = a_0 n + b_0 + \frac{a_1}{(n - n_1)^2 + (Dn_1)^2} + \frac{a_2}{(n - n_2)^2 + (Dn_2)^2} \quad (\text{A.2})$$

for two overlapped lines. Here, a_0 and b_0 are the parameters of the signal background, ν_1 and ν_2 are transition frequencies, $\Delta \nu_1$ and $\Delta \nu_2$ are half widths at half maximum of the Lamb dip, and a_1 and a_2 represent the intensities.

Appendix B: Statistical average value and uncertainty

The weighted average of two frequencies is given as

$$\bar{\nu} = \frac{\nu_1 / \sigma_1^2 + \nu_2 / \sigma_2^2}{1 / \sigma_1^2 + 1 / \sigma_2^2}, \quad (\text{B.1})$$

where ν_i ($i = 1$ and 2) and σ_i are the measured frequency and fitting uncertainty of the i -th measurement. The statistical uncertainty is given by

$$\sigma_{\text{stat}} = \sqrt{\frac{(\nu_1 - \bar{\nu})^2 + (\nu_2 - \bar{\nu})^2}{2}}. \quad (\text{B.2})$$

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Figure captions:

Fig. 1. Experiment setup. ECLD: Extended-cavity laser diode, EOM: Electro-optic

modulator, FA: Fiber amplifier, RF: RF local oscillator, PPLN: Periodically-poled lithium niobate, BP: Brewster plate, ECAC: Enhanced-cavity absorption cell, PZT: Piezoelectric transducer, PID Controller: Proportional-integral-derivative controller, D1, D4: Liquid nitrogen cooled InSb detector, D2, D3: InGaAs detector, Counter: Frequency counter, Mix: RF mixer, PC: Personal computer, OFC: Optical frequency comb.

Fig. 2. Sub-Doppler resolution spectrum of the ν_1 band $^qQ(3, 3)$ transitions of $^{12}\text{CH}_3\text{D}$. The A_1 - A_2 splitting is barely resolved.

Fig. 3. Sub-Doppler resolution spectra of the ν_4 band $^pP(J, 3)$ transitions of $^{12}\text{CH}_3\text{D}$. The A_1 and A_2 components are largely separated.

Fig. 4. Sub-Doppler resolution spectra of the ν_4 band $^rQ(J, 3)$ transitions of $^{12}\text{CH}_3\text{D}$. The A_1 - A_2 splitting is not resolved for the $^rQ(6, 3)$ transition, but the spectral line is broader than the other lines and flattened at the top.

Fig. 5. Energy levels of the ground vibrational and $\nu_4 = 1$ states associated with the A_1 - A_2 splitting. (a) $^pP(J, 3)$ and $^pQ(J, 3)$ transitions (b) $^rR(J, 3)$ and $^rQ(J, 3)$ transitions.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Tables

Table 1. Transition frequencies list of the v_1 band

Transition	Assignment	Obs. (kHz)	Ref. (MHz)	δ (MHz)
$^aQ(3, 3)$	A_2	89 012 513 353.4(39)	89 012 489.08	24.28
	A_1	89 012 513 474.8(29)	89 012 489.08	24.40
$^aQ(4, 3)$	A_1	89 023 546 946.2(39)	89 023 535.26	11.69
	A_2	89 023 547 881.6(39)	89 023 535.26	12.62
$^aQ(5, 3)$	A_2	89 037 747 401.2(52)	89 037 735.26	12.14
	A_1	89 037 751 253.2(41)	89 037 735.26	15.99
$^aQ(6, 3)$	A_1	89 055 573 618.1(35)	89 055 567.48	6.13
	A_2	89 055 585 361.9(31)	89 055 567.48	17.88
$^aQ(7, 3)$	A_2	89 077 712 222.7(41)	89 077 714.53	-2.31
	A_1	89 077 740 724.3(31)	89 077 714.53	26.19

Assignment: Assignment of the ground vibrational state, Obs.: Measured frequency, Ref.:

HITRAN2012 [17], δ : Difference between measured frequency and

HITRAN2012[17].

