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Extension of the millimeter- and submillimeter-wave spectral databases of deuterated methyl cyanides (CH_2DCN and CHD_2CN)⋆

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ABSTRACT

Context. The study of deuterated abundant molecules is recognized as important in understanding molecular complexity in star-forming regions.

Aims. We seek to assign the laboratory millimeter and submillimeter wave rotational spectra of the CHD_2CN and CH_2DCN deuterated isotopologues of methyl cyanide over a wide frequency range in order to provide precise spectral predictions for observations.

Methods. Using the solid-state submillimeter-wave spectrometer in Lille, we measured and assigned 723 new lines for CHD_2CN and 307 new lines for CH_2DCN. The observed rotational transition frequencies were fitted with the ASFIT program to determine the spectroscopic parameters. The prediction of transition frequencies was performed using the SPCAT program.

Results. Measurements for both isotoplogues were taken up to 945 GHz and are made available at the CDS. For CHD_2CN this is significantly higher than the previous range of measurement up to 40 GHz. For CH_2DCN many more lines of high K_a have been measured than previously.

Conclusions. Our work confirms the recent analysis for CHD_2CN given in the CDMS database and extends the number of determined molecular parameters from 10 to 19. For CH_2DCN, 3 new parameters including D_K have been determined, and the uncertainty on parameters has been decreased by a factor of approximately 2. For both isotopologues the measured data show shifts in the frequency of some high K_a transitions that are attributed to interactions with a low-lying vibrational state. The availability of more directly measured data and the increase in confidence of the predictions to higher quantum numbers and frequencies will be helpful for the radio astronomical detection of deuterated isotopologues of methyl cyanide in the interstellar medium.

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

1. Introduction

With its high abundance and symmetric top spectral pattern, methyl cyanide (or acetonitrile), CH_3CN, is known as an excellent probe-molecule for deriving the kinetic temperature and density of interstellar objects. It is thus not surprising that its rotational spectrum has been comprehensively studied (see Cazzoli & Puzzarini 2006, for references and a very recently published paper of Müller et al. 2009). However, the ambition of astronomers does not stop at investigating abundant molecules like CH_3CN. The astrophysical study of the isotopologues of abundant molecules provides valuable clues for understanding the complex physical and chemical phenomena occurring in the interstellar medium (ISM). The average atomic deuterium-to-hydrogen ratio in the local interstellar medium is around 10^{-5}. However, exceptionally high deuterium-to-hydrogen ratios have been observed for certain molecules in hot cores and especially in hot corinos (Ceccarelli et al. 2007). This enrichment in deuterium is explained by reactions taking place both in the gas phase and on the surface of grains, however, the enrichment appears to change from species to species and from one object to another, and the precise mechanisms taking place are still subject to debate. Observations of deuterated species are thus extremely valuable for constraining chemical models that may allow us to reconstruct the past history of protostars (Taquet et al. 2012). For this purpose, it is essential to know in advance precise rotational transition frequencies for these isotopologues, and other spectral information needed to model intensities. The necessary data is provided from laboratory measurements and their analysis, as reported here for CH_2DCN and CHD_2CN.

Concerning the substituted ^{13}C and ^{15}N isotopologues, after some investigations dating from the 1980's (Demaison et al. 1979; Boucher et al. 1980, etc.), Pearson & Müller (1996) reported in 1996 the spectra of $^{13}CH_3CN$, $CH_3{}^{13}CN$, and $CH_3C^{15}N$ in the 294–607 GHz frequency range. Recently, Müller et al. (2009) have extended the studied frequency range up to about 1.2 THz. In addition to the measurements of the singly substituted ^{13}C isotopologues, the previous publication also reports the high-resolution spectrum of the doubly substituted one (i.e. $^{13}CH_3{}^{13}CN$), for which only measurements up to 72 GHz were previously available (Tam et al. 1988).

⋆ Full Tables B.1 and B.2 are only available in electronic form 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/553/A84`

As for laboratory measurements of deuterated methyl cyanide, the ground state microwave spectrum of CD_3CN (triply deuterated methyl cyanide) was measured between 8 and 240 GHz by Demaison et al. (1979). Later, Brown et al. (1989) extended the measurements to the submillimeter region. Moreover, the rotational spectrum of CD_3CN in excited vibrational states has already been the subject of several publications (Matsumura et al. 1962; Cosleou et al. 1989, 1991; Chen et al. 1991).

