# Total internal partition sums for 166 isotopologues of 51 molecules important in planetary atmospheres: Application to HITRAN2016 and beyond

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## ABSTRACT

Total internal partition sums (TIPS) are reported for 166 isotopologues of 51 molecules important in planetary atmospheres. Molecules 1 to 50 are taken from the HITRAN2016 list, and, in some cases, additional isotopologues are considered for some of the molecules. Molecules 51–53 are $C_3H_4$, $CH_3$, and $CS_2$, respectively. TIPS are not reported for the O atom and $CF_4$; thus, while there are 53 species in the list, data are reported for 51 molecules. The TIPS are determined by various methods from 1 K to a $T_{max}$ that ensures the TIPS reported have converged. These data are provided with HITRAN2016 and a new version of the TIPS code is available in both FORTRAN and python languages.

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## 1. Introduction

The Total Internal Partition Sums (TIPS), also called internal partition functions, describe the statistical properties of a gas in thermodynamic equilibrium. The TIPS are needed to determine the population of different quantum energy states. These population factors are used in determining the intensity of ro-vibrational transitions. The partition sum appears in the relationships between the intensity of a spectral line and the square of the transition moment, the Einstein-A coefficient, or the oscillator strength [1]. Because planetary atmospheres are not isothermal, radiative-transfer (RT) studies need to determine the line intensity at a number of temperatures from reference line intensities that can be found in molecular spectroscopic databases such as HITRAN [2,3] or GEISA [4]. A minimal set of input values needed by RT codes requires a knowledge of the line position, lower-state energy, intensity at a reference temperature, half-width for most atmospheric pressure regimes, and the partition functions at both the temperature of interest and a reference temperature.

The study of stellar atmospheres requires the partition function to high temperatures. In 1984, Sauval and Tatum [5] determined partition functions for some 300 diatomic molecules of astrophysical interest over a temperature range of 1000 to 9000 K. Irwin [6] later refined the work of Sauval and Tatum for $H_2$ and CO and later [7] 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 [8]. In 2016, this work was extended by Barklem and Collet [9] to partition functions and dissociation equilibrium constants for 291 diatomic molecules for temperatures in the range from near absolute zero to 10,000 K.

The equation of state of a gas, the thermodynamic functions (internal energy, enthalpy, entropy, Helmholtz free energy, and Gibbs free energy), heat capacity, etc. can be written in terms of the TIPS and its dependence on temperature [10]. Note that, in the literature, the terms partition function and partition sum are often interchanged. Here the standard chemistry notation, $Q(T)$, for the total internal partition sum as a function of temperature $T$ is adopted. The total partition function is assumed to be the product of the internal and the translational partition functions.

This work is an update and extension of previous works [11–17] to determine TIPS for molecules present on the HITRAN database and for astrophysical applications. In 1990 Gamache et al. [11] presented TIPS for 11 closed shell linear molecular species and their isotopic variants contained in HITRAN86 [18]. The data were given as polynomial expansions in two temperature regimes: 70–400 and 400–2005 K. In addition, a logarithmic expansion was presented for extrapolation to 3000 K. In 2000, this work was extended [12] to all molecular/isotopologue species on HITRAN92 [19] and three additional molecular/isotopologue species from HITRAN96 [20]. The calculations were made for temperatures from 70 to 3005 K and the data divided into three regions and fit by a 3$^{rd}$ order polynomial for rapid retrieval. In 2002 and 2003, Fischer and Gamache [14] extended the TIPS calculations to include 16 isotopologues of 5 molecules which are abundant in planetary atmospheres and made TIPS calculations for non-equilibrium applications. The same temperature range was employed. However, a 4$^{th}$ order polynomial was used for the fitting in the three temperature regions. In 2003, Fischer et al. [16] provided TIPS for the 40 molecules and 95 isotopologues/isotopomers on the HITRAN2000 database [21] with an additional 13 rare isotopologues/isotopomers of ozone and carbon dioxide. The calculations reported were over the same temperature range as previous studies, 70–3000 K. However, now the $Q(T)$ data were determined using a Lagrange 4-point interpolation scheme. Finally, Laraia et al. [17] determined TIPS for 33 isotopologues of 14 molecules needed to support planetary remote sensing. For the most part, the molecules considered in this work were to be added to the HITRAN database. In all of the above studies the methods of calculating $Q(T)$ were improved upon earlier studies.