Table 2. Transition frequencies list of the v_4 $I = -1$ subband

Transition	Assignment	Obs. (kHz)	Ref. (MHz)	δ (MHz)
$^pP(3, 3)$	A_1	89 579 142 364.1(31)	89 579 144.40	-2.03
	A_2	89 579 144 824.4(27)	89 579 144.40	0.43
$^pP(4, 3)$	A_2	89 344 491 937.8(27)	89 344 493.81	-1.88
	A_1	89 344 504 665.4(28)	89 344 493.81	10.85
$^pP(5, 3)$	A_1	89 109 271 815.9(27)	89 109 278.54	-6.72
	A_2	89 109 311 879.0(28)	89 109 278.54	33.34
$^pP(6, 3)$	A_2	88 873 563 830.7(27)	88 873 543.64	20.19
	A_1	88 873 663 358.4(28)	88 873 601.11	62.25
$^pP(7, 3)$	A_1	88 637 467 220.7(27)	88 637 559.84	-92.62
	A_2	88 637 682 706.0(27)	88 637 660.66	22.04
$^pQ(3, 3)$	A_2	90 274 418 455.1(33)	90 274 411.56	6.90
	A_1	90 274 431 160.2(79)	90 274 411.56	19.60
$^pQ(4, 3)$	A_1	90 271 396 966.5(30)	90 271 401.28	-4.31
	A_2	90 271 436 993.6(29)	90 271 401.28	35.71
$^pQ(5, 3)$	A_2	90 267 699 339.5(27)	90 267 733.32	-33.98
	A_1	90 267 798 738.1(28)	90 267 733.32	65.42
$^pQ(6, 3)$	A_1	90 263 387 502.4(27)	90 263 477.28	-89.78
	A_2	90 263 602 651.7(29)	90 263 580.59	22.06

Assignment: Assignment of the ground vibrational state, Obs.: Measured frequency, Ref.:

HITRAN2012 [17], δ : Difference between measured frequency and

HITRAN2012[17].

Table 3. Transition frequencies list of the v_4 $I = +1$ subband

Transition	Assignment	Obs. (kHz)	Ref. (MHz)	δ (MHz)
$^rQ(4, 3)$	A^*	90 621 902 004.1(73)	90 621 919.07	-17.07
$^rQ(5, 3)$	A^*	90 616 775 399.3(36)	90 616 775.59	-0.19
$^rQ(6, 3)$	A_2^{**}	90 610 702 534.5(72)	90 610 685.46	17.08
	A_1^{**}	90 610 702 622.3(61)	90 610 685.46	17.16
$^rQ(7, 3)$	A_1	90 603 739 403.0(38)	90 603 724.01	15.40
	A_2	90 603 739 634.9(33)	90 603 724.01	15.63
$^rQ(8, 3)$	A_2	90 595 966 750.8(36)	90 595 950.39	16.36
	A_1	90 595 967 245.9(27)	90 595 950.39	16.86
$^rQ(9, 3)$	A_1	90 587 505 479.5(27)	90 587 487.01	18.47
	A_2	90 587 506 416.0(31)	90 587 487.01	19.41
$^rQ(10, 3)$	A_2	90 578 547 116.2(60)	90 578 536.82	10.29
	A_1	90 578 548 703.2(27)	90 578 536.82	11.88
$^rQ(11, 3)$	A_1	90 569 420 659.7(27)	90 569 400.95	19.71
	A_2	90 569 422 935.2(27)	90 569 400.95	21.99
$^rR(3, 3)$	A^*	91 551 828 514.0(34)	91 551 811.15	17.36

