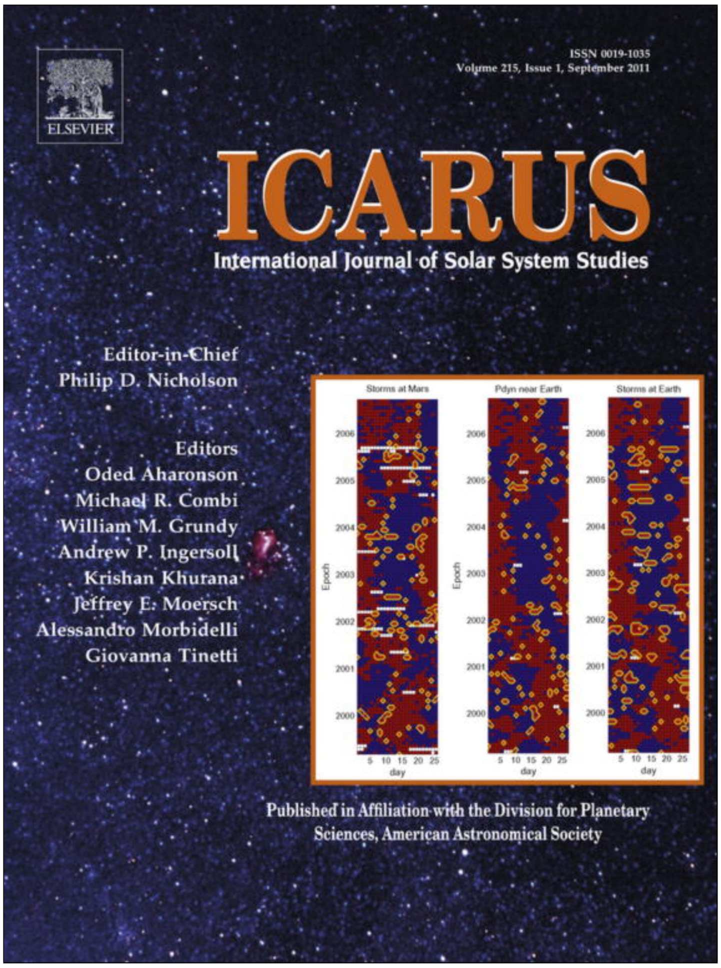

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Total internal partition sums to support planetary remote sensing

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ABSTRACT

Total internal partition sums are determined from 65 to 3010 K for $^{13}C^{18}O_2$, $^{13}C^{18}O^{17}O$, $^{12}CH_3D$, $^{13}CH_3D$, $H^{12}C^{12}CD$, $^{13}C^{12}CH_6$, $^{12}CH_3{}^{79}Br$, $^{12}CH_3{}^{81}Br$, $^{12}CF_4$, $H^{12}C^{12}C^{12}C^{12}CH$, $H^{12}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{13}C^{14}N$, $H^{12}C^{13}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{12}C^{15}N$, $D^{12}C^{12}C^{12}C^{14}N$, $^{14}N^{12}C^{12}C^{14}N$, $^{15}N^{12}C^{12}C^{15}N$, $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, $^{13}C^{32}S$, H_2, HD, $^{32}S^{16}O$, $^{32}S^{18}O$, $^{34}S^{16}O$, $^{12}C_3H_4$, $^{12}CH_3$, $^{12}C^{32}S_2$, $^{32}S^{12}C^{34}S$, $^{13}C^{32}S_2$, and $^{32}S^{12}C^{33}S$. These calculations complete the partition sum data needed for additional isotopologues in HITRAN2008 and also extend the partition sums to molecules of astrophysical interest. These data, at 25 K steps, are incorporated into a FORTRAN code (TIPS_2011.for) that can be used to rapidly generate the data at any temperature in the range 70–3000 K.

1. Introduction

The total internal partition sum (TIPS) is an important physical parameter that is necessary for a variety of purposes. From the TIPS, a number of thermodynamic quantities can be derived. An accurate value of the partition sum is required for the determination of relationships between the intensity of a spectral line and the square of the transition moment, the Einstein A coefficient, or the oscillator strength (Gamache and Goldman, 2001). The spectral line intensity at a particular temperature can be computed from knowledge of the line position, lower state energy, intensity at a reference temperature, and the partition sums at both temperatures. These relationships are essential when studying planetary atmospheres, because these systems are not isothermal. With a database of spectral lines of important atmospheric molecules, such as the HIgh-resolution TRANsmission molecular absorption database (HITRAN) (Rothman et al., 2009), and the partition sum at relevant temperatures, atmospheric spectra can be inverted to obtain concentration profiles. Partition functions are also needed for the study of stellar atmospheres. Sauval and Tatum (1984) determined partition functions over a temperature range of 1000–9000 K for some 300 diatomic molecules of astrophysical interest. Irwin (1987) later refined the work of Sauval and Tatum for H_2 and CO and later Irwin (1988) extended the partition functions to consider polyatomic molecules that significantly affect the stellar atmospheric equation of state and which were of interest to the JANAF (Joint-Army–Navy–Air Force) program. Note that, in the literature, the terms partition function and partition sum are often interchanged.

In 2003, Fischer et al. (2003) made calculations for all species present on the HITRAN'2000 database (Rothman et al., 2003). This database has been updated and expanded since then, with the most recent version being the 2008 version (Rothman et al., 2009). In the present study, theoretical calculations of partition sums are made for the species that were introduced in HITRAN'2008. These species include two minor (in the sense of terrestrial abundance) isotopologues of carbon dioxide ($^{13}C^{18}O_2$ and $^{13}C^{18}O^{17}O$), a minor isotopologue of ethane ($^{13}C^{12}CH_6$), two isotopologues of monodeuterated methane ($^{12}CH_3D$ and $^{13}CH_3D$), a carbon-13 isotopologue of ethylene ($^{13}C^{12}CH_6$), methylbromide ($^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$), and carbon tetrafluoride ($^{12}CF_4$). The $^{12}CH_3D$ isotopologue was already present in the database, but the TIPS was recalculated using improved molecular parameters.

Also a number of molecules (and isotopologues) important in planetary, stellar, and cometary atmospheres as well as in interstellar media will soon be introduced into HITRAN and therefore the TIPS were calculated for them as well. For instance, sulfur monoxide (SO) is present in the atmosphere of Venus (Na et al., 1990), and it has also been detected in the atmospheres of Io (de Pater et al., 2002), and comets (Boissier et al., 2007). The CS_2 molecule has been detected in the atmosphere of Jupiter after its collision with the Shoemaker–Levy 9 comet (Atreya et al., 1995), and it was also tentatively detected in comets (Crovisier, 2006) and the atmosphere of Venus (Hua et al., 1979). An analogous situation

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exists for carbon monosulfide (CS). The methyl radical (CH_3) has been detected in the atmospheres of Neptune (Bézard et al., 1999) and Saturn (Bézard et al., 1998) by the Infrared Space Observatory (ISO). CH_3 also plays an important role in Titan's methane cycle, although no direct spectroscopic observations have yet been reported. The recent studies of Titan's atmosphere by the spectrometers on the Cassini mission (Coustenis et al., 2007) as well as 3 μm high-resolution ground-based studies with NIRSPEC/Keck II (Seo et al., 2009) revealed a number of molecules not currently present in HITRAN, such as propane (C_3H_8), diacetylene (C_4H_2), cyclopropene (C_3H_4), cyanoacetylene (HC_3N) and cyanogen (C_2N_2). Finally, molecular hydrogen (H_2) is the most abundant gas in the atmosphere of gas giants and knowledge of its partition sum is essential.

