A&A, 685, C1 (2024)
https://doi.org/10.1051/0004-6361/202449899e

Astronomy & Astrophysics

Impact of nonconvergence and various approximations of the partition function on the molecular column densities in the interstellar medium*

(Corrigendum)

M. Carvajal[1], C. Favre[2,3], I. Kleiner[4], C. Ceccarelli[3], E. A. Bergin[5], and D. Fedele[2]

[1] Dept. Ciencias Integradas, Facultad de Ciencias Experimentales, Centro de Estudios Avanzados en Física, Matemática y Computación, Unidad Asociada GIFMAN, CSIC-UHU, Universidad de Huelva, Spain, Instituto Universitario "Carlos I" de Física Teórica y Computacional, Universidad de Granada, Granada, Spain
e-mail: miguel.carvajal@dfa.uhu.es
[2] INAF – Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, Firenze 50125, Italy
[3] Univ. Grenoble Alpes, CNRS, IPAG, 38000 Grenoble, France
[4] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris-Est Créteil, Université de Paris, Institut Pierre Simon Laplace (IPSL), Créteil, France
[5] Dept. of Astronomy, University of Michigan, 311 West Hall, 1085 South University Avenue, Ann Arbor, MI 48109, USA

A&A, 627, A65 (2019), https://doi.org/10.1051/0004-6361/201935469

Key words. techniques: spectroscopic – ISM: abundances – radio lines: ISM – errata, addenda

In the original version of this paper, the calculated values of the internal partition function of methyl cyanide (CH_3CN) have some errors. This miscalculation came from using different values of the nuclear spin statistical weights for CH_3CN at different stages of the work. In this erratum, we specify the values of the nuclear spin statistical weights considered in the original work and by different authors that gave rise to the miscalculations. However, using incorrect values for the internal partition function of CH_3CN did not affect our conclusions. Here, we provide some clarifying details and enumerate the corrections carried out.

The rovibrational partition function of CH_3CN, $Q(T)$, defined as a direct sum of exponential terms, is approximated as a product of the rotational contribution, $Q_{\rm rot}(T)$, and the vibrational one, $Q_{\rm vib}(T)$ (Herzberg 1991; Carvajal et al. 2019):

$$Q(T) = \sum_i g_{\rm ns}^{\rm (i)}\,(2\,J_{\rm i}+1)e^{-\frac{E_{\rm i}}{kT}} \approx Q_{\rm rot}(T)\,Q_{\rm vib}(T), \tag{1}$$

where $J_{\rm i}$, $g_{\rm ns}^{\rm (i)}$, $E_{\rm i}$, and T are the rotational angular momentum, the nuclear spin degeneracy of energy level i, the rovibrational energy levels (in this case with respect to the ground vibrational state), and the temperature of the environment, respectively.

The vibrational contribution to the internal partition function, $Q_{\rm vib}(T)$, was computed using the harmonic approximation (Herzberg 1991; Carvajal et al. 2019). This was proven to be a good approximation for computing the vibrational partition function within the typical interstellar medium temperatures (Carvajal et al. 2019). The rotational partition function, $Q_{\rm rot}(T)$ (e.g., Herzberg 1991; Groner et al. 2007; Carvajal et al. 2019), can be computed as a direct sum:

$$Q_{\rm rot}(\text{direct sum}) = \sum_i g_{\rm ns}^{(i)}\,(2\,J_{\rm i}+1)\,e^{-\frac{E_{\rm i}^{\rm (rot)}}{kT}}, \tag{2}$$

where $E_{\rm i}^{\rm (rot)}$ represents the energy for the i-th rotational state. The degeneracy $g_{\rm ns}^{\rm (i)}$ is included in the definition of the rotational contribution of the partition function (Eq. (2)) because, in general, the value of $g_{\rm ns}^{\rm (i)}$ is associated with the quantum numbers, K, for a symmetric top (or $K_{\rm a}$ and $K_{\rm c}$ for an asymmetric top).