${}^rR(4, 3)$	A^*	91 778 900 535.0(28)	91 778 883.19	17.34
${}^rR(5, 3)$	A^*	92 004 838 023.3(28)	92 004 820.64	17.39
${}^rR(6, 3)$	A_2^{**}	92 229 659 582.0(29)	92 229 647.14	12.44
	A_1^{**}	92 229 659 680.6(39)	92 229 647.14	12.54
${}^rR(7, 3)$	A_1	92 453 408 880.8(28)	92 453 401.20	7.68
	A_2	92 453 409 153.2(38)	92 453 401.20	7.95
${}^rR(8, 3)$	A_2	92 676 169 870.6(28)	92 676 149.10	20.77
	A_1	92 676 170 502.9(40)	92 676 149.10	21.41
${}^rR(9, 3)$	A_1	92 898 097 314.6(59)	92 898 073.40	23.91
	A_2	92 898 098 718.0(28)	92 898 073.40	25.32
${}^rR(10, 3)$	A_2	93 119 483 527.4(31)	93 119 472.44	11.09
	A_1	93 119 486 552.3(28)	93 119 472.44	14.11

Assignment: Assignment of the ground vibrational state, Obs.: Measured frequency, Ref.:

HITRAN2012 [17], δ : Difference between measured frequency and

HITRAN2012[17], *: Unresolved A_1 - A_2 splitting, **: Unresolved A_1 - A_2 splitting.

Two frequencies are determined by fitting.

Table 4. Frequency differences between the A_1 and A_2 components and super-combination differences

Upper state	Transition 1	Δ_1 (kHz)	Transition 2	Δ_2 (kHz)	SCD (kHz)	δ (kHz)
ν_1 band						
(3, 3 ⁰)	${}^aQ(3, 3)$	121.4(48)				
(4, 3 ⁰)	${}^aQ(4, 3)$	935.5(55)				
(5, 3 ⁰)	${}^aQ(5, 3)$	3 852.0(66)				
(6, 3 ⁰)	${}^aQ(6, 3)$	11 743.9(47)				
(7, 3 ⁰)	${}^aQ(7, 3)$	28 501.6(51)				
ν_4 band						
(2, 2 ⁻¹)	${}^pP(3, 3)$	2 460.3(41)				
(3, 2 ⁻¹)	${}^pP(4, 3)$	12 727.6(39)	${}^pQ(3, 3)$	12 705.2(85)	22.5(94)	13.4
(4, 2 ⁻¹)	${}^pP(5, 3)$	40 063.1(39)	${}^pQ(4, 3)$	40 027.1(42)	35.9(57)	-3.5
(5, 2 ⁻¹)	${}^pP(6, 3)$	99 527.7(39)	${}^pQ(5, 3)$	99 398.5(39)	129.2(55)	3.1
(6, 2 ⁻¹)	${}^pP(7, 3)$	215 485.3(38)	${}^pQ(6, 3)$	215 149.3(40)	336.0(55)	4.9
(6, 4 ⁺¹)	${}^rQ(6, 3)$	87.7(94)				
(7, 4 ⁺¹)	${}^rQ(7, 3)$	231.9(51)	${}^rR(6, 3)$	98.7(49)	330.5(70)	-0.6
(8, 4 ⁺¹)	${}^rQ(8, 3)$	495.0(45)	${}^rR(7, 3)$	272.4(47)	767.5(65)	10.7
(9, 4 ⁺¹)	${}^rQ(9, 3)$	936.5(41)	${}^rR(8, 3)$	632.4(49)	1 568.9(64)	8.0
(10, 4 ⁺¹)	${}^rQ(10, 3)$	1 587.1(66)	${}^rR(9, 3)$	1 403.5(65)	2 990.5(93)	17.5
(11, 4 ⁺¹)	${}^rQ(11, 3)$	2 275.5(38)	${}^rR(10, 3)$	3 024.9(42)	5 300.3(57)	-14.0

Δ_1 : Frequency difference between the A_1 and A_2 components of the transition 1, Δ_2 :

Frequency difference between the A_1 and A_2 components of the transition 2, SCD:

Super-combination difference, δ : Observed SCD - calculated SCD

Table 5. Calculated energy separations between the A_1 and A_2 sublevels in the ground vibrational state

J	Splitting (kHz)	σ (kHz)
3	1.1	0.0
4	7.9	0.0
5	31.5	0.0
6	94.6	0.1
7	236.5	0.4
8	520.3	0.9
9	1 040.6	1.7
10	1 932.5	3.2
11	3 381.9	5.7
12	5 636.4	9.4
13	9 018.3	15.1
14	13 937.3	23.4
15	20 906.0	35.0
16	30 555.0	51.2
17	43 649.9	73.2
18	61 109.9	102.4
19	84 026.1	140.8
20	113 682.4	190.5