There are many other examples of high-quality partition sums in the literature for one to several isotopologues of a molecule. Some recent examples include work on MgH by Szidarovszky and Császár [22], on $H_2^{16}O$ by Furtenbacher et al. [23], and on three isotopologues of $D_2O$ by Simkó et al. [24].

In the present work, total internal partition sums are determined for 166 isotopologues of 51 molecules important in planetary atmospheres. Species 1 to 50 are taken from the HITRAN2016 list, although in some cases more isotopologues are considered for some of the molecules. In the HITRAN list 1–50, no data are given here for number 34, O atom, and number 42, $CF_4$. Molecules 51–53 are $C_3H_4$, $CH_3$, and $CS_2$, respectively. For a number of molecules no new data were generated as explained below. All of the new calculations represent an improvement over the previous work. In many cases the improvements were possible due to the advances in first-principles computations of ro-vibrational energies, which can yield a complete set of rovibronic energies. Because of the more complete energy states, converged TIPS (converged in the sense that adding higher energies to the sum does not change $Q(T)$ significantly, discussed below) could be determined at higher temperatures for a number of isotopologues. In this work the calculations of the TIPS

does not consider unbound states. The temperature grid was taken from 1 K to a $T$ appropriate to ensure convergence of the partition function for the particular isotopologue. Also new with the 2016 edition of HITRAN is the distribution of programs to rapidly recall $Q(T)$ values in the FORTRAN (TIPS_2017_v1p0.for) and python (TIPS_2017_v1p0.py) languages.

In Section 2, the methods that can be used to determine the total internal partition sums are described. Section 3 describes the methods used for each molecule/ isotopologue combination. In Section 4 the codes to rapidly recall $Q(T)$ are described and Section 5 summarizes the work.

## 2. Determining the total internal partition sum

Considering a particular isotopologue of a molecule, the total internal partition sum of a molecule is given by summing the factor $e^{-hcF_s/kT}$ over all states, $s$, labeled according to the electronic, vibrational, rotational, torsional, … energy level structure of the isotopologue. Here, $h$ is the Planck constant, $c$ is the speed of light, $k$ is the Boltzmann constant, $T$ is the thermodynamic temperature in Kelvin, and $hcF_s$ is the total energy (electronic, vibrational, rotational, and any other quantized motion) of state $s$. $F_s$ is the term value [25] and has units of cm$^{-1}$. The physical constants, $h, c,$ and $k,$ have the CODATA recommended values [26],

The expression for $Q(T)$ is usually written accounting for degenerate states by

$$Q_{elec,\,vib,\,rot,\,tors,\,etc.}(T) = d_i \sum_{all\;states\;s} d_s\; e^{-hc\,F_s/k\,T} \tag{1}$$

where $d_i$ and $d_s$ account for degeneracy factors that are state independent and state dependent, respectively.

The state dependent degeneracy factors are generally composed of two components. The first is the usual $(2J+1)$ or $(2F+1)$ degeneracy factor, where $J$ and $F$ are the rotational and total angular momentum quantum numbers. However, for molecules with some degree of symmetry, whereby identical atoms are interchanged by a symmetry operation, only certain products of rotational and nuclear wavefunctions yield the proper symmetry for the complete wavefunctions. The net result is that for some molecules/isotopologues, even (eigenfunction is symmetric with respect to an exchange of the equivalent nuclei) and odd (eigenfunction is antisymmetric with respect to an exchange of the equivalent nuclei) symmetry states have different weights (nuclear spin weights) and these values must be factored in accordingly when calculating partition sums.

