Terahertz spectroscopy of methanimine and its isotopologs[★]

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ABSTRACT

Context. Methanimine (CH₂NH) is a simple molecule composed of methylene and imine. The molecule has been detected toward the Galactic center, star-forming regions, circumstellar envelopes, and other galaxies since 1973. In previous studies, the rest frequency of methanimine has been measured for normal species up to the 650-GHz region, but its ¹³CH₂NH, CH₂¹⁵NH, and CH₂ND isotopologs were limited to the 100-GHz region.

Aims. If a rotational temperature of 100 K is assumed for methanimine, the highest intensity falls at approximately 1.5 THz. In addition to normal methanimine, the ¹³CH₂NH, CH₂¹⁵NH, and CH₂ND isotopologs in their ground-vibrational states were observed in the frequency range of 120–1600 GHz to provide accurate rest frequency information. Based on this study, the calculated rest frequencies below 2 THz should be sufficiently precise and support observations using all ALMA and *Herschel*/HIFI observational bands.

Methods. Methanimine was generated by pyrolysis of diaminoethane (DAE) vapor at 850 °C. ¹³CH₂NH and CH₂¹⁵NH isotopologs were measured with their natural abundance, and deuterization of DAE was performed by mixing normal DAE with deuterated water, D₂O, and then pyrolyzed. This gives the deuterated isotopolog of methanimine, CH₂ND. Spectral measurements were performed by using the 23 kHz source-frequency modulated terahertz spectrometer at Toho University.

Results. Both *a*- and *b*-type transitions up to 1.6 THz for the three isotopologs and the normal species were measured. Rotational and centrifugal distortion constants for the three isotopologs were accurately determined. For normal species (CH₂NH), both electric quadrupole and nuclear spin-rotation coupling constants for nitrogen nucleus were determined, while for the ¹³CH₂NH and CH₂ND species, only electric quadrupole-coupling constants for nitrogen nucleus were determined.

Conclusions. Our spectral line frequencies are suitable for a future astronomical search for these isotopologs of methanimine. The 1σ frequency accuracy up to 2 THz is lower than 100 kHz.

Key words. line: identification – molecular data – ISM: molecules – submillimeter: ISM

1. Introduction

In our previous paper (Motoki et al. 2013), we have reported terahertz spectroscopy of aminoacetonitrile (NH₂CH₂CN) and its amino-deuterated isotopologs. Aminoacetonitrile is one of the key molecules in Strecker-type synthesis, which was originally proposed in the laboratory condition (Strecker 1850) to form glycine, the simplest amino acid. This synthesis procedure starts with ammonia (NH₃) and formaldehyde (H₂CO), which are well-known abundant species in interstellar space (for example, Cheung et al. 1968; Snyder et al. 1969):

To the best of our knowledge, glycine is the only one among the species appearing in the above series of reactions that has not yet been confirmed in interstellar space (Cheung et al. 1969; Buhl & Snyder 1971). The detection of glycine was reported by Kuan et al. (2003), but it was not confirmed in a subsequent study (Snyder et al. 2005). For example, aminoacetonitrile, the direct precursor to glycine, was recently confirmed toward Sgr B2(N)

with a derived abundance on the order of 10¹⁶ molecules cm⁻² (Belloche et al. 2008a,b).

In the reaction scheme of Strecker-type synthesis, methanimine (CH₂NH) is a precursor of aminoacetonitrile. Because spectroscopic information on methanimine has been available since the early 1970s and the molecule has a very simple structure consisting of methylene and imine groups, there have been numerous efforts to detect this molecule in space. On the basis of spectroscopic information, evidently, Godfrey et al. (1973) found interstellar methanimine for the first time toward the Galactic center in Sgr B2, measuring a column density of 3 × 10¹⁴ molecules cm⁻². Later, this molecule was also identified in several interstellar environments, such as hot cores associated with massive star-forming regions (for example, Qin et al. 2010), translucent molecular clouds (Turner et al. 1999), carbon-rich circumstellar envelopes (for example, Tenenbaum et al. 2010), and extragalactic environments (for example, Martin et al. 2006). Although spectroscopy of the molecule in the 1970s was limited up to the millimeter-wave region (below 100 GHz), Dore et al. (2012) recently provided the rest frequency of this molecule by measuring the spectrum in the frequency range of 329–629 GHz. This enables us to search for this molecule with a frequency uncertainty of several kilohertz, or a radial velocity of lower than 0.01 km s⁻¹ up to 1 THz. However, as shown in the figure in the paper by Dore et al. (2012), the spectral intensity of this molecule has its maximum in the submillimeter-wave region