In the present work, we focus on the millimeter and submillimeter spectra up to 945 GHz of singly and doubly deuterated methyl cyanides, i.e. CH_2DCN and CHD_2CN, in their ground vibrational states. Previous studies have been reported for these deuterated species but were limited to low-frequency measurements for CHD_2CN and could be beneficially completed for CH_2DCN. First, the three $J = 2 \leftarrow 1$ R-branch transitions were measured by Thomas et al. (1955) for both CH_2DCN and CHD_2CN, so that only the rotational constants B and C were deduced approximately. Halonen & Mills (1978) recorded about fifty microwave lines of CHD_2CN between 18 and 40 GHz. They extended the determination of the spectroscopic parameters to all three rotational constants, as well as five quartic and four sextic distortion constants. However, based on the same measurements, an alternative fit has recently been proposed by H. S. P. Müller in the CDMS database using only two sextic distortion constants. No other rotational spectra of CHD_2CN in a higher spectral region have been reported up to now. As for CH_2DCN, the spectroscopic data from laboratory measurements are more extended. Its ground-state rotational spectrum, as well as those of ^{13}C and ^{15}N isotopologues, was measured by Le Guennec et al. (1992) from 120 to 470 GHz. Recently, Müller et al. (2009) have extended the data set up to about 1.2 THz. However, since CH_2DCN was studied in natural abundance, they were not able to observe transitions with high quantum number K_a. The aim of this work is to extend the frequency range of measurements of CHD_2CN to provide accurate predictions for astrophysical research and to complete the measurements of CH_2DCN.

With regard to astrophysical observations, CH_2DCN was detected toward the hot core Orion-IRc2 and tentatively towards G34.3 by Gerin et al. (1992), which constitutes the unique published detection. They reported a D/H ratio of about 0.01 that is subject to uncertainties, such as line opacity and beam dilution (uncertainty in the emission region), referred to in the text. For example, the authors give a minimum ratio of 0.004 if the emission of all isotopes comes only from the central $1''$ region. Recent interferometric observations of Orion BN/KL by Peng et al. (2012) give a lower deuteration ratio for methanol (CH_2DOH/CH_3OH) abundance of around 10^{-3}. Further studies of CH_2DCN would, therefore, be interesting for clearing up the uncertainties in its abundance, and these should involve ideally states of widely differing energy. No identification of CHD_2CN has been reported to date, which reflects the lower abundance but also the lack of a complete spectral database to help in the identification. The possibility of detecting doubly deuterated methyl cyanide is especially interesting by interferometric observations of the hot corinos of low-mass protostars. In low-mass protostars, deuteration ratios are reported to be significantly higher than in high-mass ones, as shown for example in Parise et al. (2006).

Explanations of this high deuteration in terms of current gas and grain models show multiple inconsistencies (see for example Ratajczak et al. 2011). The deuteration, for at least two species (formaldehyde and methanol) is shown to depend critically on the precollapse phase and on D and H abstraction and substitution reactions (Taquet et al. 2012). Specifically, in the latter reference it is shown that the different deuterated species are formed at different times, so that their measure helps reconstruct the past history of the protostar. In the case of methyl cyanide, measuring the singly and doubly deuterated abundances would also help in understanding the relative contribution of the gas versus grain surface synthesis of this species (see Bottinelli et al. 2008 for a discussion of the various specific possibilities mentioned in the literature). It is, therefore, important to obtain accurate frequencies for both CH_2DCN and CHD_2CN for as many transitions as possible, to confirm or exclude their presence in radio-astronomical spectra (in particular of ALMA, in spectral surveys and/or for modeling confusion-limited detections) and to calculate significant maximum abundance limits in the case of non detection.

2. Experimental

The submillimeter-wave measurements (150–945 GHz) were performed using the Lille spectrometer (Motiyenko et al. 2010) based only on solid-state sources. The frequency of an Agilent synthesizer E8257D (12.5–17.5 GHz) was first multiplied by six and amplified by a Spacek active sextupler providing output power of +15 dBm in the W-band range (75–110 GHz). This power is high enough to use passive Schottky multipliers (×2, ×3, ×5, ×3×2, ×3×3) from Virginia Diodes Inc in the next stage of the frequency multiplication chain. As a detector we used an InSb liquid He-cooled bolometer from QMC Instruments Ltd. To improve the sensitivity of the spectrometer, the sources were frequency-modulated at 10 kHz, and a 2f phase-sensitive detection was used. The absorption cell is a stainless-steel tube (6 cm diameter, 220 cm long). The sample pressure during measurements was about 1.5 Pa (15 μbar), and the linewidth was limited by Doppler broadening. Measurements were taken at room temperature. The accuracy of the measurements for isolated lines is estimated to be 30 kHz up to 660 GHz and 50 kHz from 660 to 945 GHz. However, if the lines were blended or had a poor signal-to-noise ratio, they were given an uncertainty of 100 or even 200 kHz.

To synthesize the deuterated samples, the preparation of Anthoni and Nielsen (Anthoni & Nielsen 1984) was modified (see Appendix A).