For molecules where two identical nuclei are exchanged upon rotation, the nuclear statistical weights must be determined and are part of the state dependent degeneracy factors. For molecules where the exchanged nuclei have half-integer spins (Fermi systems) and molecules where the exchanged nuclei have integer spins (Bose systems) the state dependent degeneracy factors [25] are given by:

$$\begin{aligned}Fermi\;system\;-\;even:\\Bose\;system\;-\;odd:\end{aligned}\quad \frac{1}{2}\left[\left(2\,I_x\;+\;1\right)^2\;-\;\left(2\,I_x\;+\;1\right)\right] \tag{2a}$$

$$\begin{aligned}Fermi\;system\;-\;odd:\\Bose\;system\;-\;even:\end{aligned}\quad \frac{1}{2}\left[\left(2\,I_x\;+\;1\right)^2\;+\;\left(2\,I_x\;+\;1\right)\right] \tag{2b}$$

where $I_x$ is the nuclear spin of the atoms which are interchanged. For example, for $H_2O$, the two interchanged nuclei are the two spin-½ hydrogen atoms. Inserting this spin value into the above equations gives a three-fold degeneracy for the odd states and a one-fold degeneracy for the even states. For $^{16}O_3$, a $C_{2v}$ molecule, the interchanged nuclei are oxygen atoms with zero nuclear spin.

Substituting this value into the above equations yields a one-fold degeneracy for the even levels and a zero-fold degeneracy for the odd levels (i.e., such levels do not exist). For molecules which have more than one pair of atoms exchanged upon rotation, expressions for the number of spin functions for each state are given in Ref. [25], p17, Eqs. (I.8) and (I.9).

State dependent factors are considered explicitly when TIPS are determined by direct sums by calculating the parity of each state using an expression appropriate for the molecular symmetry of the species involved. When analytical expressions are used, an average state dependent factor is used by taking the arithmetic mean of the state dependent factors involved. For example, for $^{16}O_3$, a factor of 0.5 is used to account for the total of the state dependent factors.

In the literature, state independent factors are often omitted from partition sum calculations when the application involves a ratio of partition sums. These factors are necessary to relate the partition functions to thermodynamic quantities. State independent factors occur in species where there are atoms that are not interchanged upon rotation. This degeneracy factor is expressed as $\prod (2I + 1)$, where $I$ is the nuclear spin and the product is taken over all nuclei not interchanged by rotation [25]. In this work, the state independent factor has been included when determining the TIPS for all molecules/isotopologues, yielding partition sums that can be used to determine thermodynamic quantities. Note, when comparing the partition sums from this study to values from the literature, it is sometimes necessary to multiply the reported values by a constant value to obtain agreement due to the omission of the state independent factors. Such comparisons are discussed specifically in the text.

In order to evaluate Eq. (1), energy levels and corresponding degeneracy factors are needed for the molecule/isotopologue in question. As the energy increases, the exponential factor approaches zero and the sum can be truncated with no loss of accuracy. At which energy state this series truncation occurs depends on the temperature, since $kT$ divides the energy of the state. An accurate determination of the TIPS must sum over energy levels until the exponential factor no longer contributes significantly to the sum. This point can be determined by calculating $Q(T)$ as a function of energy and noting where $Q(T)$ no longer changes within the desired accuracy as additional energies are summed. Such a test should consider all energy levels up to dissociation. Here, the convergence test determines $dQ(T)/dE$ as a function of $E$ and looks for energies above which $Q(T)$ no longer changes within the desired accuracy. At this point the calculation of the partition sum is said to have converged.

The ideal situation is to have energy levels up to the dissociation limit of the isotopologue in question. Then a direct sum can be done. However, seldom are energy levels available up to the dissociation limit, counter examples are Refs. 22 and 23. Recently there are a number of *ab initio* calculations of ro-vibrational energies that do provide the needed energies. A number of the improved TIPS discussed below incorporate these *ab initio* energies. When energies are not available to sufficiently high states for convergence of $Q(T)$, approximations need to be made.