We therefore calculated partition sums for: mono-deuterated acetylene ($H^{12}C^{12}CD$), an isotopologue of diacetylene ($H^{12}C^{12}C^{12}C^{12}CH$), six isotopologues of cyanoacetylene ($H^{12}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{13}C^{14}N$, $H^{12}C^{13}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{12}C^{15}N$, $D^{12}C^{12}C^{12}C^{14}N$), two isotopologues of dicyanogen ($^{14}N^{12}C^{12}C^{14}N$, $^{15}N^{12}C^{12}C^{15}N$), four isotopologues of carbon sulfide ($^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, $^{13}C^{32}S$), two isotopologues of the hydrogen molecule (H_2, HD), three isotopologues of sulfur oxide ($^{32}S^{16}O$, $^{32}S^{18}O$, $^{34}S^{16}O$), methylacetylene ($^{12}C_3H_4$), methyl radical ($^{12}CH_3$), and four isotopologues of carbon disulfide ($^{12}C^{32}S_2$, $^{32}S^{12}C^{34}S$, $^{13}C^{32}S_2$, $^{32}S^{12}C^{33}S$). The methods used are based on previous work of Fischer and Gamache (2002), Gamache et al. (1998, 2000), and Gamache and Rothman (1992). Calculations are compared to values in the literature whenever possible, predominately with JPL (Pickett et al., 2003) or CDMS (Müller et al., 2005) databases depending of which one is more recent. Partition sums calculated in this work will serve as necessary supplemental information for the species that already exist in the HITRAN database, as well as for species of astrophysical importance that will be introduced to the database in the near future.

2. Method for calculating the total internal partition sum

The total internal partition sum of a molecule is defined as a direct sum over all states, *s*, of the factor $\exp(-hcE_s/kT)$, where, *h* is the Planck constant, *c* is the speed of light, *k* is the Boltzmann constant, *T* is the temperature in Kelvin, and E_s is the energy of state *s* in wavenumber units, which includes electronic, vibrational, rotational and any other quantized motion. The partition function, *Q*, a function of temperature, is written

$$Q(T) = d_i \sum_{\text{all states}\,s} d_s e^{-hcE_s/kT}, \tag{1}$$

where d_i is the state-independent degeneracy factor and d_s is the state-dependent degeneracy factor, discussed later in this section.

Because this calculation is a direct sum over all quantized energy states of a molecule, it requires that the energy levels and degeneracy factors of the molecule be known. As the energy of state *s* increases, the exponential factor approaches zero and effectively stops contributing to the sum. The state at which the sum can be truncated is said to be the state at which the calculation has converged. The values at high energies can often be difficult to obtain for various reasons, and for these cases some approximations must be made.

One useful approximation, called the product approximation (Gamache et al., 1990), is made when molecules have large separations between the ground and excited electronic states. In this case, ignoring the vibration–rotation interaction, the total energy is taken as $E_{tot} \approx E_{vib} + E_{rot}$, where E_{vib} is the vibrational energy and E_{rot} is the rotational energy. When vibration–rotation interactions can be ignored, the TIPS is written

$$Q(T) = Q_{vib}Q_{rot} = \sum_{\substack{\text{vibrational}\\ \text{states}}} d_{vib}\, e^{-hcE_{vib}/kT} \times \sum_{\substack{\text{rotational}\\ \text{states}}} d_{rot}\, e^{-hcE_{rot}/kT}. \tag{2}$$

This approximation is used when many rotational energy levels are available for the ground vibrational state but few rotational energy levels are available for excited vibrational states. Now the problem is reduced to computing Q_{vib} and Q_{rot} individually.

The product approximation was utilized for many of the molecules in this study. Rotational partition functions were determined by using McDowell's formulas (McDowell, 1988, 1990), which are a set of analytical formulas for calculating Q_{rot} for molecules with various symmetries (here for linear molecules and symmetric top molecules). For the vibrational partition function, the Harmonic Oscillator Approximation (HOA) of Herzberg (1960) was used. This approximation gives Q_{vib} as a product over the vibrational fundamentals, ω_i, and is written

$$Q_{vib} = \prod_i \left(\frac{1}{1 - e^{-hc\omega_i/kT}} \right). \tag{3}$$

Q_{vib} as calculated within the product approximation treats the vibrations as an infinite sum of harmonic oscillators, see Herzberg (1960), p. 503. This approach will include contributions from states above the dissociation level, which do not exist. As long as the temperature is low enough, these states above dissociation will not contribute significantly to Q_{tot} (see the discussion of convergence above). For the temperatures of this study, 65–3500 K, this approximation has been shown to agree quite well with direct sum calculations of the partition function (Gamache et al., 2000). However, caution should be used at the high temperatures for molecules/isotopologues with low dissociation energies.

There are two types of degeneracy factors, state dependent and state independent. Frequently, state-independent degeneracy factors are neglected from the partition sum calculation because many applications use the partition function to go from the intensity of a line at one temperature to the line intensity at another temperature. In such applications, the state-independent degeneracy factors cancel out because a ratio of partition functions is taken. For a true value of $Q(T)$ that can be used to determine thermodynamic functions, however, these factors must be included in the calculation. Therefore, in this work, efforts have been made to take all degeneracy factors into account, and thus obtain a correct value of the TIPS.

The state-dependent degeneracy factor is a product of two components in general. The first is the $(2J+1)$ factor, which is the degeneracy of a state with total angular momentum *J*. The second state-dependent component occurs in systems where the rotational wavefunction couples with the nuclear wavefunctions of the atoms in the molecule that are being interchanged in symmetry operations that leave the molecule unchanged. The net effect of this coupling is that sometimes the even and odd symmetry states have different statistical weights. These states are identified by *J* and *K*, the projection of the total angular momentum *J* along the internuclear *z*-axis. For a correct value of the TIPS, it is crucial that these values are factored into the calculation.

The formulas for the nuclear statistical weights of molecules that exchange two identical nuclei in symmetry operations have been given by Herzberg (1960) or Bunker and Jensen (1998). For Fermi or Bose systems (defined by the nuclei of the atoms being interchanged in the symmetry operations having half-integer spins or integer spins, respectively), the following equations provide the state-dependent degeneracy factors:

$$\begin{array}{l} \textit{Fermi system} - \textit{even level} \\ \textit{Bose system} - \textit{odd level} \end{array} \quad \frac{1}{2}\left[(2I_x+1)^2 - (2I_x+1)\right], \tag{4a}$$

Table 1
Nuclear spins for atomic species presented in this work.