In addition, the rotational partition function (Eq. (2)) can be obtained with the approximated expression for symmetric tops (McDowell 1990) considering the rotational constants:

$$Q_{\rm rot}^{\rm McDowell}(T) \approx g'_{\rm ns}\,\sqrt{\frac{\pi}{A\,B^2}\left(\frac{k\,T}{h}\right)^3}\,e^{\left(\frac{h\,B\left(4-\frac{B}{A}\right)}{12\,k\,T}\right)}\left(1+\frac{1}{90}\left(\frac{h\,B\left(1-\frac{B}{A}\right)}{k\,T}\right)^2\right). \tag{3}$$

We note that the nuclear spin statistical weight in Eq. (3), $g'_{\rm ns}$, takes different values than the nuclear spin statistical weight in Eq. (2), $g_{\rm ns}^{\rm (i)}$.

The following are the corrections we made to the internal partition function of methyl cyanide given in the original paper:

1. The values from Tables 2 and 3 of the original paper concerning CH_3CN were recomputed according to the nuclear spin statistical weights defined here, and are presented in Tables 1 and 2;

2. The nuclear spin statistical weights reported in the literature and given in Table A.1 of the original paper needed extra clarification because they use different values, $g_{\rm ns}^{\rm (i)}$ or $g'_{\rm ns}$, according to the mathematical expression of the rotational partition function considered (i.e., Eq. (2) or (3), respectively);

* The corrected Table D.2 is available at the CDS via anonymous ftp to cdsarc.cds.unistra.fr (130.79.128.5) or via https://cdsarc.cds.unistra.fr/viz-bin/cat/J/A+A/685/C1

Table 1. Rotational partition function for CH_3CN.

T (K)	$Q_{rot}^{approx\ (a)}$	Q_{rot}(direct sum)$^{(b)}$	Rel. Diff. (%)$^{(c)}$
2.725	4.61	6.92	–33.38
5.0	11.18	14.25	–21.54
9.375	28.33	32.05	–11.61
18.75	79.50	82.16	–3.24
37.50	224.00	224.54	–0.24
75.0	632.35	632.59	–0.04
150.0	1786.82	1788.18	–0.08
225.0	3281.54	3285.29	–0.11
300.0	5051.45	5059.15	–0.15
500.0	10866.88	10892.77	–0.24

Notes. The direct sum values are compared to the classical approximation. $^{(a)}$Approximated expression of the rotational partition function for symmetric tops given in Eq. (3) (McDowell 1990). For this expression, the nuclear spin statistical weight is taken as $g'_{ns} = 2/3$. $^{(b)}$Rotational partition function computed as a direct sum with Eq. (2) using all the predicted rotational energy levels up to $J = 99$ (Müller et al. 2009). The nuclear spin degeneracy is considered to be $g_{ns} = 1$. $^{(c)}$Relative differences of Q_{rot}^{approx} with respect to the rotational direct sum values, Q_{rot}(direct sum).

3. According to the first two corrections, the values of the polynomial coefficients fitted to the rovibrational partition function values, given in Table B.2 of the original paper, were also corrected and are presented in Table 5;

4. The corrected values of the internal partition function of CH_3CN at the excitation temperature deduced for this molecule in NGC 7538 ($T = 350$ K) and the column density estimates for CH_3CN given in Table 7 of the original paper are reported in Table 6.

In Table 1 of this erratum, the classical approximation of the rotational partition function (Eq. (3)) for CH_3CN is compared to the direct sum expression for the rotational partition function (Eq. (2)). The nuclear spin weight of Eq. (2) of this erratum was omitted as in the original paper and, therefore, considered to be $g_{ns} = 1$. The classical approximation (Eq. (3)) was computed using the rotational constants from Müller et al. (2015) considering $g'_{ns} = 2/3$. The direct sum was computed for all the rotational energy levels up to $J = 99$ (Müller et al. 2009). This set of rotational energies is enough to make Q_{rot}(direct sum) reach convergence for temperatures up to $T = 500$ K (for more details, see Carvajal et al. 2019). In addition, the classical approximation for the rotational partition function contribution is not accurate enough for temperatures below 18.75 K. If the estimate of the molecular column density of CH_3CN for a cold interstellar medium region with a temperature around 10 K were carried out with the classical approximation (Eq. (3)), the molecular column density would be around 10% smaller than the estimate obtained with Q_{rot}(direct sum).