[★] The full line list is only available at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via <http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/566/A28>

Fig. 1. Spectral intensity distribution of CH_2NH at 100 K Both *a*-type and *b*-type transitions are depicted. The ALMA and *Herschel* band designations are also shown. As described in the text, the most intense peak appeared around 1.5 THz, which is a common feature for all other isotopologs studied in the present paper.

at rotational temperature conditions of 50–100 K. The calculated spectral intensity of CH_2NH at 100 K up to 2 THz is shown in Fig. 1. The band designations of ALMA and *Herschel*/HIFI are also shown in the figure. The most intense lines lie at around 1.5 THz and are stronger by three orders of magnitude than those in the millimeter-wave region. The molecule CH_2NH was already identified in the millimeter-wave region and it is strongly expected to be observed in the submillimeter-wave to terahertz-frequency region. The isotopologs $^{13}\text{CH}_2\text{NH}$, $\text{CH}_2^{15}\text{NH}$, and CH_2ND may be detectable in the higher frequency region. Relevant spectroscopic information will be indispensable for their detection. Although the methylene-hydrogen deuterated methanimine can be considered as the singly substituted isotopologs, we have not tried to measure these species (two kinds of CHD_2NH) primarily because of the difficulty in the sample preparation. We therefore focused on the three isotopologs in the present work.

Methanimine spectroscopy was performed for the first time by Johnson & Lovas (1972). They measured the normal species of methanimine, CH_2NH , in the frequency region of 60–120 GHz and determined rotational constants and quadrupole coupling constants of the nitrogen nucleus. Later, the measurement was extended by several investigators and were summarized by Kirchhoff et al. (1973), and parts of the lines were remeasured precisely by Krause et al. (1989). Pearson & Lovas (1977) have been measuring various isotopologs of methanimine including $^{13}\text{CH}_2\text{NH}$, $\text{CH}_2^{15}\text{NH}$, and three kinds of deuterium isotopologs (CD_2ND , CD_2NH , and CH_2ND) in the millimeter-wave region to determine their molecular structure.

Very recently, two spectroscopic studies have been reported by Dore and his collaborators (Dore et al. 2010, 2012), as mentioned before. The former study describes the determination of very precise hyperfine structure of CH_2NH by using the Lamb-dip technique in the millimeter-wave region, by which not only electric quadrupole coupling constants of the nitrogen nucleus, but also the nuclear spin-rotation and nuclear spin-nuclear spin coupling constants of both N and H nuclei have been precisely determined. The latter study was mainly devoted to providing accurate rest frequencies of CH_2NH for astronomers in the submillimeter-wavelength region. The rest frequencies provided were claimed to be sufficiently accurate for whole ALMA observational bands (with 1σ uncertainties lower than 0.01 km s^{-1} in equivalent radial velocity). By combining their data with their analysis, Dore et al. (2010, 2012) provided not only extremely precise data in the millimeter-wave region, but also relatively higher frequency data.

We report in this paper terahertz spectroscopy of the three isotopologs ($^{13}\text{CH}_2\text{NH}$, $\text{CH}_2^{15}\text{NH}$, and CH_2ND) as well as main species. The measurements have been taken up to 1.6 THz to provide accurate rest frequencies up to at least 2 THz, covering all ALMA and *Herschel*/HIFI observational bands and with sufficient accuracy of $<0.1 \text{ MHz}$, corresponding to radial velocities of $<0.02 \text{ km s}^{-1}$.