Atom	Spin	Atom	Spin
H	1/2	^{14}N	1
D (^2H)	1	^{15}N	1/2
^{12}C	0	^{19}F	1/2
^{13}C	1/2	^{32}S	0
^{16}O	0	^{33}S	3/2
^{17}O	5/2	^{34}S	0
^{18}O	0	^{79}Br	3/2
		^{81}Br	3/2

$$\begin{array}{l} \textit{Fermi system} - \textit{odd level} \\ \textit{Bose system} - \textit{even level} \end{array} \frac{1}{2}[(2I_x+1)^2+(2I_x+1)], \tag{4b}$$

where I_x is the nuclear spin of the atoms that are exchanged during the symmetry operations. For molecules that have more than one pair of atoms exchanged, Herzberg (1960) gives expressions for the number of spin functions for each state. For symmetric top molecules, $^{12}CH_3D$ for example, the state-dependent degeneracy factors are

$$\frac{1}{3}(2I+1)(4I^2+4I+3) \tag{4c}$$

for K divisible by 3 (including 0) and

$$\frac{1}{3}(2I+1)(4I^2+4I) \tag{4d}$$

for K not divisible by 3.

For spherical rotors the determination of the spin factors is slightly more complicated. The statistical weights for CF_4 levels are 5, 2, and 3 for the A, E, and F states respectively. For details see Herzberg (1960) or Bunker and Jensen (1998); in fact as molecules become more complicated the symmetry methods of Bunker and Jensen (1998) are easier to apply.

For reference, Table 1 gives nuclear spins for relevant atoms in this work.

State-independent factors occur in molecules that have atoms that are not interchanged during symmetry operations. The factor is expressed in the form $\Pi\ (2I+1)$, where I is the nuclear spin and the product is done over all atoms that are not exchanged. Since these factors are often neglected, it may be necessary to multiply or divide by an integer value to obtain agreement with values found the literature, if these factors have in fact been omitted in the study.

FORTRAN codes were written to perform the calculations, and the TIPS were computed at 1 K intervals from 1 to 3500 K. The results for $Q(T)$ were taken at 25 K intervals from 65 K to 3010 K to be used in a four-point Lagrange interpolation scheme. The reasons for using this interpolation over a four or five-coefficient polynomial fit are numerous and are discussed by Fischer et al. (2003). The partition functions computed here will be added to a new version of the partition function code (TIPS_2011.for).

3. Calculations

3.1. CO_2

Two isotopologues of carbon dioxide were considered in this study: $^{13}C^{18}O_2$ and $^{13}C^{18}O^{17}O$ (HITRAN codes 838 and 837, respectively). The rotational state-dependent factor for 838 was calculated using basic spectroscopic rules (Herzberg, 1960). The two identical nuclei exchanged in this molecule are the ^{18}O atoms, which have a nuclear spin $I = 0$, hence a Bose system. The rules yield a onefold degeneracy for even energy levels and a zerofold degeneracy for odd levels, meaning that odd levels do not exist (i.e. half of the states *do not* exist for the molecule). The state-independent factor is simply $(2I+1)$ of the central atom, which for ^{13}C ($I = 1/2$) is 2. In the analytical model of McDowell (1988) the average number of states is needed. The state-independent factor is 2 but half the states are missing so the average degeneracy is 1 for 838. Note, the $(2J+1)$ factor is accounted for in McDowell's formulation. For 837, there is no state-dependent factor since the molecule is not symmetric, so the state-independent factor is

$$\prod_{x=1}^{3}(2I_x+1) = (2(1/2)+1)(2(0)+1)(2(5/2)+1) = 12. \tag{5}$$

For both isotopologues, the partition sums were calculated using McDowell's analytical formula for linear molecules (McDowell, 1988). Rotational constants were taken from Toth et al. (2008) for 838, and from Teffo et al. (1998) for 837, and are listed in Table 2. Vibrational fundamentals were estimated for 838 using a scheme that considers the isotopic shift relation in the molecule and using $^{12}C^{16}O_2$ (626), $^{13}C^{16}O_2$ (636) and $^{12}C^{18}O_2$ (828) as references, since they have known vibrational fundamentals. The ratios of the fundamental vibrations (*e.g.* $\nu_1(^{13}C^{16}O_2)/\nu_1(^{12}C^{16}O_2)$, etc.) between the two isotopologues were determined. The fundamental vibrations for $^{13}C^{18}O_2$ were estimated using the fundamental values for $^{12}C^{18}O_2$ and the computed ratios. For the $^{18}O^{13}C^{17}O$ molecule, the data from $^{16}O^{12}C^{17}O$ and $^{16}O^{13}C^{17}O$ were used in a similar method to estimate the fundamental vibrations. The resulting estimated frequencies are a few percent lower than those of the related isotopologue. The final estimated vibrational fundamentals for 838 and 837 are tabulated in Table 3.

A search of the literature yielded no values for comparison. However, a check of the calculations is desirable. Because the molecular constants (both vibrational and rotational) for $^{12}C^{16}O_2$, $^{13}C^{18}O_2$ and $^{18}O^{13}C^{17}O$ are similar, the $Q(T)$s computed here can be compared with those for $^{12}C^{16}O_2$ by scaling out the degeneracy factors. Setting the average degeneracy factors to 1 is accomplished by multiplying the $Q(T)_{rot}$ by 2 for 626 (since the total degeneracy of isotopologue 626 is ½). For 838 the factor is already 1, and $Q(T_{rot})$ for 837 is divided by 12. At 296 K, this procedure yields the values (scaled values are denoted by the asterisk) $Q^*_{rot\text{-}626} = 529.4$, $Q_{rot\text{-}838} = 595.5$, and $Q^*_{rot\text{-}837} = 578.7$; a −12% difference between 626 and 838 and a −9% difference between 626 and 837 for the rotational partition functions. The vibrational partition function data at 296 K are $Q_{vib\text{-}626} = 1.084$, $Q_{vib\text{-}838} = 1.098$, (1.3% difference compared to 626), and $Q_{vib\text{-}837} = 1.097$ (1.2% difference compared to 626). Both the rotational and vibrational partition functions are larger for the species considered here compared to 626, which is expected since the rotational constants and the vibrational fundamentals are smaller than those of 626. The product $Q_{vib} * Q_{rot}$ is used to generate the TIPS for these isotopologues.

3.2. CH_3D

The partition sums for $^{12}CH_3D$ were recalculated (see Fischer et al. (2003)) in this study using the correct vibrational fundamentals for this isotopologue (Young, N., Descent of Symmetry and Correlation Diagrams in Vibrational Spectroscopy, Department of Chemistry, University of Hull, UK, 2010, see http://www.hull.ac.uk/chemistry/courseNotes.php?year=pt&course=37). Degeneracy factors and rotational constants remain unchanged from Fischer

Table 2
Rotational constants in cm^{-1} for $^{13}C^{18}O_2$ from Toth et al. (2008) and $^{13}C^{18}O^{17}O$ from Teffo et al. (1998).