In Table 2 of this erratum, the values and their uncertainties of the rovibrational partition function (Eq. (1)), calculated as the product of the direct sum of the rotational contribution and the harmonic vibrational approximation, are given from 2.725 to 500 K (Col. 3). These values are compared with those of the rovibrational partition function provided by the CDMS catalog (our Col. 4; see also Endres et al. 2016). To allow for a comparison, the nuclear spin statistical weight has been reduced in both contributions and considered to be $g_{ns} = 1$. The values computed in this work and the CDMS ones disagree at temperatures higher than 300 K. The uncertainties of the internal partition

Table 2. Vibrational and rotational-vibrational partition function for CH_3CN.

		CH_3CN		
T (K)	$Q_{vib}^{harm\ (a)}$	Q_{rv}(present work)$^{(b)}$	Q(CDMS)$^{(c)}$	Rel. Diff. (%)$^{(d)}$
2.725	1.000000	6.9178(57)	6.9177	0.00
5.0	1.000000	14.2462(49)	14.2462	0.00
9.375	1.000000	32.0478(45)	32.0478	0.00
18.75	1.000000	82.1586(42)	82.1586	0.00
37.50	1.000002	224.5412(40)	224.5412	0.00
75.0	1.001822	633.747(16)	633.8360	–0.01
150.0	1.063424	1901.60(80)	1903.8737	–0.12
225.0	1.233076	4051.0(39)	4022.6080	0.71
300.0	1.507618	7627.(11)	7341.8162	3.89
500.0	2.970625	32 358.(72)	24 312.9485	33.09

Notes. The values obtained in the present erratum are compared to those published in the CDMS catalog. The nuclear spin degeneracy was considered to be $g_{ns} = 1$ in this work. $^{(a)}$The vibrational partition function was computed with the harmonic approximation. $^{(b)}Q_{rv}$(present work)= Q_{rot}(direct sum) Q_{vib}^{harm}. An upward estimate of the uncertainties are given in parentheses in units of the last quoted digits. $^{(c)}$Partition function in the CDMS catalog computed considering the rotational contribution as a direct sum and vibrational states up to about 1200 cm^{-1} (Endres et al. 2016). Unlike the values reported in the CDMS catalog, the nuclear spin statistical weight is taken here, for the sake of comparison, to be $g_{ns} = 1$ instead of 2. $^{(d)}$Relative difference between the partition function given in the present work and the values in the CDMS catalog.

function are rather small despite being estimated upward, considering the high rotational energy uncertainties of 100 MHz and uncertainties of 1 cm^{-1} for the vibrational fundamentals. In fact, the rovibrational partition function of CH_3CN at $T = 500$ K is 32 358. and has an uncertainty of 72.; in other words, even with an upward estimate of the uncertainties, the relative uncertainty for the partition function at $T = 500$ K is around 0.2%.

In Table D.2 (available at the CDS) of this erratum, the rotational, vibrational, and rovibrational partition function calculated in the present work for CH_3CN are provided in intervals of 1 K up to $T = 500$ K. In addition, the values for the temperatures 2.725, 5, 9.375, 18.75, 37.5, 75, 150, 225, 300, and 500 K are also provided (without any truncation or rounding). In Table 2, these values for the rovibrational partition function are truncated and rounded off according to their uncertainties.