3. Analysis and discussion

Both CH_2DCN and CHD_2CN are near prolate asymmetric top molecules with $\kappa = -0.9973$ and -0.9965, respectively. The parent molecule CH_3CN or the totally deuterated CD_3CN are symmetric tops, with the dipole moment along the symmetry (molecular) axis. The substitution of one H atom by D in the case of CH_2DCN, or one D by H in the other case, gives rise to a small rotation of the dipole moment from the molecular axis. This shift leads to CH_2DCN having a much smaller $\mu_b \approx 0.12$ D component, as well as a large dipole moment component μ_a (≈3.92 D) along the molecular axis. Similarly, $\mu_c \approx 0.11$ D for CHD_2CN. In the ground vibrational state, these two species therefore exhibit strong a-type transitions and very weak b (or respectively c)-type transitions. The dipole moments are taken from a recent entry in the CDMS database and were derived from the value determined for the main isotopologue by Gadhi et al. (1984) taking the rotation of the inertial axes into account. The selection rule for the quantum number J ($\Delta J = 0, \pm 1$ corresponding to Q, R and P branches, respectively) is completed by the selection rule for K_a and K_c that depends on the non zero components of the dipole moment (i.e. $\mu_a \neq 0{:}\Delta K_a = 0, \pm 2 ...$;

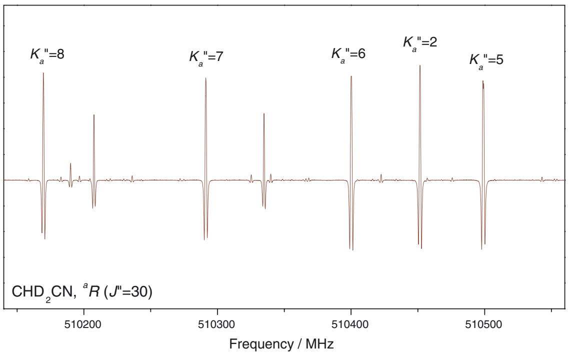

Fig. 1. Part of the submillimeter spectrum of CHD$_2$CN.

$\Delta K_c = \pm1, \pm3...$; $\mu_b \neq 0{:}\Delta K_a = \pm1, \pm3...$; $\Delta K_c = \pm1, \pm3...$; $\mu_c \neq 0{:}\Delta K_a = \pm1, \pm3...$; $\Delta K_c = 0, \pm2...$ (Kroto 1975)). The majority of our measured lines were a-type transitions belonging to the R-branch with $\Delta K_a = 0$ and $\Delta K_c = 1$ that are the strongest in the frequency range measured. The a-type transitions with $\Delta K_a = \pm2$ are very weak for asymmetric molecules close to the prolate symmetric limit, so were not measured. Some very weak b-type (or c-type) transitions could be observed but their identification demanded more caution.

Figure 1 gives an example of spectra recorded around 510 GHz for CHD$_2$CN. The five labeled lines are a-type R-branch transitions with $J'' = 30$ and different K''_a as given in the figure. The remaining unlabeled transitions (that probably correspond to the excited vibrational states) have not been assigned in the present work.

With the ASFIT program[1], the identified transitions were fitted to the asymmetric top S-reduction of the rotational Hamiltonian in the I^r representation (Watson 1977). The asymmetric top A-reduction was also tried but did not give a better fit. Predictions were made using the SPCAT program (Pickett et al. 1998) with the parameter set resulting from ASFIT and the dipole moments reported above.

3.1. CHD$_2$CN

Our initial identifications were based on the predictions that we made using the measurements of Halonen & Mills (1978) between 18 and 40 GHz. First, we identified the strong a-type transitions of the R-branch from 150 to 250 GHz. 32 lines (with J'' varying from 9 to 14 and K''_a from 0 to 6) were measured with a systematic shift from the predictions (for example, about 3 MHz at $J'' = 14$ and $K''_a = 6$). These newly identified lines were then included in the fit. They fitted correctly, and the shifts decreased to below the experimental uncertainty. Next, we identified lines by progressively extending the frequency and systematically increasing K_a. At $K''_a = 17$, we observed a significant disagreement between the measured and predicted frequencies of the transitions with $J'' = 29{-}37$ and $J'' = 49{-}54$. The maximum differences were observed for two transitions $J = 37 \leftarrow 36$ (about 3 MHz) and $J = 38 \leftarrow 37$ (about 7 MHz), while the others (of from 0.1 to 0.9 MHz) were also significant compared to the estimated experimental uncertainty of 0.05 MHz. This discrepancy between measurement and prediction was not resolved by adding more lines to refine parameters. Reasonable agreement was obtained for 14 transitions with $J'' = 18{-}28$, as well as with $J'' = 47$ (other J'' values were not observed). In the final analysis, transitions with $K''_a = 17$ and shifted by more than 0.1 MHz were omitted from the fit, and assumed perturbed (see Sect. 3.3). Transitions with $K''_a = 18$ to 20 fitted correctly. Transitions with $K''_a = 21$, 22, and 23 were also observed, but no possible combination of parameters was found that allowed to fit them correctly. Lines of higher K_a were too weak to be observed, so the highest K_a included in the final fit is 20, with a maximum J of 56.

The c-type transitions belonging to the R- and Q-branches were then identified and progressively included in the fit, but only a very minor improvement was seen in the determined spectroscopic parameters. On the other hand, including 11 very weak c-type P-branch transitions (with $\Delta K_a = 1$ and $\Delta K_c = -2$) allowed us to determine the sextic centrifugal distortion constant H_K.