	$^{13}C^{18}O_2$	$^{13}C^{18}O^{17}O$
B	$3.46834282 \times 10^{-1}$	3.5694456×10^{-1}
D	1.05943×10^{-7}	1.1113×10^{-7}
H	1.49×10^{-13}	-1.8×10^{-13}

Table 3
Calculated vibrational fundamentals in cm^{-1} for $^{13}C^{18}O_2$ and $^{13}C^{18}O^{17}O$.

	$^{13}C^{18}O_2$	$^{13}C^{18}O^{17}O$
ν_1	1332.7300	1335.06
ν_2	638.4371	640.871
ν_3	2248.41	2257.02

Table 4
Rotational constants in cm^{-1} for $^{13}CH_3D$ from Ulenikov et al. (2000).

Constant	Value/cm^{-1}
A	5.25082109
B	3.876884527
D_j	5.243010×10^{-5}
D_{jk}	1.276156×10^{-4}
D_k	-7.896593×10^{-5}
H_j	1.43479×10^{-9}
H_{jk}	1.214490×10^{-8}
H_{kj}	-6.7214×10^{-9}
H_k	-1.6436×10^{-9}

et al. (2003), with the only improvement being the vibrational fundamentals, which are from Young. The minor isotopologue $^{13}CH_3D$ was also considered in this work. McDowell's analytical formula for spherical top molecules was used to calculate both rotational partition sums. For $^{13}CH_3D$, rotational constants were taken from Ulenikov et al. (2000) (given in Table 4). The vibrational partition sum was calculated using the same constants as $^{12}CH_3D$, with the exception of the ν_2 fundamental, which was taken from Chackerian and Guelachvili (1980) and are given in Table 5.

The state-independent factor for $^{13}CH_3D$ is given by:

$$\prod_{x=1}^{2}(2I_x+1) = (2(1)+1)(2(1/2)+1) = 6, \tag{6}$$

where the two nuclei that are not interchanged during rotation are the deuterium (D, *i.e.* ^2H) and ^{13}C. The state-dependent factors are given by Eqs. (4a) and (4b) which gives an average factor of $\sigma^* = 8/3$. Thus the total degeneracy for this isotopologue is $6 \times 8/3 = 16$.

In future calculations, the vibrational fundamentals specific to $^{13}CH_3D$ will be utilized. The product $Q_{vib} * Q_{rot}$ is used to determine Q_{tot} for the TIPS code. In Table 6, Q_{rot} (300 K) for $^{12}CH_3D$ and $^{13}CH_3D$ are compared with the CDMS/JPL values. Note, the values computed here agree well (~0.9%) with the classical rotational partition sum Herzberg (1960) but are roughly a factor of 2 larger than those reported by CDMS/JPL. It appears that the CDMS/JPL calculations did not include the spin factor for the D atom.

3.3. $H^{12}C^{12}CD$

The $H^{12}C^{12}CD$ isotopologue of acetylene was considered in this study. The rotational and vibrational constants of Jolly et al. (2008) were used in the determination of energy levels, in Q_{rot} calculations via direct sum and analytical solutions, and in the calculations of vibrational partition sums via the HOA. The state-dependent degeneracy factor is 1 and the state-independent degeneracy factor is 6 for this isotopologue. The linear molecule analytical model of McDowell (1988) was used to determine Q_{rot}. The minimum difference (−0.76%) between the analytical and direct sum Q_{rot} is at 378 K. Thus, for this isotopologue, the direct sum is used from 1 to 378 K, and the analytical Q_{rot} is used form 379 to 3500 K. The product approximation was used to determine the total internal partition sum. Q_{rot} (300 K) determined here agrees very well with the value reported by CDMS, see Table 6.

Table 5
Vibrational fundamentals in cm^{-1} for $^{12}CH_3D$ and $^{13}CH_3D$ from Young (see Section 3.2) except ν_2 of $^{13}CH_3D$ which is from Chackerian and Guelachvili (1980).

	$^{12}CH_3D$	$^{13}CH_3D$
ν_1	2982	2982
ν_2	2205	2190.0485
ν_3	1306	1306
ν_4	3030	3030
ν_5	1477	1477
ν_6	1156	1156

Table 6
Q_{rot} (300 K) from CDMS or JPL catalogues and from this work for certain isotopologues studied here.

Molecule	MW catalogue	Q_{rot} (CDMS/JPL)	Q_{rot} (this work)[a]
$^{12}CH_3D$	CDMS/JPL	806.8997	1613.8
$^{13}CH_3D$	CDMS/JPL	807.8471	1615.2
$H^{12}C^{12}CD$	CDMS	210.7267	211.3977
$H^{12}C^{12}C^{12}C^{14}N$	CDMS	1374.9098	1379.055
$H^{12}C^{12}C^{13}C^{14}N$	CDMS	1380.6343	1387.85
$H^{12}C^{13}C^{12}C^{14}N$	CDMS	1380.7674	1383.01
$H^{13}C^{12}C^{12}C^{14}N$	CDMS	1418.7542	1434.08
$H^{12}C^{12}C^{12}C^{15}N$	CDMS	1416.0846	1421.79
$D^{12}C^{12}C^{12}C^{14}N$	CDMS	1481.5213	1486.05
$^{12}C^{32}S$	CDMS	256.3136	256.5262
$^{12}C^{33}S$	CDMS	1033.8369	1034.63736
$^{12}C^{34}S$	CDMS	260.506	260.69237
$^{13}C^{32}S$	CDMS	543.2265	543.44647
HD	CDMS	5.0418	5.0426
$^{32}S^{16}O$	CDMS	850.2167	851.33597
$^{32}S^{18}O$	CDMS	917.685	918.81647
$^{34}S^{16}O$	CDMS	867.035	868.15984
$^{12}C_3H_4$	CDMS	17826.072[b]	21709.27

[a] State independent degeneracy factor removed to facilitate comparison.
[b] The CDMS partition function contains contributions from $\nu_{10} = 1$, $\nu_9 = 1$ and $\nu_{10} = 2$. Removing these contributions and adding a state independent factor of 2 for the H atom gives a value of 21729.69 in excellent agreement with our value.

Table 7
Rotational constants in cm^{-1} for $^{13}C^{12}CH_6$ from Weber et al. (1994).

Constant	Value cm^{-1}
A	2.66852
B	0.6497649
D_j	0.99385×10^{-6}
D_{jk}	2.6088×10^{-6}
D_k	9.54×10^{-6}

3.4. C_2H_6

The minor isotopologue $^{13}C^{12}CH_6$ (HITRAN code 1231) of ethane was considered in this study. To calculate the rotational partition sum, McDowell's formula for symmetric top molecules (McDowell, 1990) was used. Molecular constants are listed in Table 7 and were taken from Weber et al. (1994). The state-independent factor was calculated by

$$\prod_{x=1}^{2}(2I_x+1) = (2(1/2)+1)(2(0)+1) = 2. \tag{7}$$

Since isotopologue 1231 possesses C_{3v} point group symmetry, meaning that it has a threefold symmetry axis, the levels with $K = 0, 3, 6, 9, \ldots$ have a larger statistical weight than those with $K = 1, 2, 4, 5, 7, 8, \ldots$ The weight factors due to the spin can be determined by Eqs. (4c) and (4d). This gives a weight of 4 for K divisible by three and 2 for K not divisible by three. Hence the average weight of states, σ^*, is $\frac{4+2+2}{3} = \frac{8}{3}$. Thus the analytical $Q(T)$ must be multiplied by 2 and by 8/3.