In practice, the energy states are usually not known for all rotational levels of all vibrational states of all electronic states. When there are other complications, such as lambda doubling, torsional motion, etc. the situation for the energy states is more complex. In such cases it is assumed that the energy is additive

$$E(elec,\ vib,\ rot,\ tors,\ \ldots) = E_{elec} +\ E_{vib} +\ E_{rot} +\ E_{tors} + \bullet \bullet \bullet \quad (3)$$

from which follows the product approximation

$$Q(elec,\ vib,\ rot,\ tors,\ \ldots) = Q_{elec} \times\ Q_{vib} \times\ Q_{rot} \times\ Q_{tors} \times \bullet \bullet \bullet \quad (4)$$

The problem is now reduced to calculating the electronic, vibrational, rotational, … partition sums. Which approach is used is determined by the availability of energy states for the molecule/isotopologue in question. For discussion, the general case is considered where $Q_{elec}(T)=1$ and there is no torsional or other structure (e.g. lambda doubling, inversion, etc.). Ignoring vibration-rotation interaction, Eq. (4) can be written

$$Q(T) = \sum_{\substack{vibrational \\ states}} d_{vib}\ e^{-hc\ G_{vib}/k\ T} \sum_{\substack{rotational \\ states}} d_{rot}\ e^{-hc\ F_{rot}/k\ T}$$

$$= Q_{vib}(T) \times\ Q_{rot}(T) \quad (5)$$

where $d_{vib}$ and $d_{rot}$ are the degeneracy factors for the states, and $G_{vib}$ and $F_{rot}$ are the term values of the vibrational and rotational states, respectively. The problem now reduces to computing the rotational and vibrational partition sum.

If a complete set of rotational energies are available to a high enough limit, a direct sum can be made

$$Q_{rot}(T) =\ d_i \sum_{\substack{all \\ rotational \\ states}} d_r\ e^{-hc\ F_r/k\ T}. \quad (6)$$

In many cases there is not available a complete set of energies to a high enough limit to obtain a converged partition sum. For such cases analytical expressions [27–30] for the partition sums must be used. Since the analytical models are developed by mapping the quantum structure of the energy to a classical structure, the analytical rotational partition sums do not work well at low temperatures where quantum structure of the energy level density is important. Thus corrections must be made; this fact is discussed below.

The vibrational partition function can be approximated by the harmonic oscillator approximation of Herzberg [25], using vibrational fundamentals taken from the literature

$$Q_{vib}(T) =\ \prod_{\substack{vibrational \\ fundamentals}} \frac{1}{1\ -\ e^{-hc\ G_v/k\ T}} \quad (7)$$

If anharmonic constants are available, the vibrational fundamentals can be calculated [25] to high energy and a direct sum performed to determine $Q_{vib}(T)$.

Given the above discussion, the method chosen below for the molecule/isotopologue under study depends on the availability of energy levels and a lower bound $T_{max}$ of 3500 K. The actual $T_{max}$ was determined by studying the convergence of $Q(T)$.

Extensive comparison with literature values of the partition sums was done in previous studies [11–17] and will not be repeated here. Where there are new data some comparisons will be made.