Table 1 gives the rotational and centrifugal distortion parameters of CHD$_2$CN in comparison with two lists of previously available parameters; one resulting from the fit by Halonen & Mills (1978) and the other from a recent alternative fit given on the CDMS database[2] and based on the same experimental data. In our work six sextic centrifugal distortion constants (all except h_3) were determined reliably. As mentioned previously, H_K could also be determined thanks to a small number of c-type transitions, and its value (49.9 Hz) was very different from the −1941 Hz obtained by Halonen & Mills (1978) but very close to the 51 Hz of the parent molecule CH$_3$CN estimated by Müller et al. (2009). This parameter was appropriately constrained to zero in the CDMS fit. We observed close agreement between our parameters and those that were determined in the CDMS fit, pointing out the very good choice made in the latter. For example, while two values of H_{JK} and h_2 provided by the CDMS are close to those obtained in the present work, all four sextic H_{KJ}, H_K, h_1, and h_2 distortion constants determined by Halonen & Mills (1978) show significant disagreements. Similarly, agreements between the predictions in CDMS and our measurements are closer than those based on the original fit. For example, the CDMS prediction of the a-type transition with $J'' = 14$ and $K''_a = 6$ mentioned above differs by only about 200 kHz. Our work thus confirms the high quality of the original low-frequency data of Halonen & Mills (1978) and of the fit carried out on the CDMS that exploits this data the most reliably. Our fit differs from the latter on being based not only on much higher frequency data but also on many lines containing higher J and much higher K_a transitions. Along with the full set of sextic paramaters, three octic (L_{JJK}, L_{JK}, L_{KKJ}) and two decatic (P_{KJ}, P_{KKJ}) centrifugal distortion constants were also needed to correctly fit all of our data.

For predictions of lines of higher J and moderate K_a that are still strong at temperatures of the 100–200 K found typically in hot cores and corinos, the new data differ by 1 to several MHz with the present CDMS fit and these differences increase at higher frequency. The differences become important in the case such as for lower abundance species in star-forming regions of spectral congestion and multi-species analysis where best candidates for detection depend not only on absolute intensity but also on minimum convolution with other nearby lines.

The final fit given in Table B.1 (Appendix B) contains 773 lines (723 new lines) and 1177 transitions with 404 unresolved doublets. Only the first 15 lines are listed, but a full list of measurements is available in electronic form at the CDS. The measured transitions not included in the fit are also shown in the full Table B.1 (noted by "e").

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[1] Kisiel, PROSPE, `http://www.ifpan.edu.pl/~kisiel/prospe.htm`

[2] `http://www.astro.uni-koeln.de/cdms`

Table 1. CHD_2CN rotational and centrifugal distortion parameters.

	This work	Halonen & Mills (1978)	CDMS database*
A/MHz	96 500.2696 (22)	96 500.2674 (373)	96 500.2310 (530)
B/MHz	8320.07278 (10)	8320.0735 (30)	8320.0706 (44)
C/MHz	8164.42785 (10)	8164.4282 (30)	8164.4253 (44)
D_J/kHz	3.103685 (65)	3.0903 (34)	3.10466 (259)
D_{JK}/kHz	126.7475 (21)	126.2140 (808)	126.833 (47)
D_K/kHz	1206.37 (24)	1213.57 (319)	1202.06 (159)
d_1/kHz	–0.047756 (23)	–0.04786 (14)	–0.048006 (47)
d_2/kHz	–0.0105627 (84)	–0.010712 (15)	–0.0105365 (46)
H_J/Hz	0.000472 (11)	0.0	0.0
H_{JK}/Hz	0.72260 (83)	0.0	0.7172 (188)
H_{KJ}/Hz	0.774 (21)	60.14 (418)	0.0
H_K/Hz	49.9 (67)	–1941 (275)	0.0
h_1/mHz	–0.0615 (65)	–0.40 (3)	0.0
h_2/mHz	0.0643 (43)	0.26 (1)	0.0637 (64)
L_{JJK}/mHz	–0.00472 (11)		
L_{JK}/mHz	–0.0451 (43)		
L_{KKJ}/mHz	–0.590 (86)		
P_{KJ}/μHz	0.2188 (83)		
P_{KKJ}/μHz	–8.27 (11)		
Freq$_{\rm max}$[a]/MHz	940 798.15	39 473.20	39 473.20
nbr of transitions[b]	1177	50	50
$J''_{\rm max}$, $K''_{a\,\rm max}$[c]	56, 20	53, 4	53, 4
rms[d]/kHz	30.6	26.2	21.5
wrms[e]	0.864		0.649

Notes. (*) Revised fit by H. S. P. Müller using the data of Halonen & Mills (1978), (a) maximum line frequencies assigned; (b) number of transitions included in the fit; (c) maximum values of J and K_a (of lower state); (d) standard deviation of fit; (e) weighted standard deviation of fit.