While it is expected that the torsional partition function will contribute significantly to the total partition sum, the torsional splitting of ethane was not included in these calculations, but will be added in the future. Weber et al. (1994) do calculate torsional partition functions for $^{13}C^{12}CH_6$. At 294 K they report vibrational, rotational, and torsional partition sums; $Q_{vib} = 1.058$, $Q_{rot} = 18{,}613$, $Q_{tor} = 4.063$. The rotational and vibrational values for the TIPS at 294 K computed here are $Q_{vib} = 1.367$ and $Q_{rot} = 26{,}083$. Note that because torsion was not included in our calculation, the ν_4 torsional fundamental is included in the Q_{vib} computed here. Removing ν_4 in the calculation gives the same Q_{vib} as Weber et al. However, the calculations of Q_{rot} presented here do not agree well with the Q_{rot} of Weber et al. (1994). The classical rotational partition function formula of Herzberg (1960) is:

$$Q_{rot}^{classical}(T) = \sigma^* \times d_i \times 1.02718\sqrt{\frac{T^3}{B^2A}}, \tag{8}$$

where T is the temperature in Kelvin, B and A are rotational molecular constants, d_i is the state-independent factor, and σ^* is the average weight of states. Using the rotational constants from Weber et al. (1994) gives the classical rotational partition function $Q_{rot}^{classical}(294\text{ K}) = 26020.6$, which agrees well (0.2% difference) with our value at 294 K.

3.5. CH_3Br

The partition sums were calculated for the $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$ isotopologues. The rotational constants are from Brunetaud et al. (2002) for both isotopologues and the vibrational fundamentals from Anderson and Overend (1971), Betrencourt et al. (1975), Betrencourt-Stirnemann and Graner (1974), Deroche and Betrencourt-Stirnemann (1976), and Graner and Blass (1975) are given in Table 8. The rotational partition sums were determined using the symmetric-top analytical formula of McDowell (1990). The nuclear spin of both ^{79}Br and ^{81}Br is 3/2 and that of ^{12}C is 0 giving a state-independent factor of 4. The average weight of the states in McDowell's formula is $(2 * I_H + 1)^3/3 = 8/3$. The vibrational partition sums used the HOA method of Herzberg. The total partition sum was calculated using the product approximation.

The vibrational partition sums computed here compare very well with those reported by Brunetaud et al. (2002), 0.004% and 0.009% difference for $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$, respectively. Their total internal partition functions, when corrected to have the state-independent factor of 4, are 83048.78 and 83397.08, compared to our values of 83051.98 and 83395.21 for $^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$, respectively.

Table 9
Vibrational fundamentals and degeneracy, g_v, for diacetylene from Guelachvili et al. (1984).

State	Fundamental (cm^{-1})	g_v
ν_1	3332.1	1
ν_2	2188.9	1
ν_3	872.0	1
ν_4	3333.7	1
ν_5	2022.2	1
ν_6	625.6	2
ν_7	482.7	2
ν_8	627.9	2
ν_9	220.1	2

3.6. CF_4

The partition function values for $^{12}CF_4$ are taken from Boudon (Boudon, V., Calculation of $^{12}CF_4$ partition sum using the method of: Ch. Wenger, J.P. Champion, V. Boudon, J. Quant. Spectrosc. Radiat. Transfer 109(2008) 2697-2706, private communication, University of Dijon, Dijon, France, 2009). These values are used in TIPS_2011.for. The states of CF_4, a spherical rotor, are labeled by A_1, A_2, E, F_1, and F_2. The state dependent statistical weight factors are 5 for the A_1 and A_2 species, 2 for the E species, and 3 for the F_1 and F_2 species. The method used to calculate the partition sum was that of a previous study by Wenger et al. (2008) in which partition functions for methane were calculated.

3.7. $^{12}C_4H_2$

Calculations of the total, rotational, and vibrational partition sums at temperatures from 1 to 3500 K were made for diacetylene, $H^{12}C^{12}C^{12}C^{12}CH$ (common name butadiyne). This is a symmetric linear molecule, so the odd states have a statistical weight factor of 3 and the even states 1. The rotational partition sums were determined using McDowell's analytical formula for linear molecules with 2 as the average spin factor. The rotational constants are those of Arié and Johns (1992). The vibrational partition sums were determined using the HOA method with the fundamentals given in Table 9 from Guelachvili et al. (1984). The total partition sums were calculated using the product approximation.

The rotational partition sum at 300 K is 2850.085, which compares well with the classical partition sum, 2848.286.

3.8. HC_3N

The partition sums of cyanoacetylene were determined from 1 to 3500 K for six isotopologues of the molecule: $H^{12}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{13}C^{14}N$, $H^{12}C^{13}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{12}C^{15}N$,

Table 8
Vibrational fundamentals and degeneracy, g_v, for CH_3Br.

State	Fundamental (cm^{-1})	g_v	Reference
$CH_3{}^{79}Br$			
ν_1	2973.184	1	Betrencourt et al. (1975)
ν_2	1305.907	1	Graner and Blass (1975)
ν_3	611.112	1	Anderson and Overend (1971)
ν_4	3056.4037	2	Betrencourt-Stirnemann and Graner (1974)
ν_5	1442.885	2	Graner and Blass (1975)
ν_6	954.8672	2	Deroche and Betrencourt-Stirnemann (1976)
$CH_3{}^{81}Br$			
ν_1	2973.183	1	Betrencourt et al. (1975)
ν_2	1305.907	1	Graner and Blass (1975)
ν_3	609.933	1	Anderson and Overend (1971)
ν_4	3056.4002	2	Betrencourt-Stirnemann and Graner (1974)
ν_5	1442.885	2	Graner and Blass (1975)
ν_6	954.8044	2	Deroche and Betrencourt-Stirnemann (1976)

Table 10
Vibrational fundamentals and degeneracy, g_v, for HC_3N.