σ . Estimated uncertainty

Table 6. Determined and calculated energy separations between the A_1 and A_2 sublevels of the $\nu_1 = 1$ state

Upper level	Transition	δ_3 (kHz)	calc. (kHz)	$\delta_3 - \text{calc.}$ (kHz)
(3, 3)	$^aQ(3, 3)$	122.5(48)	126.1	-3.7
(4, 3)	$^aQ(4, 3)$	943.3(55)	932.3	11.0
(5, 3)	$^aQ(5, 3)$	3 881.0(40)	3 887.5	-6.5
(6, 3)	$^aQ(6, 3)$	11 838.5(47)	11 836.7	1.7
(7, 3)	$^aQ(7, 3)$	28 738.1(51)	28 738.2	-0.1

δ_3 : Determined energy separation between the A_1 and A_2 sublevels in the $\nu_1 = 1$ state, calc.:

Calculated energy separation between the A_1 and A_2 sublevels in the $\nu_1 = 1$ state

Table 7. Determined and calculated energy separations between the A_1 and A_2 sublevels of the $\nu_4 = 1$ $I = -1$ state

Upper level	Transition	δ_3 (kHz)	calc. (kHz)	$\delta_3 - \text{calc.}$ (kHz)
(2, 2 ⁻¹)	$^pP(3, 3)$	2 459.2(41)	2 460.5	-1.4
(3, 2 ⁻¹)	$^pP(4, 3)$	12 719.7(39)	12 723.6	-3.8
	$^pQ(3, 3)$	12 706.3(85)	12 723.6	-17.3
(4, 2 ⁻¹)	$^pP(5, 3)$	40 031.6(39)	40 024.5	7.1
	$^pQ(4, 3)$	40 035.0(42)	40 024.5	10.6
(5, 2 ⁻¹)	$^pP(6, 3)$	99 433.1(39)	99 434.6	-1.5

	${}^pQ(5, 3)$	99 430.0(39)	99 434.6	-4.6
(6, 2 ⁻¹)	${}^pP(7, 3)$	215 248.8(38)	215 245.9	2.9
	${}^pQ(6, 3)$	215 243.9(40)	215 245.9	-2.0

δ_3 : Determined energy separation between the A_1 and A_2 sublevels in the $\nu_4 = 1$ $l = -1$ state,

calc.: Calculated energy separation between the A_1 and A_2 sublevels in the $\nu_4 = 1$ $l = -1$ state

Table 8. Determined and calculated energy separations between the A_1 and A_2 sublevels of the $\nu_4 = 1$ $l = +1$ state

Upper level	Transition	δ_3 (kHz)	calc. (kHz)	$\delta_3 - \text{calc.}$ (kHz)
(6, 4 ¹)	${}^rQ(6, 3)$	6.9(94)	-1.2	8.1
(7, 4 ¹)	${}^rQ(7, 3)$	4.6(51)	0.6	4.1
	${}^rR(6, 3)$	3.1(85)	0.6	2.5
(8, 4 ¹)	${}^rQ(8, 3)$	25.3(46)	19.1	6.2
	${}^rR(7, 3)$	35.9(48)	19.1	16.9
(9, 4 ¹)	${}^rQ(9, 3)$	104.1(44)	100.5	3.6
	${}^rR(8, 3)$	112.1(50)	100.5	11.6
(10, 4 ¹)	${}^rQ(10, 3)$	345.4(74)	366.4	-21.0
	${}^rR(9, 3)$	362.9(67)	366.4	-3.6
(11, 4 ¹)	${}^rQ(11, 3)$	1 106.4(69)	1 096.2	10.2
	${}^rR(10, 3)$	1 092.4(53)	1 096.2	-3.8

δ_3 : Determined energy separation between the A_1 and A_2 sublevels in the $\nu_4 = 1$ $l = +1$ state,

calc.: Calculated energy separation between the A_1 and A_2 sublevels in the $\nu_4 = 1$ $l = +1$ state