2. Experiment

Methanimine was generated by pyrolysis of the alkylamine diaminoethane ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) in the present study. A quartz

Fig. 2. Observed spectra (solid line) of CH_2ND ($N_{K_a K_c} = 10_2 8 \leftarrow 9_1 9$). The nitrogen hyperfine structure (quadrupole coupling) was partially resolved. They are completely decomposed into two spectral components (overlapping of $F = 11-10$ and $9-8$ and $F = 10-9$ components) shown as dotted lines, each of which has been simulated by giving appropriate parameters to make the second derivative of Voigt line shapes. The residual between observed and simulated spectra was satisfactorily small, as shown at the bottom of the figure. The spectrum was recorded by integrating 30 scans with a 0.5 Hz repetition rate and a 1 ms time constant of the lock-in amplifier.

tube of 1/4 inch in diameter and 50 cm in length was heated in a furnace over a length of approximately 30 cm. The pyrolysis temperature was optimized to 850 °C by monitoring the intensity of known spectral lines of the normal species in the millimeter-wave region (Dore et al. 2010). Diaminoethane was continuously flowed through the heated quartz tube and the pyrolysis product was directly introduced into the absorption cell. No other buffer gas was introduced into the absorption cell. The pressure of the cell was kept at approximately 2–4 Pa. Observation of $^{13}\text{CH}_2\text{NH}$ and $\text{CH}_2^{15}\text{NH}$ was made in natural abundances. The imino-hydrogen deuterated methanimine (CH_2ND) was from the deuterium-enriched precursor, which was prepared by mixing deuterated water with diaminoethane in a volume ratio of 1:2. All spectral lines were measured with the 23 kHz-frequency modulated terahertz spectrometer at Toho University. The details of our spectrometer have been described extensively in our previous study (Motoki et al. 2013). Millimeter-wave to terahertz radiation in the frequency range of 120–1600 GHz was provided by the state-of-the-art frequency multiplier chains (VDI Inc.) output from a microwave synthesizer (Agilent 8257D). Both a GaAs solid-state zero-bias detector that operates at room temperature (VDI Inc.) and a liquid-helium-cooled InSb bolometer (QMC Instruments Ltd.) were used. The former was used mainly for detection below 1 THz and the latter above 1 THz. The 40–60 dB preamplified signal is detected at twice the modulation frequency, giving a second-derivative line shape. An example of the measured spectrum is shown in Fig. 2 to show the signal-to-noise ratio of CH_2ND . Because the spectra of $^{13}\text{CH}_2\text{NH}$ and $\text{CH}_2^{15}\text{NH}$ were recorded in natural abundances, numerous scans were necessary to obtain the same signal-to-noise ratio as that for the normal species. In Table 1, a part of the observed frequencies at around 1.5 THz is listed. The frequency measurement error in this frequency region is approximately 70 kHz. We estimated the error of the measured frequency in the present study to be between 30 and 70 kHz depending on the observed frequencies. Of course, the given frequency error becomes smaller as the measurement frequency becomes lower.

Table 1. Selection of observed transition frequencies of CH_2NH and its isotopologs around 1500 GHz.