State	Fundamental (cm^{-1})	g_v	Reference
HC_3N			
ν_1	3327.37	1	Winther et al. (1996)
ν_2	2272	1	Uyemura and Maeda (1974)
ν_3	2077	1	Uyemura and Maeda (1974)
ν_4	863	1	Uyemura and Maeda (1974)
ν_5	663.4	2	Uyemura et al. (1982)
ν_6	498.7	2	Uyemura et al. (1982)
ν_7	223	2	Winther et al. (1996)
DC_3N			
ν_1	2607	1	Uyemura and Maeda (1974)
ν_2	2251	1	Uyemura and Maeda (1974)
ν_3	1956	1	Uyemura and Maeda (1974)
ν_4	855	1	Uyemura et al. (1982)
ν_5	522.6	2	Uyemura et al. (1982)
ν_6	494.6	2	Uyemura et al. (1982)
ν_7	213	2	Uyemura et al. (1982)

$D^{12}C^{12}C^{12}C^{14}N$. The rotational constants are from Lafferty and Lovas (1978). The rotational partition sums employ the analytical formula of McDowell (1988). There are no state-dependent degeneracy factors from the coupling of the rotational and nuclear wavefunctions. The state-independent degeneracy factors are 6, 12, 12, 12, 4, and 9, respectively. The vibrational partition sums were determined using the HOA method with the vibrational fundamentals given in Table 10 for all isotopologues taken from Uyemura et al. (1982), Uyemura and Maeda (1974), and Winther et al. (1996). The total internal partition sums were determined using the product approximation.

In Table 6 the total internal partition sums at 300 K calculated in this work are compared with those from the CDMS catalogue Müller et al. (2005) for the isotopologues studied here. Note, to compare the CDMS values with the calculations of this work the state-independent degeneracy factors were removed from our values. The percent differences are 0.3, −0.1, 0.2, 1., 0.4, and 0.3 for the $H^{12}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{13}C^{14}N$, $H^{12}C^{13}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, $H^{12}C^{12}C^{12}C^{15}N$, $D^{12}C^{12}C^{12}C^{14}N$ isotopologues, respectively.

3.9. C_2N_2

Two isotopologues of dicyanogen were considered in this work: $^{14}N^{12}C^{12}C^{14}N$ and $^{15}N^{12}C^{12}C^{15}N$. The rotational constants are those of Maki (1965). Because of the symmetry of the isotopologues, state-dependent degeneracies arise from the coupling of rotational and nuclear wavefunctions. The $^{14}N^{12}C^{12}C^{14}N$ isotopologue has a threefold degeneracy associated with the odd J states and a sixfold degeneracy with the even J states. For the $^{15}N^{12}C^{12}C^{15}N$ isotopologue, these degeneracies are threefold for the odd J levels and onefold for the even J level. The state-independent degeneracy factor is 1 for both isotopologues. The rotational partitions sums were calculated using McDowell's linear molecule analytical formula with the average spin degeneracy of 4.5 and 2, respectively. The vibrational partition sums were determined via the HOA method with the vibrational fundamentals given in Table 11 from Grecu et al. (1993).

Table 11
Vibrational fundamentals and degeneracy, g_v, for C_2N_2 from Grecu et al. (1993).

State	Fundamental (cm^{-1})	g_v
ν_1	2330.5	1
ν_2	845.5	1
ν_3	2157.8	1
ν_4	502.8	2
ν_5	233.9	2

There are no partition sum data to compare with; however the rotational partition sum at 300 K for $^{14}N^{12}C^{12}C^{14}N$ is about 0.1% larger than the $Q_{classical}$ determined using the formula of Herzberg (1960).

3.10. CS

Total internal partitions sums were calculated for four isotopologues of CS: $^{12}C^{32}S$, $^{12}C^{34}S$, $^{12}C^{33}S$, and $^{13}C^{32}S$. The rotational constants of Burkholder et al. (1987a) were used to determine energies and Q_{rot} (analytical) using the model of McDowell (1988) for linear molecules. The energies were used to determine Q_{rot} (DS) by direct summation. The state-independent degeneracy factors for $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, and $^{13}C^{32}S$, are 1, 4, 1, and 2, respectively. The direct sum and analytical Q_{rot} agree best at roughly 10 K, hence the analytical Q_{rot} data are used for the temperatures of this study. The fundamental vibrational frequencies were taken from Burkholder et al. (1987a); 1272.16211 cm^{-1}, 1262.02624 cm^{-1}, 1266.94361 cm^{-1}, and 1236.31586 cm^{-1} for $^{12}C^{32}S$, $^{12}C^{34}S$, $^{12}C^{33}S$, and $^{13}C^{32}S$, respectively. The Harmonic Oscillator Approximation was used to determine the vibrational partition sums. The final TIPS were determined using the product approximation.

Table 6 reports Q_{rot} (300 K) values for these isotopologues of CS from the CDMS catalogue and from the calculations made here. The agreement is excellent; 0.08%, 0.08%, 0.07%, 0.04% for the $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, and $^{13}C^{32}S$ isotopologues, respectively.

3.11. H_2

For two isotopologues of hydrogen, H_2 and HD, the TIPS were calculated via direct sum using *ab initio* energies. For H_2 the energies were derived from the dissociation energies reported by Piszczatowski et al. (2009) for $v = 0–14$ and $J = 0–31$. These energies are complete to 35,242 cm^{-1}, ensuring convergence of the partition sums at all temperatures of this study. The energies were used to compute the direct sum. The state-independent factor for H_2 is 1, but because H_2 is a Fermi system, there is a state-dependent statistical weight determined using Eqs. (4a) and (4b). From these expressions, the calculated weight for an odd state is 3 and the weight for an even state is 1. The value of Q_{tot} at 1000 K computed here, 24.822, can be compared with that of Irwin (1987), 6.1501. It was then noted that Irwin used statistical weights of ¾ and ¼ for the odd and even states. Multiplying his value by 4 yields 24.600, within 0.9% of the value determined in this work.

Determination of the partition sums for HD also used direct summation of the energy levels provided in this case by the work of Pachucki and Komasa (2010). These data provide energy levels for 400 states from $v = 0–17$ and $J = 0–36$ and are complete to 35,506 cm^{-1}. Thus all partition sums are converged at all temperatures of this study. There is no coupling of nuclear spins and rotational states for this isotopologue. The state independent degeneracy factor is 6 for HD.

The value of the TIPS computed here for HD is compared in Table 6 to the value from the CDMS Catalogue at 300 K showing a 0.02% difference.

3.12. SO

Three isotopologues of SO were considered in this study: $^{32}S^{16}O$, $^{32}S^{18}O$, and $^{34}S^{16}O$. For the rotational partition function, energy levels were calculated using the formula and constants of Burkholder et al. (1987b). Note, the formulas for the $J = N \pm 1$ contain a typographical error, see Mizushima (1975) for details. It should also be noted that the sign of the square root term is flipped for the $J = 0$, $N = 1$ state (Herzberg, 1950), Tinkham and Strandberg, 1955). The energies were calculated up to $J = 150$, and were scaled