As previously noted, the value of the nuclear spin statistical weight in Eq. (3), g'_{ns}, is different than the nuclear spin statistical weight in Eq. (2), $g_{ns}^{(i)}$. The values of g'_{ns} and $g_{ns}^{(i)}$ used in this work are given in Table 3 and are compared with others from the literature (Gordy & Cook 1984; Blake et al. 1987; Bunker & Jensen 1989; Turner 1991; Pickett et al. 1998; Rinsland et al. 2008; Mangum & Shirley 2015; Endres et al. 2016). In Table 3, the nuclear spin statistical weight in Eq. (2) for CH_3CN is given as $g_{ns}^{(i)} = g_{ns}$ because it has the same value for the three possible symmetries of the rotational states, A_1, A_2, and E (see our Table 4 and Bunker & Jensen 1989). In this erratum we use $g_{ns} = 1$, which, when applying the temperature diagram method, should be substituted in Eq. (2) of the original paper to compute the degeneracy of the upper level before including it in the intensity expressions (Eqs. (3) and (4) of the original paper). Nevertheless, the values of g_{ns} for the rotational states with quantum number $K = 0$ or $K \neq 3n$ (n is an integer) are taken as half the value of the $K = 3n$ states because the two $K = 3n$ rotational states

Table 3. Nuclear spin statistical weight values – g_{ns} in Eq. (2) and g'_{ns} in Eq. (3) – for all symmetries of methyl cyanide considered in this work compared with others used in the literature.

	g_{ns}	g'_{ns}
This work/Blake et al. (1987)	$1^{(a)}$	2/3
Bunker & Jensen (1989)/Rinsland et al. (2008)	12	8
JPL/CDMS	2	4/3
Mangum & Shirley (2015)/Turner (1991)/Gordy & Cook (1984)	1/2	1/3

Notes. $^{(a)}$ The value of g_{ns} in Eq. (2) considered in this work is 1 and it is the same for the three possible symmetries (A_1, A_2, and E) of the rotational states of CH_3CN (Bunker & Jensen 1989).

Table 4. Symmetry of the rotational states (Γ_{rot}) for a $C_{3v}(M)$ molecule obtained according to the rotational quantum numbers (J,K) (Bunker & Jensen 1989).

K	Γ_{rot}
0	A_1 (J even)
0	A_2 (J odd)
$3n \pm 1^{(a)}$	E
$3n^{(a,b)}$	$A_1 \oplus A_2$

Notes. $^{(a)}n$ is an integer. $^{(b)}$The two rotational states with $K = 3n$ are labeled with symmetries A_1 and A_2. Therefore, when the two $K = 3n$ states are considered as a degenerate K doublet, the g_{ns} value for $K = 3n$ states in Eq. (2) is taken to be two times the nuclear spin statistical weights of the rotational states with $K = 0$ or $K \neq 3n$ (see, e.g., Loren & Mundy 1984; Turner 1991).

Table 5. Polynomial coefficients fitted to the rovibrational partition function values of the present work for CH_3CN.

Sixth-order polynomial$^{(a)}$		$\log_{10}(Q)$ expansion$^{(b)}$	
A_0	–1.13655	a_0	0.331365
A_1	2.55403	a_1	1.19788
A_2	0.112615	a_2	–0.132771
A_3	–0.000657908	a_3	0.115758
A_4	3.21106×10^{-6}	a_4	0.110291
A_5	-6.30594×10^{-9}	a_5	–0.104387
A_6	5.21834×10^{-12}	a_6	0.0225974
T	Rel. Diff. (%)$^{(c)}$		Rel. Diff. (%)$^{(c)}$
2.725	3.92		0.05
5.0	–0.86		–0.27
9.375	–0.44		0.54
18.75	–0.28		–0.48
37.50	0.15		–0.03
75	–0.02		0.50
150	0.00		–0.47
225	0.00		–0.11
300	0.00		0.32
500	0.00		–0.07