Species	$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$	Frequency ^a	obs. – calc. ^a
CH_2NH	$4_4 0 \leftarrow 3_3 1$	1 404 238.028(70) ^b	0.140
	$5_4 2 \leftarrow 4_3 1$	1 468 185.402(70)	–0.007
	$5_4 1 \leftarrow 4_3 2$	1 468 199.075(70)	–0.023
	$12_5 7 \leftarrow 12_4 8$	1 471 199.202(70)	–0.012
	$12_5 8 \leftarrow 12_4 9$	1 471 499.403(70)	–0.027
	$9_5 4 \leftarrow 9_4 5$	1 473 861.534(70)	–0.018
	$9_5 5 \leftarrow 9_4 6$	1 473 892.068(70)	–0.014
	$8_5 3 \leftarrow 8_4 4$	1 474 356.250(70)	0.024
	$8_5 4 \leftarrow 8_4 5$	1 474 367.926(70)	–0.089
	$11_3 9 \leftarrow 10_2 8$	1 484 492.817(70)	–0.011
	$12_3 10 \leftarrow 11_2 9$	1 532 209.417(70)	–0.076
	$11_3 8 \leftarrow 10_2 9$	1 548 586.974(70)	0.002
	$13_3 11 \leftarrow 12_2 10$	1 576 363.188(70)	–0.010
$^{13}\text{CH}_2\text{NH}$	$21_2 19 \leftarrow 20_2 18$	1 352 287.798(70)	0.012
	$22_1 21 \leftarrow 21_1 20$	1 357 924.664(70)	–0.046
	$4_4 1 \leftarrow 3_3 0$	1 403 358.349(70)	0.052
	$4_4 0 \leftarrow 3_3 1$	1 403 359.871(70)	–0.096
	$11_3 9 \leftarrow 10_2 8$	1 474 883.686(70)	–0.022
	$14_5 9 \leftarrow 14_4 10$	1 475 381.288(70)	0.058
	$14_5 10 \leftarrow 14_4 11$	1 476 200.023(70)	–0.039
	$13_5 9 \leftarrow 13_4 10$	1 477 506.681(70)	–0.015
	$12_5 7 \leftarrow 12_4 8$	1 478 359.598(70)	0.083
	$11_5 6 \leftarrow 11_4 7$	1 479 383.508(70)	0.023
	$11_5 7 \leftarrow 11_4 8$	1 479 506.536(70)	–0.022
	$10_5 5 \leftarrow 10_4 6$	1 480 174.884(70)	–0.010
	$10_5 6 \leftarrow 10_4 7$	1 480 232.612(70)	–0.001
	$9_5 4 \leftarrow 9_4 5$	1 480 778.809(70)	0.070
	$9_5 5 \leftarrow 9_4 6$	1 480 803.406(70)	–0.177
	$12_3 10 \leftarrow 11_2 9$	1 522 368.746(70)	–0.126
	$6_4 3 \leftarrow 5_3 2$	1 528 120.333(70)	–0.016
	$6_4 2 \leftarrow 5_3 3$	1 528 167.416(70)	0.024
	$13_3 11 \leftarrow 12_2 10$	1 566 486.726(70)	0.011
$\text{CH}_2^{15}\text{NH}$	$22_3 20 \leftarrow 21_3 19$	1 372 963.250(70)	–0.039
	$22_6 17 \leftarrow 21_6 16$	1 376 401.678(70)	0.044
	$22_6 16 \leftarrow 21_6 15$	1 376 428.341(70)	0.061
	$22_5 18 \leftarrow 21_6 17$	1 379 173.653(70)	–0.043
	$22_5 17 \leftarrow 21_6 16$	1 379 791.274(70)	–0.082
	$22_4 18 \leftarrow 21_4 17$	1 389 424.015(70)	0.017
	$21_4 20 \leftarrow 20_1 19$	1 392 881.468(70)	–0.081
	$24_0 24 \leftarrow 23_1 23$	1 401 369.234(70)	–0.042
	$24_1 24 \leftarrow 23_1 23$	1 403 565.546(70)	–0.034
	$24_0 24 \leftarrow 23_0 23$	1 404 280.946(70)	0.010
	$24_1 23 \leftarrow 23_2 22$	1 407 122.642(70)	–0.042
	$23_1 22 \leftarrow 22_1 22$	1 413 143.255(70)	–0.037
	$22_5 18 \leftarrow 22_4 19$	1 455 861.400(70)	–0.046
	$24_2 23 \leftarrow 23_2 22$	1 457 357.254(70)	0.000
	$25_0 25 \leftarrow 24_1 24$	1 459 068.714(70)	0.032
	$7_5 2 \leftarrow 7_4 3$	1 477 594.406(70)	0.073
	$7_5 3 \leftarrow 7_4 4$	1 477 597.522(70)	–0.060
	$5_5 \leftarrow 5_4$	1 478 001.450(70)	–0.064
	$24_4 21 \leftarrow 23_4 20$	1 507 131.016(70)	0.009
CH_2ND	$25_2 24 \leftarrow 24_2 23$	1 515 322.641(70)	0.024
	$24_2 23 \leftarrow 23_1 22$	1 519 421.807(70)	0.061
	$24_4 20 \leftarrow 23_4 19$	1 520 980.865(70)	0.007
	$8_4 5 \leftarrow 7_3 4$	1 365 724.764(70)	0.002
	$8_4 4 \leftarrow 7_3 5$	1 366 494.752(70)	0.014
	$9_4 6 \leftarrow 8_3 5$	1 423 367.321(70)	0.009
	$9_4 5 \leftarrow 8_3 6$	1 425 064.589(70)	0.012
	$5_5 \leftarrow 4_4$	1 446 408.397(70)	0.077
CH_2ND	$10_4 7 \leftarrow 9_3 6$	1 480 328.684(70)	0.017
	$10_4 6 \leftarrow 9_3 7$	1 483 724.746(70)	0.009
	$11_4 8 \leftarrow 10_3 7$	1 536 302.549(70)	0.000
	$11_4 7 \leftarrow 10_3 8$	1 542 599.447(70)	0.012
	$7_5 3 \leftarrow 6_4 2$	1 563 606.214(70)	–0.031
	$7_5 2 \leftarrow 6_4 3$	1 563 609.067(70)	0.105