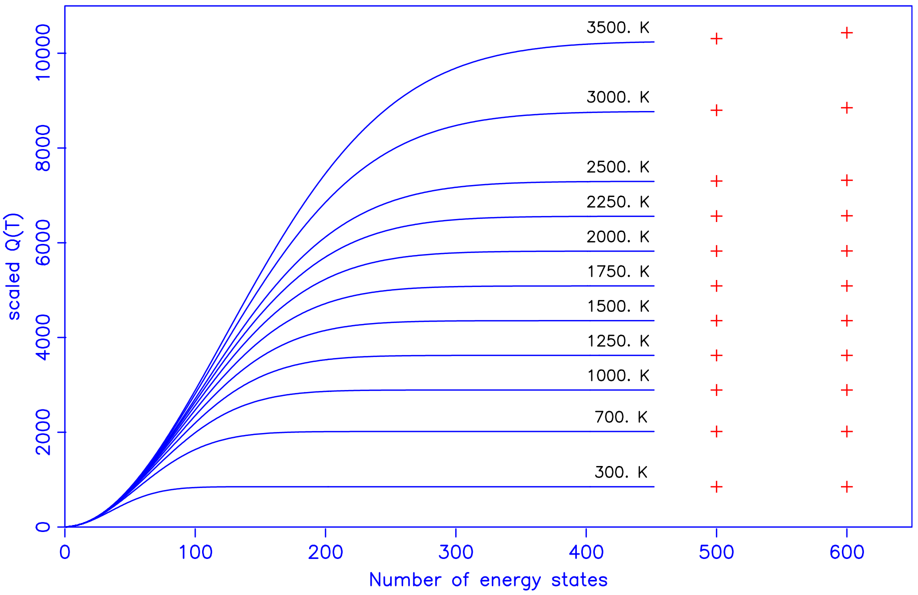

Fig. 1. Convergence of Q(T) for $^{32}S^{16}O$ as a function of number of energy states (solid line) with extrapolation to energy states number 500 and 600 (+ symbol).

to set the energy of the state for $J = 0$, $N = 1$ to zero. These energies were used to calculate $Q(T)$ by direct summation with a state-independent factor of 1 for each isotopologue. There is no analytical formula for this $X^3\Sigma$ molecule so convergence tests were made for the direct sum $Q(T)$ determined for each isotopologue. The convergence curves and the extrapolated points (described below) versus the number of energy states are shown in Fig. 1 for the $^{32}S^{16}O$ isotopologue for the temperatures 300, 700, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 3000, and 3500 K. As the number of states increases the partition sums level off. To develop a sense of the convergence, the energies at levels number 375–452 were taken with the number of energy states and a linear regression was made to determine the slope and intercept. The straight-line formula was used to extrapolate the partition sums to energy numbers 500 and 600. This procedure allows an estimation of the convergence of the partition sums. Comparing the partition sum at energy number 4500 to that from the direct sum gives 0.03%, 0.1%, 0.25%, 0.5%, 1.4%, 2.8% difference for 1750, 2000, 2250, 2500, 3000, and 3500 K respectively. Similar results are obtained for the other isotopologues of this study. In Table 6 the rotational partition sums computed here and those given in the CDMS catalogue at 300 K are reported. The percent differences are all roughly 0.1 where the partition sums computed here are somewhat larger, which is expected since the calculations presented here sum over more states. These additional states will have more of an effect at higher temperatures.

The vibrational partition functions were calculated using Herzberg's HOA method (Herzberg, 1960) with the vibrational fundamentals from Burkholder et al. (1987b). The final partition sums were determined using the product approximation.

3.13. C_3H_4

Calculations were made for the principal isotopologue, $^{12}C_3H_4$, of methylacetylene (common name propyne). The rotational constants are those of Cazzoli and Puzzarini (2008). The energy levels were determined using Eq. (2) of Pracna et al. (1996) and $Q_{rot}(T)$ determined by direct summation. The state-independent degeneracy factor is 2. McDowell's analytical formula for symmetric tops (McDowell, 1990) was also used to determine Q_{rot} where the average state degeneracy is $2 * 8/3$. The minimum difference between the two methods (−0.0003%) occurs at 288 K. Thus the direct sum Q_{rot} is used from 1 to 288 K and the analytical Q_{rot} is used from 289 to 3500 K. The vibrational fundamentals used are $\nu_1 = 3335.61\ \text{cm}^{-1}$ (1), $\nu_2 = 1853.78\ \text{cm}^{-1}$ (1), $\nu_3 = 2583.60\ \text{cm}^{-1}$ (1), $\nu_4 = 519.80\ \text{cm}^{-1}$ (2), $\nu_5 = 678.80\ \text{cm}^{-1}$ (2) (Pracna, P., Vibrational fundamentals for C_3H_4, private communication, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 18223 Prague 8, Czech Republic, 2010), where the number in the parenthesis is the degeneracy of the level. The total internal partition sums were determined via the product approximation.

The analytical model rotational partition sum computed here at 300 K with the state-independent factor of 2 removed is given in Table 6 along with the value from the CDMS catalogue. They differ by about 18%. Comparing our value to the classical rotational value (Herzberg, 1960) gives a 0.2% difference.

3.14. CH_3

Methyl radical ($^{12}CH_3$) is a planar symmetric top. Rotational energies up to $J = 50$ were determined using the molecular constants of Yamada et al. (1981) and their Eq. (2). These energies, complete to 17,545 cm^{-1} for the ground rotational state, were used to determine Q_{rot} where the state-dependent degeneracies were taken from Weber (1980). The weights, in addition to $(2J + 1)$ are: when $K = 0$ and J is even $d_s = 0$ and when J is odd $d_s = 4$; when $K > 0$ and is a multiple of $3d_s = 4$, otherwise $d_s = 2$. Note that the different weighting for states with $K = 0$ causes complications for determining the analytical partition functions since the average weight per state is difficult to determine. Q_{rot} from the analytical model depends strongly on the average weight, σ^*, and which energy levels contribute to Q_{rot} depends on temperature; adjusting σ^* should only be done for very high temperatures. Thus the direct sum Q_{rot} is used at all temperatures of the study. To check for convergence of the partition sums, the 2601 energy levels were sorted and the partition sum calculated as a function of the energy state. Next, the energies at levels 2000–2601 were taken with the count and a linear regression was made to determine the slope and intercept. Using these values the partition sums were extrapolated to energy numbers 3500 and 4500. The convergence curves and the extrapolated points are shown in Fig. 2 for the temperatures 300,

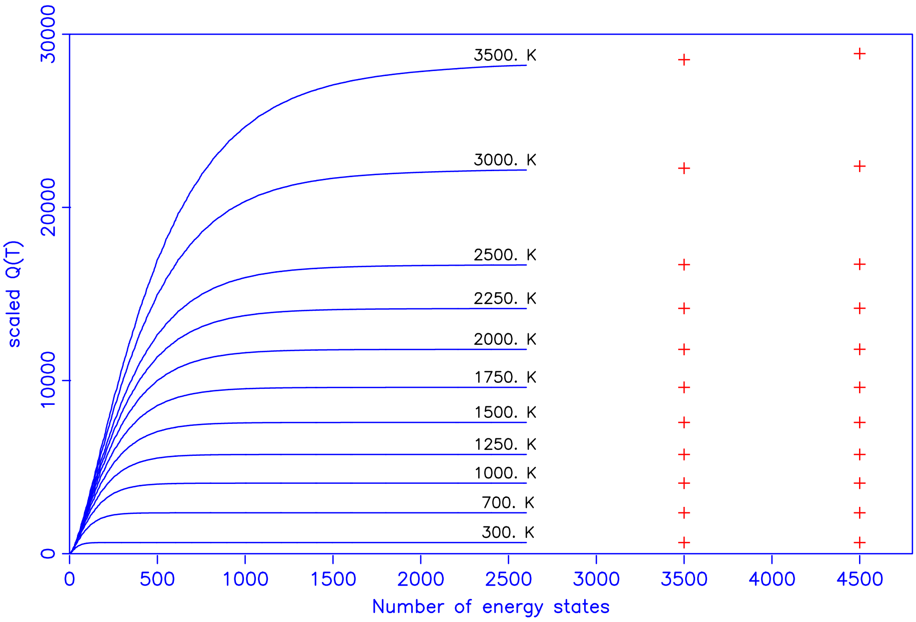

Fig. 2. Convergence of $Q(T)$ for $^{12}CH_3$ as a function of number of energy states (solid line) with extrapolation to energy states number 3500 and 4500 (+ symbol).