3.2. CH_2DCN

Since an extensive set of measurements up to 1.2 THz was already available by Müller et al. (2009), identification of a-type transitions was immediate. Besides the measurements of the authors (10 lines recorded in Cologne and 109 lines at JPL), the previous data set contained data from Thomas et al. (1955) and from Le Guennec et al. (1992). We decided to measure all possible transitions, so we remeasured lines already cited in the previous work that were within our frequency scans. As expected, the difference between the two sets of measurements was within the experimental uncertainty. The previous data were included in the fit without changes except for the remeasured lines that were replaced by the new ones. We then proceeded to measure lines with K_a greater than ten, most of which had not been observed previously because of low sensitivity. Measurements were taken up to $K''_a = 20$ and $J'' = 53$.

The problems with fitting observed for CHD_2CN occurred for CH_2DCN at lower K_a. We were not able to simultaneously fit transitions with $K''_a = 14$ and $K''_a = 15$ having high J ($J'' = 45–51$). A perturbation was again assumed, leading to the shift of all or some of these transitions. Since it was not possible to determine which of the transitions were unaffected, we decided to omit them all from the final fit. We were then, however, able to fit all the measured transitions with $K''_a = 16$ correctly. We were also able to observe transitions with $K''_a = 17–20$; however, no possible combination of parameters allowed us to fit these transitions correctly. This appeared similar to the problems encountered for fitting transitions with $K''_a > 20$ for CHD_2CN as described above.

To determine the K-dependent parameters that could not be determined from the a-type R-branch $\Delta K_a = 0$ transitions, we also searched for b-type transitions. Only transitions belonging to the R-branch with $K_a = 1 \leftrightarrow 0$ (13 transitions) and $K_a = 2 \leftarrow 1$ (4 transitions) were strong enough to be identified and measured. The resulting rotational, centrifugal distortion constants are given in Table 2. This is also the set that allows the best comparison with the di-deuterated and main isotopologues, as well as with previous results. Other parameter sets were tried with similar or worse results. A further discussion on the parameters is given in Sect. 3.3. The D_K parameter was determined, and its value (2.22 MHz) is bigger than the 1.97 MHz fixed by Müller et al. (2009) and also than the 1.83 MHz obtained by Le Guennec et al. (1992). The higher order K-dependent parameters, such as H_K and L_K were not determined reliably by the limited number of b-type transitions we identified. We therefore fixed $H_K = 100$ Hz to be consistent with Müller et al. (2009), and a comparison of the derived parameters is given in Table 2. Additionally, decatic centrifugal distortion constants P_{KJ} and P_{KKJ} were needed to correctly fit our data that include high K_a transitions. In the analysis of Müller et al. (2009), two very weak $K_a = 1 \leftrightarrow 2$ b-type transitions measured by Le Guennec et al. (1992) were excluded: one (the $9_{2,8} \leftarrow 10_{1,9}$) that did not fit and one ($31_{1,31} \leftarrow 30_{2,28}$) that the authors did not trust. After including our b-type transitions, neither of these latter lines fitted correctly.

The final fit given in Table B.2 (Appendix B) contains 491 lines (307 new lines) and 733 transitions with 242 unresolved doublets. Only the first 14 lines are listed, but a full list of measurements is available in electronic form at the CDS.

3.3. Discussion

The weighted standard deviation of the fits is 0.864 for CHD_2CN and 0.807 for CH_2DCN, indicating that, on average, the data have been fitted within experimental uncertainties, and that the latter may be slightly overestimated.

The analysis section reports a failure in fitting for some transitions above $K''_a = 17$ for CHD_2CN and $K''_a = 14$ for CH_2DCN. An analogous shift from the predictions has already

Table 2. CH_2DCN rotational and centrifugal distortion parameters.

	This work	Müller et al. (2009)
A/MHz	121 074.919 (10)	121 074.677 (20)
B/MHz	8759.19798 (12)	8759.197 94 (23)
C/MHz	8608.54244 (11)	8608.542 55 (24)
D_J/kHz	3.469947 (55)	3.469 982 (137)
D_{JK}/kHz	143.3383 (60)	143.336 1 (138)
D_K/kHz	2224.2 (21)	1970.0
d_1/kHz	–0.079204 (23)	–0.079164 (46)
d_2/kHz	–0.004876 (16)	–0.004776 (35)
H_J/Hz	0.0004003 (82)	0.0004004 (191)
H_{JK}/Hz	0.8437 (18)	0.8375 (49)
H_{KJ}/Hz	1.150 (91)	1.688 (192)
H_K/Hz	100.	100.
h_1/mHz	0.1544 (53)	0.1490 (84)
L_{JJK}/mHz	–0.00565 (20)	–0.00537 (55)
L_{JK}/mHz	0.017 (13)	0.058 (28)
L_{KKJ}/mHz	–2.84 (52)	–10.82 (68)
P_{KJ}/μHz	0.324 (39)	
P_{KKJ}/μHz	–28.3 (10)	
Freq$_{\max}$^{a}/MHz	1 196 285.09	1 196 285.09
nbr of transitions^b	733	274
$J''_{\max}$, $K''_{a\max}$^{c}	68, 16	68, 14
rms^d/kHz	57.7	
wrms^e	0.808	0.740