## 3. Calculations

### 3.1. Water vapor

Nine isotopologues of $H_2O$ are considered in this study: $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, $HD^{16}O$, $HD^{18}O$, $HD^{17}O$, $D_2^{16}O$, $D_2^{18}O$, and $D_2^{17}O$. For $H_2^{16}O$ the energy levels are taken from the *ab initio* derived BT2 data [31]. The term values go to 30,000 cm$^{-1}$ ($J_{max}=50$) and are complete to 29,967 cm$^{-1}$. The partition sums were calculated by direct summation. $Q(T)$ can also be calculated using the experimental MARVEL term value data [23,32], where the MARVEL term values, determined by the Rayleigh-Ritz principle, are considered
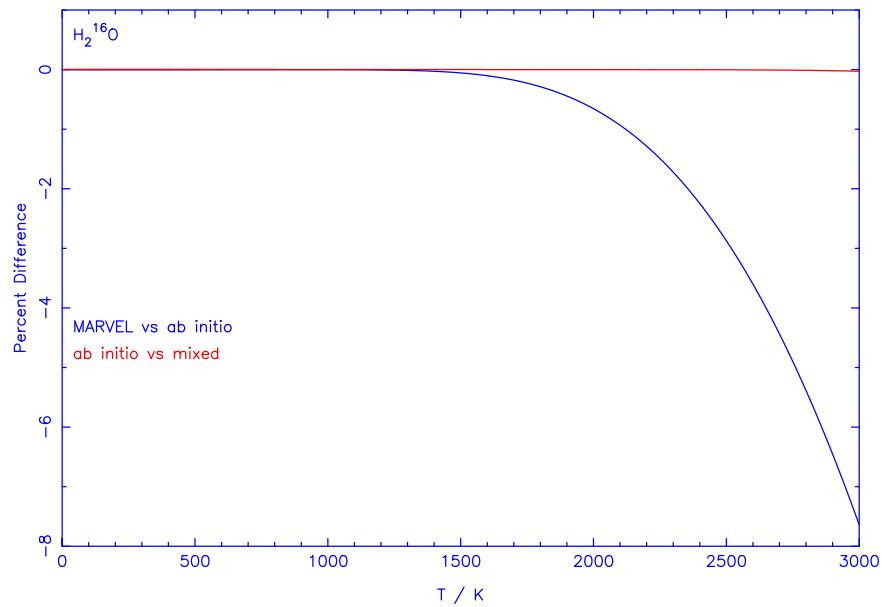
**Fig. 1.** The percent difference between $Q(T)$ determined with purely MARVEL term values and $Q(T)$ determined with *ab initio* term values (blue curve) and $Q(T)$ determined with mixed term values and $Q(T)$ determined with *ab initio* term values (red curve) for $H_2^{16}O$ versus temperature in K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the best measured term values for water. The $Q(T)$ values from the MARVEL term values provide a check on the low temperature partition sums from the *ab initio* term values. There are small differences between the MARVEL and *ab initio* term values. A better set of term values can be obtained by replacing the *ab initio* term values by MARVEL term values when possible, here called mixed term values. Fig. 1 shows the percent difference between $Q(T)$ determined with MARVEL term values and $Q(T)$ determined with *ab initio* term values (blue curve) and $Q(T)$ determined with mixed term values and $Q(T)$ determined with *ab initio* term values (red curve) for $H_2^{16}O$ versus temperature. The figure shows little difference between the TIPS determined with MARVEL term values and *ab initio* term values at low temperatures. The figure also shows that by about 1200 K the TIPS determined with purely

MARVEL term values no longer converge, due to the large number of missing experimental energy values. The final TIPS were determined using the mixed term value data. Using these data a convergence test was made. Fig. 2 shows $Q(T)$ versus the term value, $F$, in wavenumbers for $T$ values: 1000, 2000, 3000, 3500, 4000, 4500, and 5000 K. The figure shows that the TIPS have converged up to ~4000 K. The TIPS agree with the reported UCL (University College London) data [31], which are reported to 3000 K. The final TIPS are reported to 5000 K. Table 1 lists the chemical formula, isotopologue number (ISO#), AFGL code, state independent degeneracy factor ($g_i$), $Q(296 K)$, $J_{max}$, $F_{max}$ in cm$^{-1}$, and $T_{max}$ in K. Blank entries imply the data are not applicable; e.g., $F_{max}$ for a product approximation $Q(T)$.