Notes. $^{(a)}$Fitted coefficients of a sixth-order polynomial of Q in terms of the temperature, T, according to the equation $Q(T) = \sum_{n=0}^{6} A_n T^n$. $^{(b)}$A nonlinear fit of a power expansion of $\log_{10}(Q)$ in terms of the $\log_{10}(T)$ according to the equation $\log_{10} Q(T) = \sum_{n=0}^{6} a_n (\log_{10} T)^n$. $^{(c)}$Relative difference between the rovibrational partition function computed in the present work (Table 2, Col. 3) and the values provided by the polynomial expansions.

of CH_3CN (with A_1 and A_2 symmetries) are considered to be a degenerate K doublet (see Table 4 and Loren & Mundy 1984; Turner 1991). Hence, in this erratum, the nuclear spin weight of $K = 3n$ states is taken to be 2, whereas it is 1 for the rotational states with $K = 0$ or $K \neq 3n$. Therefore, the rotational partition function calculated as a direct sum is Q_{rot}(direct sum) = 5059.15 at T=300 K assuming $g_{ns} = 1$ (see Table 1), whereas the one published by the JPL and in the CDMS catalog is around 10118 (2 Q_{rot}(direct sum)) and the one calculated by Rinsland et al. (2008) is about 60709 (12 Q_{rot}(direct sum)). These three values agree with one another, differing only by a normalization factor that is due to the different nuclear spin statistical weights considered (see Table 3).

It is worth mentioning that the internal partition function values obtained in this erratum are in general comparable with those provided in HITRAN2020 (Gamache et al. 2021). Gamache et al. (2021) computed the internal partition function as the product of the classical approximation for the rotational partition function (Eq. (3)), with a nuclear spin degeneracy $g'_{ns} = 8$, and the harmonic approximation for the vibrational partition function. To compare our results with those from HITRAN2020, we reduced the HITRAN2020 nuclear spin statistical weight by dividing their values by 12. Below 3 K, the HITRAN2020 result is smaller than ours, with a relative difference of 2.8% at $T = 3$ K, 9.2% at $T = 2$ K, and 26.7% at $T = 1$ K. Above 4 K, HITRAN2020 provides practically the same result as this work, with relative differences of less than 1%. In fact, at T=500 K, the partition function of HITRAN2020 is 32363.33, essentially the same as our value of 32358.34 (i.e., a relative difference of 0.02%). This comparison with HITRAN2020 corroborates what was confirmed in the original paper: (a) the classical expression of the rotational partition function for symmetric tops (Eq. (3)) is a good approximation for higher temperatures and, (b) it is preferable to calculate the vibrational partition function with the harmonic approximation, considering all the fundamental vibrational energies, rather than using the direct sum for the vibrational energies when the available vibrational energy term values are limited to the lower energies.

The rovibrational partition function has been tabulated to a nonlinear sixth-order power expansion in terms of the temperature and a nonlinear sixth-order power expansion of $\log_{10}(Q)$ in terms of the $\log_{10}(T)$. The polynomial coefficients have been fitted to the rovibrational partition function values obtained in the present work (see Table 2). Table 5 provides the polynomial coefficients derived from the fitting as well as the corresponding relative differences between the fitted polynomial expansions and the rovibrational partition function values computed for this erratum. The sixth-order expansion is in good agreement for temperatures above 5 K, and the logarithm polynomial is generally in reasonable agreement with Q_{rv}(present work) from $T = 2.725$ K up to $T = 500$ K. Because of the small relative differences between these two power expansions and the internal partition function values computed for CH_3CN in this erratum (see Table 5), both power expansions can be used to interpolate the rovibrational partition function at any temperature from 2.725 to 500 K. Nevertheless, in the present work, the fitted polynomial expansion has a better agreement at higher temperatures than the nonlinear fit of the logarithm polynomial expansion.

Table 6. Column density estimates of CH_3CN in the NGC 7538 survey according to the partition function computed in the present work (rovibrational partition functions are computed as the product of the rotational contribution, given as a direct sum, and the harmonic approximation of the vibrational partition function) and in the CDMS and JPL databases.