Notes. Hyperfine splitting due to the nitrogen nucleus is not resolved for the tabulated lines. See text for the detail. ^(a) Units are in MHz. ^(b) Experimental frequency accuracy in the present study.

Table 2. Molecular constants of methanimine and its isotopologs.

Parameter	CH ₂ NH	¹³ CH ₂ NH	CH ₂ ¹⁵ NH	CH ₂ ND
<i>A</i> (MHz)	196 210.87629(49) ^a	196 195.4866(44)	195 737.5201(43)	157 673.92406(169)
<i>B</i> (MHz)	34 641.699423(87)	33 747.23050(117)	33 735.38602(79)	32 069.00792(41)
<i>C</i> (MHz)	29 351.496787(81)	28 706.32768(110)	28 687.85279(65)	26 563.45064(44)
<i>D_J</i> (kHz)	56.00411(44)	53.4737(49)	53.43278(237)	49.92710(163)
<i>D_{JK}</i> (kHz)	598.6775(54)	585.589(39)	580.029(34)	327.4730(110)
<i>D_K</i> (kHz)	6383.483(36)	6393.40(35)	6356.61(43)	4998.306(74)
<i>d₁</i> (kHz)	−9.973179(80)	−9.24134(313)	−9.26331(162)	−10.90309(63)
<i>d₂</i> (kHz)	−2.007905(34)	−1.83540(104)	−1.83380(52)	−2.069013(219)
<i>H_J</i> (Hz)	0.01736(48)	0.0208(69)	0.01895(253)	0.04504(186)
<i>H_{JK}</i> (Hz)	2.6068(112)	2.445(77)	2.370(41)	1.9751(232)
<i>H_{KJ}</i> (Hz)	6.125(69)	7.38(74)	7.69(78)	−32.070(180)
<i>H_K</i> (Hz)	877.75(104)	861.8(90)	876.6(117)	779.52(147)
<i>h₁</i> (mHz)	33.067(164)	26.7(53)	30.35(200)	43.08(92)
<i>h₂</i> (mHz)	32.462(61)	23.9(34)	25.85(96)	36.91(60)
<i>h₃</i> (mHz)	9.091(39)	7.38(190)	9.11(96)	10.013(224)
<i>L_K</i> (mHz)	−163.0(47)			
<i>l₁</i> (μHz)	−0.541(97)			
<i>l₃</i> (μHz)	−0.472(34)			
<i>χ_{aa}</i> (N) (MHz)	−0.91523(141)	−0.568(109)		−0.5268(316)
<i>χ_{bb}</i> (N) (MHz)	−2.66739(126)	−2.881(71)		−3.0186(209)
<i>C_{aa}</i> (N) (kHz)	53.16(71)	53.2 ^b		42.8 ^b
<i>C_{bb}</i> (N) (kHz)	9.351(230)	9.09 ^b		8.64 ^b
<i>C_{cc}</i> (N) (kHz)	1.214(215)	1.17 ^b		1.09 ^b
# of newly measured lines	201	143	136	239
# of fitted lines ^c	389 ^d	146 ^e	139 ^e	268 ^e
rms	0.869	0.908	0.750	0.619

Notes. ^(a) Values in parentheses denote one standard deviation and apply to the last digits of the constants. ^(b) Fixed. See text in detail. ^(c) In addition to the newly observed lines in the present study, available data have been included for the analysis. ^(d) Data observed by Johnson & Lovas (1972); Kirchhoff et al. (1973); Krause et al. (1989); Dore et al. (2010); and Dore et al. (2012) are also included in the analysis. ^(e) Data observed by Pearson & Lovas (1977) are also included in the analysis.