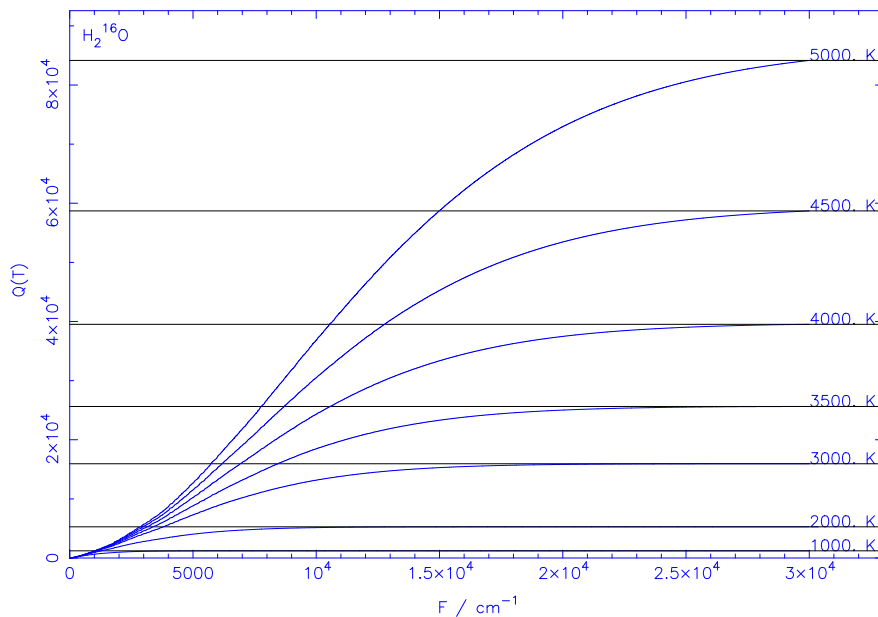For $H_2^{18}O$ and $H_2^{17}O$ the available *ab initio* energies were not



**Fig. 2.** $Q(T)$ for $H_2^{16}O$ versus the term value, $F$, in wavenumbers for the following $T$ values: 1000, 2000, 3000, 3500, 4000, 4500, and 5000 K.

**Table 1**

Molecule number, chemical formula, isotopologue number (ISO#), AFGL code, state independent degeneracy factor ($g_i$), $Q(296 K)$, $J_{max}$, $F_{max}$ in cm$^{-1}$, and $T_{max}$ in K. Blank entries imply the data are not applicable.