Table 12
Vibrational fundamentals (cm^{-1}) for CS_2 from Smith and Overend (1971), degeneracy in parentheses.

State	$^{12}C^{32}S_2$	$^{32}S^{12}C^{34}S$	$^{13}C^{32}S_2$	$^{32}S^{12}C^{33}S$
ν_1 (1)	658.013	648.37	657.24	653.192
ν_2 (2)	396.092	395.13	388.275[b]	395.611
ν_3 (1)	1535.353	1518.85[a]	2332.1363	1527.102

[a] Estimated from $3\nu_3$.
[b] Estimated from $2\nu_2$.

700, 1000, 1250, 1500, 1750, 2000, 2250, 2500, 3000, and 3500 K. This procedure allows an estimation of the convergence of the partition sums. Comparing the partition sum at energy number 4500 to that from the direct sum gives 0.01%, 0.05%, 0.14%, 0.32%, 1.1%, 2.6% difference for 1750, 2000, 2250, 2500, 3000, and 3500 K respectively.

The vibrational partition sums were determined using the HOA and the following fundamental frequencies: $\nu_1 = 3004.43$ cm^{-1} (Zahedi et al., 1994), $\nu_2 = 606.4531$ cm^{-1} (Yamada et al., 1981), $\nu_3 = 3160.821$ cm^{-1} (Davis et al., 1997), and $\nu_4 = 1397$ cm^{-1} (Jacox, 1994).

The TIPS were determined using the product approximation.

3.15. CS$_2$

Total internal partition sums were calculated for $^{32}S^{12}C^{32}S$, $^{32}S^{12}C^{34}S$, $^{32}S^{13}C^{32}S$, and $^{32}S^{12}C^{33}S$. The rotational constants reported by Maki and Sams (1974) were used for all isotopologues. Energy levels were calculated using the standard B, D, H expression (Herzberg (1960) (note that Maki and Sams (1974) do not provide the rotational constant H, so it is set to zero) and direct sums calculated. The analytical model of McDowell for linear molecules was also used to determine the partition sums. For the principal isotopologue, $^{32}S^{12}C^{32}S$, identical sulfur atoms are exchanged in 180 degree rotations or inversion. This isotopologue is a Bose system ($I(^{32}S) = 0$) and even states have a degeneracy factor of 1 and the odd states have a degeneracy factor of 0, *i.e.* the odd states are missing. For the other isotopologues, there are no identical atoms interchanged in symmetry operations, hence $d_s = 1(2J + 1)$. The state-independent degeneracy factors are 1, 1, 2, and 4, respectively. The best agreement between the analytical and direct sum $Q(T)$ is at 9 K, well below the temperatures of this study. The vibrational fundamentals are from Smith and Overend (1971) and are reported in Table 12. Q_{vib} was determined by the HOA and used with Q_{rot} to form the total internal partition function.

Table 13
Total internal partition functions at 296 K for the isotopologues/isotopomers considered in this study.

Isotopologue	Q (296 K)	Isotopologue	Q (296 K)
$^{13}C^{18}O_2$	653.76	$^{15}N^{12}C^{12}C^{15}N$	7365.1
$^{18}O^{13}C^{17}O$	7615.2	$^{12}C^{32}S$	253.62
$^{12}CH_3D$	4795.5	$^{12}C^{33}S$	1023.0
$^{13}CH_3D$	9599.2	$^{12}C^{34}S$	257.77
$H^{12}C^{12}CD$	1581.8	$^{13}C^{32}S$	537.50
$^{13}C^{12}CH_6$	36,192	H_2	7.6724
$CH_3{}^{79}Br$	83,052	HD	29.963
$CH_3{}^{81}Br$	83,395	$^{32}S^{16}O$	843.04
$^{12}CF_4$	121,270	$^{32}S^{18}O$	910.68
$^{12}C_4H_2$	9826.0	$^{34}S^{16}O$	859.88
$H^{12}C^{12}C^{14}N$	24,706	$^{12}C_3H_4$	74,897
$H^{12}C^{12}C^{13}C^{14}N$	49,724	$^{12}CH_3$	668.84
$H^{12}C^{13}C^{12}C^{14}N$	49,555	$^{12}C^{32}S_2$	1352.6
$H^{13}C^{12}C^{12}C^{14}N$	51,373	$^{32}S^{12}C^{34}S$	2798.0
$H^{12}C^{12}C^{12}C^{15}N$	16,980	$^{13}C^{32}S_2$	2739.7
$D^{12}C^{12}C^{12}C^{14}N$	45,915	$^{32}S^{12}C^{33}S$	11,007
$^{14}N^{12}C^{12}C^{14}N$	15,582		

4. Determining $Q(T)$ data for applications

A four-point Lagrange interpolation of $Q(T)$ versus T was used in this work. In a previous study (Fischer et al., 2003), it was shown that a $Q(T)$ versus T scheme was a more accurate and efficient method of interpolation than either the $\ln(Q(T))$ versus $\ln(T)$ or the $\ln(Q(T))$ versus T scheme. A four-point Lagrange interpolation is used for the temperature range 70–3000 K with data tables generated listing values of $Q(T)$ at intervals of 25 K starting at 65 and going to 3010 K. Other temperature step sizes were tested and a 25 K step was found adequate to reproduce the data well within its uncertainty. The 4-point Lagrange interpolation scheme and the tables were then coded into a FORTRAN program (TIPS_2011.for) and subroutine (BD_TIPS_2011.for) and are available on one of the authors' website (RRG, faculty.uml.edu/Robert_Gamache) and the HITRAN ftp website (ftp://cfa-ftp.harvard.edu/pub/HITRAN2008/Global_Data/).

5. Conclusion

The partition functions calculated above serve to complete the data for isotopologues/isotopomers present in the HITRAN‘2008 database and to extend the TIPS to molecules important in astrophysical applications. Q_{tot} values at 296 K for the species considered in this work are provided in Table 13. A FORTRAN program to evaluate the TIPS at any temperature in the range 70–3000 K can also be obtained (see above). Improvements to the partition sums are planned for the future, such as including torsional splitting of energy levels for the ethane molecule and extending the partition sums to lower temperatures.

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