For the lines showing asymmetric line shape, we tried to obtain each frequency by decomposing each hyperfine component frequency as shown in Fig. 2. When hyperfine components were not resolved, the frequency of the overlapping line is the intensity-weighted average of the corresponding components. The expected intensity of normal methanimine is so high (as can be seen in Fig. 1) that we may observe the distorted spectral line shape due to optical thickness for the intense line over 1 THz. However, we did not observe this effect because we were able to fit the spectral profile normally with a simple Voigt function for all the observed lines, probably because our pyrolysis condition was not efficient and the optically thin condition was virtually realized.

3. Spectral analysis

CH₂NH is a nearly prolate rotor ($\kappa = -0.937$) and the CN molecular axis lies almost along the *a* axis. The dipole moment of the molecule is mainly governed by CN and NH groups, with a CNH angle of approximately 110° (Pearson & Lovas 1977). This means that the dipole moment lies in the middle of the *a* and *b* axes. The dipole moment of the normal species was measured by Allegrini et al. (1978) by laser Stark spectroscopy, giving quite similar components for both *a* and *b* axes (μ_a and μ_b of 1.3396(30) and 1.4461(90) Debyes, respectively). From the view point of astronomical observation, both types of transitions are important.

The observed spectral-line frequency data were analyzed using the following S-reduced Hamiltonian for an asymmetric top molecule:

$$H = H_{\text{rot}} + H_{\text{eQq,N}} + H_{\text{nsr,N}}, \quad (4)$$

where H_{rot} represents the rotational Hamiltonian including the centrifugal distortion effect. For the analysis of the normal species, three octic centrifugal terms were needed because we included higher *N* and *K_a* lines in the fitting. This choice of molecular parameter set is coherent with the data set archived in the Cologne Database for Microwave Spectroscopy (CDMS; Müller et al. 2001, 2005). For other isotopologs, sextic centrifugal distortion constants are sufficient to explain all the observed line frequencies. $H_{\text{eQq,N}}$ and $H_{\text{nsr,N}}$ denote the Hamiltonians for an electric quadrupole interaction and nuclear spin-rotation interaction for the nitrogen nucleus, respectively. The former was taken for all species with nitrogen-14 nuclei; for the latter interaction term, however, it was included only for the normal species because we also fitted the line frequency observed previously by Dore et al. (2010) using the Lamb-dip technique in the millimeter-wave region. In the present analysis, we only considered the nitrogen hyperfine coupling described above because we were not able to observe any spectral line splitting from nuclei other than nitrogen. Thus, the coupling scheme we employed in the present analysis is

$$N + I(N) = F \quad \text{with} \quad I(N) = 1. \quad (5)$$

The observed data were combined with the data obtained previously (Johnson & Lovas 1972; Kirchhoff et al. 1973; Pearson & Lovas 1977; Krause et al. 1989; Dore et al. 2010, 2012) and were analyzed by using the SPFIT/SPCAT suite of programs (Pickett 1991). The number of measured lines in the present study and the fitted lines as well as the determined molecular constants for all four isotopologs are summarized in Table 2. Among hyperfine coupling constants, nitrogen nuclear spin-rotation coupling constants for the ¹³CH₂NH and CH₂ND isotopologs were poorly

Table 3. Partition function of methanimine and its isotopomers.

Temperature (K)	CH ₂ NH	¹³ CH ₂ NH	CH ₂ ¹⁵ NH	CH ₂ ND
300	5903.9	6048.5	2019.3	7195.1
225	3834.9	3928.7	1311.8	4673.2
150	2088.6	2139.7	714.43	2544.9
100	1138.34	1166.15	389.36	1386.78
75	740.42	758.48	253.25	901.87
37.5	263.37	269.76	90.069	320.60
18.75	94.295	96.554	32.238	114.64
9.375	34.207	35.007	11.688	41.482

Notes. Tabulated are spin-rotation partition functions, for which only ¹⁴N spin is considered.

determined mainly because of paucity of observed hyperfine resolved spectral lines. These constants were estimated from corresponding constants for normal species by scaling the ratio of rotational constants, and were included as the fixed constants in the present analysis. We will deposit the line lists in the CDMS¹, the Toyama Microwave Atlas (ToyaMA)², and Strasbourg astronomical Data Center (CDS)³ for the creation of new or/and updated entries.