Notes. $^{(a)}$ Maximum line frequencies assigned; $^{(b)}$ number of transitions included in the fit; $^{(c)}$ maximum values of J and K_a (of lower state); $^{(d)}$ standard deviation of fit; $^{(e)}$ weighted standard deviation of fit.

been shown in the work of Simečková et al. (2004) for two transitions $J = 39 \leftarrow 38$, $K = 14$ and $J = 40 \leftarrow 39$, $K = 14$ of CH_3CN in the ground vibrational state. The authors successfully explained this shift by resonances between the ground state rotational levels with $J > 34$, $K = 14$ and the $+l$ levels of the ν_8 excited vibrational state with $K = 12$. We assumed that a similar phenomenon occurred here for the deuterated isotopologues and that the problems observed with the fit for high K_a arise from an interaction between high rotational energy levels in the vibrational ground state and other levels in an excited vibrational state. There are several low-energy excited vibrational states of CH_3CN, and the two lowest $\nu_8 = 1$ and $\nu_8 = 2$ are, respectively, at 365 cm^{-1} (Koivusaari et al. 1992) and 717 cm^{-1} (Tolonen et al. 1993) from the ground state well below, for example, the maximum rotational energy 2175 cm^{-1} of CH_2DCN at $J'' = 48$ and $K_a'' = 20$ that we measured in the vibrational ground state. We were not able to find precise energies for similar vibrations in the deuterated isotopologues, so that a detailed analysis of perturbations was not possible. Furthermore, such an analysis is outside the main objectives of this publication since the lines in question are weak so not the best candidates for astrophysical use. Lines assumed to be perturbed have therefore been excluded from the fit but given in the data for future use.

Since both isotopologues are strongly prolate, with the A rotational constant more than ten times larger than B, the energy of the rotational levels increases much more rapidly with K_a than with J. This explains the lower limit in K_a that could be measured compared to J, since the intensity decreases more rapidly with an increase in the former. It could also explain the limitation in K_a for lines that could be included in the fit because of the increased possibility of resonance with a rovibrational level at higher energy. Similarly that the A constant of CH_2DCN is 25% larger than that of CHD_2CN explains why K_a is more limited for the former. However, lines of somewhat lower K_a may show the same effect at high J. For example, the transition $J = 50 \leftarrow 49$, $K_a'' = 13$ is observed with the shift of 0.2 MHz, which is slightly higher than those obtained for the other $K_a'' = 13$ transitions.

Since perturbation depends on the (accidental) presence of a close-by lying rovibrational level, then there may be areas in energy where many lines are shifted and others where they are not. This is most clearly seen for CHD_2CN where many lines cannot be fitted for $K_a'' = 17$, but fitting was then possible up to $K_a'' = 20$. Furthermore, even in the same energy region, some lines may be perturbed and others not. Above a certain value of K_a'' (22 for CHD_2CN and 18 for CH_2DCN) it was not possible to fit the measured lines correctly. It is difficult to know whether to attribute this to perturbations, a breakdown in the approximations used in the calculations of energy levels, or too limited a number of measurements to correctly determine the higher order constants combined with an inability to correctly determine which lines are perturbed and which are not.

In principle, the more lines with high K_a that are included in the fit, the better the determination of the higher order parameters and the more precise the prediction of other higher K_a transitions. However, including lines with high K_a demanded particular attention. We observed that lines with $K_a'' = 17$ for CH_2DCN could be fit acceptably with enough parameters. However, we were not satisfied with the fit for several reasons. First, the prediction of higher K_a lines is then degraded. Second, the higher-order centrifugal distortion constants change their value significantly or become undetermined when these transitions are included. Third, some lines of lower K_a that fit previously become badly predicted. This last problem also affected the $K_a'' = 21$ transitions of CHD_2CN. For these reasons we preferred the fit for CH_2DCN where lines are only included up to $K_a'' = 16$. Similarly, only lines up to $K_a'' = 20$ are fit for CHD_2CN.

It should be noted that two decatic centrifugal distortion constants P_{KJ} and P_{KKJ} were particularly needed by our high K_a measured transitions (from $K_a'' = 19$ of CHD_2CN and from $K_a'' = 16$ of CH_2DCN). Furthermore, the higher order centrifugal constants (H_{KJ}, and especially L_{JK} and L_{KKJ}) vary somewhat according to the exact choice of lines included in the fit and should be regarded as "fitting constants" rather than having high physical signification. However, a careful choice of lines to include and of the exact parameters to be fitted leads to the best prediction of higher K_a lines as shown by comparison with the measurements. These considerations concern only the lines of high K_a. Regardless of the exact (sensible) choice, the stronger lower K_a lines that are candidate for a first astrophysical detection are always predicted at the same frequency.

4. Conclusion

The rotational spectra of singly and doubly deuterated methyl cyanides, CH_2DCN and CHD_2CN, in the ground vibrational state have been recorded up to 945 GHz. The existing data set of CHD_2CN has been extended greatly and permits reliable predictions for a first astronomical identification of this molecule. For CH_2DCN, the prediction has been improved for high values of K_a. For both isotopologues, the extension of our data in high K_a transitions permitted observing an apparent interaction for the first time between the rotational energy levels of the ground and excited vibrational states, as already suggested for the parent species. This is an interesting spectroscopic aspect that could be pursued in later work.