	Linear interpolation [(a)]			Nonlinear interpolation [(c)]			Present work [(d)]
CH_3CN	Present work	CDMS	Rel. Diff. [(b)]	Present work	CDMS	Rel. Diff. [(b)]	
$Q(T = 350$ K)	13810.0	11584.6		11139.0	10264.2		11209.6
N (cm^{-2})	$(53.1\pm3.5)\times10^{13}$	$(44.5\pm3.0)\times10^{13}$	18%	$(42.8\pm2.9)\times10^{13}$	$(39.5\pm2.6)\times10^{13}$	8%	$(43.1\pm2.9)\times10^{13}$

Notes. The interpolated partition function at the excitation temperatures deduced (350.33 K) is compared with the value computed in the present work. [(a)]The linear interpolation was carried out using the values of Q_{rv} at $T = 300$ K and 500 K. [(b)]Relative difference between the column density estimates obtained from the partition functions computed in the present work and those given in the CDMS and JPL catalogs, using the formalism Rel. Diff = $\frac{|a-b|}{(a+b)/2}$. [(c)]The nonlinear interpolation was carried out with the fitted sixth-order polynomial expansion of Q_{rv} in terms of the temperature. The polynomial coefficients for the partition function of this work are given in Col. 2 of Table 5. [(d)]Partition function computed with Eqs. (1) and (2) for the excitation temperature deduced for the NGC 7538 survey and provided in Table D.2, available at the CDS.

Therefore, we decided to use the former to interpolate the partition function at the excitation temperature of the NGC 7538 survey to estimate the molecular column density.

The results of the different approximations of the rovibrational partition function used to derive the total beam-averaged column density for CH_3CN are given in Table 6 at the specific temperature of $T = 350.33$ K from the NGC 7538 survey. The more reliable estimate of the total column density is given in Col. 8 of Table 6; it was obtained with the partition function computed in the present work at $T = 350$ K and reported in Table D.2 (available at the CDS) of this erratum. The result obtained in the present work with the rotational-vibrational partition function for CH_3CN is compared with the results obtained with the partition function values reported in the JPL or CDMS catalogs and considering the linear and nonlinear interpolation approximations at $T = 350$ K. For the nonlinear interpolation at $T = 350$ K, we used the fitted sixth-order polynomial expansion of Q_{rv} in terms of the temperature. The coefficients of Q_{rv} (present work) can be found in Col. 2 of Table 5. The nonlinear interpolation of the partition function given in this erratum (Col. 5 of Table 6) provides practically the same result for the total column density as that obtained with the partition function values of Table D.2, available at the CDS (Col. 8 of Table 6). The linear interpolation at $T = 350$ K was carried out using the values of Q_{rv} at $T = 300$ K and 500 K. In the present work, the values of Q_{rv}(present work) at $T = 300$ K and 500 K can be found in Table 2. The relative differences between the column densities estimated with the different methods are also given in Table 6. The relative difference between the column densities estimated using the partition function of this work (Col. 8 in Table 6) and that of the CDMS and JPL databases obtained with a nonlinear interpolation (Col. 6 in Table 6) is 9%. The relative differences for the cases of the linear and nonlinear interpolations between the partition function values of this work and those obtained from the CDMS and JPL databases for CH_3CN are 18% and 8%, respectively. The new and corrected values of Table 6 are practically two-thirds the values given in Carvajal et al. (2019) for both the partition function values and the column densities.

Acknowledgements. We acknowledge the comments and useful discussions with Dr. Edgar Mendoza. This work has received funding from the European Union's Horizon 2020 research and innovation program under Marie Sklodowska-Curie grant agreement No. 872081 and grant PID2022-136228NB-C21 funded by MICIU/AEI/10.13039/501100011033 and, as appropriate, by "ERDF A way of making Europe", by "ERDF/EU", by the "European Union" or by the "European Union NextGenerationEU/PRTR".

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