4. Results and discussion

We measured pure rotational spectra of methanimine and its isotopologs ¹³CH₂NH, CH₂¹⁵NH, and CH₂ND up to 1.6 THz. This enabled us to predict astronomically important rotational line frequencies of these species with accuracies of <100 kHz even at 1.91 THz, the upper frequency limit of *Herschel*/HIFI band 7. This error corresponds to a radial velocity of 15 m s⁻¹. The frequency accuracy becomes better with lower frequency. For example, at 1 THz, the typical frequency error for the line whose upper state energy is below 100 cm⁻¹ for CH₂ND is ≤10 kHz, corresponding to a radial velocity of 3 m s⁻¹.

The rotational partition functions for several temperatures were calculated and are listed in Table 3. It is worth mentioning that the intensity of the spectra for all isotopologs was estimated by using the estimated values of electric dipole moments for three isotopologs from the corresponding values of CH₂NH, which are experimentally determined. Upon exchanging an isotopic atom, the molecular axis should rotate by several degrees, while the direction of the electric dipole moment should be essentially unchanged. The projection onto each molecular axis is thus changed in accordance with the rotation angle of the *a*–*b* molecular axes. This effect is most prominent in the case of deuterated methanimine, CH₂ND, as the molecular axis will rotate by several degrees with respect to the normal species within an *a*–*b* molecular axis plane. This rotation of the molecular axis results in a change of the electric dipole moment components for CH₂ND, i.e., the estimated μ_a and μ_b are 1.23 and 1.54 Debyes, respectively. This leads to a change in the calculated intensity by approximately 20% compared with the values without this correction. As already mentioned above, since both carbon and nitrogen nuclei lie almost along the *a* axis, the effect of substituting N or C atoms is weaker than substituting imino-hydrogen by a deuterium atom. This estimation of the spectral intensity is probably sufficiently accurate at a level

of 5%. Other contributions to the uncertainties of the spectral intensity are the low-lying vibrationally excited state and truncation of rotational levels in calculating the partition function. For methanimine, most of the vibrational frequencies have been already measured by other authors (Allegrini et al. 1978; Duxbury et al. 1981; Hamada et al. 1984; Halonen & Duxbury 1985). We found that all the reported vibrational frequencies are higher than 1000 cm⁻¹; the effect on the spectral intensity from this factor is thus negligibly small under the conditions of relatively cold interstellar space of 10 to 100 K, for example. The effect of truncation of rotational levels ($J \leq 99$ in the present study) was also checked by making a comparison with the approximate formula (Gordy & Cook 1984), and we confirmed that the effect on the spectral intensity is also negligibly small.

Finally we would like to mention the astronomical implication of this molecule. The normal species of methanimine has been observed toward several objects as described in the introduction section, to the best of our knowledge, however, no reports have been made with respect to the detection of the isotopologs, except for that of Cummins et al. (1986) who described the possible detection of ¹³C isotopolog at 124 GHz region toward Sgr B2. This assignment was based on the frequency coincidence of the single transition that has been measured in the laboratory (Pearson & Lovas 1977). It is hard to confirm the detection of the molecules from this report alone. Another assignment of the transitions based on the present work will be necessary.

5. Conclusions

Spectral lines of methanimine and its three isotopologs (CH₂NH, ¹³CH₂NH, CH₂¹⁵NH, and CH₂ND) were observed in the laboratory up to 1600 GHz. The obtained frequency data were analyzed and the molecular constants as well as spin-rotational partition function at various temperatures were revised. The frequency error for spectral lines with upper-state energy below 100 cm⁻¹ is <100 kHz even at 2 THz, corresponding to a radial velocity of 15 m s⁻¹. The accuracy of the intensity is expected to be within 5%. Our provided spectral line list will be cataloged in several spectral line databases and is valid for astronomical searches for methanimine in all ALMA and *Herschel*/HIFI observational bands.

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¹ <http://www.astro.uni-koeln.de/cdms>

² <http://www.sci.u-toyama.ac.jp/phys/4ken/atlas/>

³ <http://cdsweb.u-strasbg.fr/>

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