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Appendix A: Synthesis of the deuterated isotopologues

In a Schlenk flask, equipped with a stirring bar, was introduced powdered potassium cyanide (1.17 g, 17.7 mmol), dry triethylene glycol (2 ml), and deuteromethyl iodide (2.00 g, 14.0 mmol). The mixture was cooled to 77 K, the flask was evacuated, and the stopcock was closed. The solution was then stirred for 6 h at 40 °C. After cooling at room temperature, the flask was connected to a vacuum line (0.1 mbar) equipped with two U-tubes with stopcocks (Fig. A.1). The first one was immersed in a bath at −30 °C to condense the high boiling impurities and the second one in a bath at −90 °C to selectively trap deuteroacetonitrile in a vacuum. Yield: 89%. *NMR data.* Synthesis of CH_2DCN: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.96 (t, $^2J_{HD}$ = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.71 ($^1J_{CD}$ = 20.7 Hz (t), $^1J_{CH}$ = 135.0 Hz (t), CH_2D); 116.5 (s, CN). Synthesis of CHD_2CN: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.96 (q, $^2J_{HD}$ = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.58 ($^1J_{CD}$ = 21.0 Hz (q), $^1J_{CH}$ = 135.0 Hz (d), CH_2D); 116.5 (s, CN).

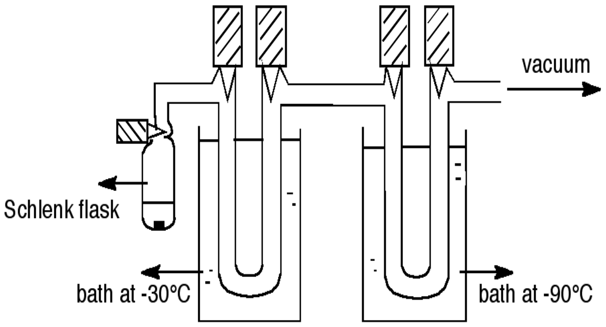

Fig. A.1. Synthesis scheme for the deuterated methyl cyanides.

Appendix B: Observed frequencies and fit of CHD_2CN and CH_2DCN in the ground state

Table B.1. Observed frequencies and fit of CHD_2CN in the ground state.

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	Uncertainty (MHz)	Obs.-Calc. (MHz)
10	1	10	9	1	9	164 043.8545	0.0300	–0.0041
10	6	4	9	6	3	164 742.8533+	0.0300	0.0732
10	6	5	9	6	4	164 742.8533+	0.0300	0.0732
10	5	5	9	5	4	164 771.0991+	0.0300	0.0271
10	5	6	9	5	5	164 771.0991+	0.0300	0.0271
10	4	7	9	4	6	164 794.7045+	0.0300	–0.0080
10	4	6	9	4	5	164 794.7045+	0.0300	–0.0080
10	0	10	9	0	9	164 798.6268	0.0300	–0.0157
10	3	8	9	3	7	164 814.4499	0.0300	0.0812
10	2	9	9	2	8	164 817.3348	0.0300	0.0334
10	2	8	9	2	7	164 851.1481	0.0300	–0.0190
10	1	9	9	1	8	165 599.7877	0.0300	–0.0045
37	5	32	38	4	34	166 150.9717c	0.0300	0.0654
37	5	33	38	4	35	166 164.1827c	0.0300	–0.0208
17	0	17	16	1	15	180 733.0036c	0.0300	0.0456

Notes. The full Table B.1 is available in electronic form at the CDS. A portion with only the 15 lowest frequency transitions is shown here for guidance regarding its form and content. Transitions are assigned with the rotational quantum numbers of the upper (first) and lower (second) levels. Observed frequencies are given. A "c" shows the *c*-type transitions. Transitions without "c" are of *a*-type. Sign "+" shows the blended transitions. An "e" (seen in the full table) shows the transitions observed but rejected from the fit as described in the text, because of the significant difference between observed and calculated frequencies; the observed minus calculated difference (Obs.-Calc.) is not given for these transitions.

Table B.2. Observed frequencies and fit of CH_2DCN in the ground state.

J'	K'_a	K'_c	J''	K''_a	K''_c	Frequency (MHz)	Uncertainty (MHz)	Obs.-Calc. (MHz)
28	20	8	27	20	7	482 765.4041e	0.0500	
28	20	9	27	20	8	482 765.4041e	0.0500	
28	17	11	27	17	10	483 686.7272e	0.0300	
28	17	12	27	17	11	483 686.7272e	0.0300	
28	16	12	27	16	11	483 953.9374+	0.0300	–0.0416
28	16	13	27	16	12	483 953.9374+	0.0300	–0.0416
28	15	13	27	15	12	484 203.4077+	0.0300	0.0576
28	15	14	27	15	13	484 203.4077+	0.0300	0.0576
28	14	14	27	14	13	484 435.8082+	0.0300	–0.0195
28	14	15	27	14	14	484 435.8082+	0.0300	–0.0195
28	13	15	27	13	14	484 651.8126+	0.0300	0.0072
28	13	16	27	13	15	484 651.8126+	0.0300	0.0072
28	12	16	27	12	15	484 851.5592+	0.0300	–0.0161
28	12	17	27	12	16	484 851.5592+	0.0300	–0.0161

Notes. The full Table B.2 is available in electronic form at the CDS. A portion with only the 14 lowest frequency transitions is shown here for guidance regarding its form and content. Transitions are assigned with the rotational quantum numbers of the upper (first) and lower (second) levels. Observed frequencies are given. A "b" (seen in the full table) shows the *b*-type transitions. Transitions without "b" are of *a*-type. Sign "+" shows the blended transitions. An "e" shows the transitions observed but rejected from the fit as described in the text, because of the significant difference between observed and calculated frequencies; the observed minus calculated difference (Obs.-Calc.) is not given for these transitions.

References

Anthoni, U., & Nielsen, H. 1984, J. Labelled Cmpds. Radiopharm., 21, 375

Bottinelli, S., Ceccarelli, C., Neri, R., & Williams, J. P. 2008, in Organic Matter in Space, Proc. IAU Symp., 251

Boucher, D., Burie, J., Bauer, A., Dubrulle, A., & Demaison, J. 1980, J. Phys. Chem. Ref. Data, 9, 659

Brown, F. X., Cosleou, J., Dangoisse, D., Demaison, J., & Wlodarczak, G. 1989, J. Mol. Spectrosc., 134, 234

Cazzoli, G., & Puzzarini, C. 2006, J. Mol. Spectrosc., 240, 153

Ceccarelli, C., Caselli, P., Herbst, E., Tielens, A. G. G. M., & Caux, E. 2007, in Protostars and Planets V, eds. B. Reipurth, D. Jewitt, & K. Keil (Tucson, AZ: Univ. Arizona Press), 951, 47

Chen, W., Bocquet, R., Boucher, D., Demaison, J., & Wlodarczak, G. 1991, J. Mol. Spectrosc., 150, 470

Cosleou, J., Wlodarczak, G., J., B., & Demaison, J. 1989, J. Mol. Spectrosc., 137, 47

Cosleou, J., Lopéz, J. C., L, A. J., Wlodarczak, G., & Demaison, J. 1991, J. Mol. Spectrosc., 149, 242

Demaison, J., Dubrulle, A., Boucher, D., & Burie, J. 1979, J. Mol. Spectrosc., 76, 1

Gadhi, J., Lahrouni, A., Legrand, J., & Demaison, J. 1984, J. Chim. Phys., 92, 1984

Gerin, M., Combes, F., Wlodarczak, G., et al. 1992, A&A, 259, L35

Halonen, L., & Mills, I. M. 1978, J. Mol. Spectrosc., 73, 494

Koivusaari, M., Horneman, V. M., & Antilla, R. 1992, J. Mol. Spectrosc., 152, 377

Kroto, H. W. 1975, in Molecular Rotation Spectra (John Wiley & Sons Ltd)

Le Guennec, M., Wlodarczak, G., Burie, J., & Demaison, J. 1992, J. Mol. Spectrosc., 154, 305

Matsumura, C., Hirota, E., Oka, T., & Morino, Y. 1962, J. Mol. Spectrosc., 9, 366

Müller, H. S. P., Drouin, B. J., & Pearson, J. C. 2009, A&A, 506, 1487

Motiyenko, R. A., Margulès, L., Alekseev, E. A., Guillemin, J. C., & & Demaison, J. 2010, J. Mol. Spectrosc., 264, 94

Parise, B., Ceccarelli, C., Tielens, A. G. G. M., et al. 2006, A&A, 453, 949

Pearson, J. C., & Müller, H. S. P. 1996, ApJ, 471, 1067

Peng, T. C., Despois, D., Brouillet, N., Parise, B., & Baudry, A. 2012, A&A, 543, A152

Pickett, H. M., Poynter, R. L., Cohen, E. A., et al. 1998, J. Quant. Spec. Radiat. Transf., 60, 883

Ratajczak, A., Taquet, V., Kahane, C., et al. 2011, A&A, 528, L13

Simečková, M., Urban, S., Fuchs, U., et al. 2004, J. Mol. Spectrosc., 226, 123

Tam, H., An, I., & Roberts, J. A. 1988, J. Mol. Spectrosc., 129, 202

Taquet, V., Ceccarelli, C., & Kahane, C. 2012, ApJ, 748, L3

Thomas, L. F., Sherrard, E. J., & Sheridan, J. 1955, Trans. Faraday Soc., 51, 619

Tolonen, A., Koivusaari, M., Paso, R., et al. 1993, J. Mol. Spectrosc., 160, 554

Watson, J. K. G. 1977, in Vibrational Spectra and Structure (Amsterdam: Elsevier)