| Molecule # | Formula | ISO# | AFGL code | $g_i$ | $Q(296 K)$ | $J_{max}$ | $F_{max}$ cm$^{-1}$ | $T_{max}$ K |
|---|---|---|---|---|---|---|---|---|
| 1 | $H_2^{16}O$ | 1 | 161 | 1 | $1.7458 \times 10^2$ | 50 | 30000 | 5000 |
| | $H_2^{18}O$ | 2 | 181 | 1 | $1.7605 \times 10^2$ | 50 | 53501 | 5000 |
| | $H_2^{17}O$ | 3 | 171 | 6 | $1.0521 \times 10^3$ | 50 | 55273 | 5000 |
| | $HD^{16}O$ | 4 | 162 | 6 | $8.6474 \times 10^2$ | 50 | 29665 | 5000 |
| | $HD^{18}O$ | 5 | 182 | 6 | $8.7557 \times 10^2$ | 30 | 42008 | 5000 |
| | $HD^{17}O$ | 6 | 172 | 36 | $5.2268 \times 10^3$ | 30 | 42074 | 5000 |
| | $D_2^{16}O$ | 7 | 262 | 1 | $1.0278 \times 10^3$ | 98 | 42000 | 6000 |
| | $D_2^{18}O$ | 8 | 282 | 1 | $1.0434 \times 10^3$ | 98 | 42000 | 6000 |
| | $D_2^{17}O$ | 9 | 272 | 6 | $6.2160 \times 10^3$ | 98 | 42000 | 6000 |
| 2 | $^{12}C^{16}O_2$ | 1 | 626 | 1 | $2.8609 \times 10^2$ | 150 | 30385 | 5000 |
| | $^{13}C^{16}O_2$ | 2 | 636 | 2 | $5.7664 \times 10^2$ | 150 | 30438 | 5000 |
| | $^{16}O^{12}C^{18}O$ | 3 | 628 | 1 | $6.0781 \times 10^2$ | 150 | 19445 | 3500 |
| | $^{16}O^{12}C^{17}O$ | 4 | 627 | 6 | $3.5426 \times 10^3$ | 150 | 19429 | 3500 |
| | $^{16}O^{13}C^{18}O$ | 5 | 638 | 2 | $1.2255 \times 10^3$ | 150 | 19498 | 3500 |
| | $^{16}O^{13}C^{17}O$ | 6 | 637 | 12 | $7.1413 \times 10^3$ | 150 | 19482 | 3500 |
| | $^{12}C^{18}O_2$ | 7 | 828 | 1 | $3.2342 \times 10^2$ | 150 | 30452 | 5000 |
| | $^{17}O^{12}C^{18}O$ | 8 | 827 | 6 | $3.7666 \times 10^3$ | 150 | 19462 | 3500 |
| | $^{12}C^{17}O_2$ | 9 | 727 | 1 | $1.0972 \times 10^4$ | 150 | 30420 | 5000 |
| | $^{13}C^{18}O_2$ | 0 | 838 | 2 | $6.5224 \times 10^2$ | 150 | 30506 | 5000 |
| | $^{18}O^{13}C^{17}O$ | 11 | 837 | 12 | $7.5950 \times 10^3$ | 150 | 19516 | 3500 |
| | $^{13}C^{17}O_2$ | 12 | 737 | 2 | $2.2120 \times 10^4$ | 150 | 30474 | 5000 |
| | $^{14}C^{16}O_2$ | 13 | 646 | 1 | $2.9048 \times 10^2$ | 150 | 30484 | 5000 |
| 3 | $^{16}O_3$ | 1 | 666 | 1 | $3.4837 \times 10^3$ | | | 3500 |
| | $^{16}O^{16}O^{18}O$ | 2 | 668 | 1 | $7.4657 \times 10^3$ | | | 3500 |
| | $^{16}O^{18}O^{16}O$ | 3 | 686 | 1 | $3.6471 \times 10^3$ | | | 3500 |
| | $^{16}O^{16}O^{17}O$ | 4 | 667 | 6 | $4.3331 \times 10^4$ | | | 3500 |
| | $^{16}O^{17}O^{16}O$ | 5 | 676 | 6 | $2.1405 \times 10^4$ | | | 3500 |
| | $^{18}O^{18}O^{16}O$ | 6 | 886 | 1 | $7.8232 \times 10^3$ | | | 3500 |
| | $^{18}O^{16}O^{18}O$ | 7 | 868 | 1 | $4.0062 \times 10^3$ | | | 3500 |
| | $^{16}O^{17}O^{18}O$ | 8 | 678 | 6 | $4.5896 \times 10^4$ | | | 3500 |
| | $^{17}O^{16}O^{18}O$ | 9 | 768 | 6 | $4.6468 \times 10^4$ | | | 3500 |
| | $^{17}O^{18}O^{16}O$ | 10 | 786 | 6 | $4.5388 \times 10^4$ | | | 3500 |
| | $^{17}O^{17}O^{16}O$ | 11 | 776 | 36 | $2.6630 \times 10^5$ | | | 3500 |
| | $^{17}O^{16}O^{17}O$ | 12 | 767 | 1 | $1.3479 \times 10^5$ | | | 3500 |
| | $^{18}O_3$ | 13 | 888 | 1 | $4.2015 \times 10^3$ | | | 3500 |
| | $^{18}O^{18}O^{17}O$ | 14 | 887 | 6 | $4.8688 \times 10^4$ | | | 3500 |
| | $^{18}O^{17}O^{18}O$ | 15 | 878 | 6 | $2.4641 \times 10^4$ | | | 3500 |
| | $^{17}O^{17}O^{18}O$ | 16 | 778 | 36 | $2.8573 \times 10^5$ | | | 3500 |
| | $^{17}O^{18}O^{17}O$ | 17 | 787 | 1 | $1.4126 \times 10^5$ | | | 3500 |
| | $^{17}O_3$ | 18 | 777 | 6 | $8.2865 \times 10^5$ | | | 3500 |
| 4 | $^{14}N_2^{16}O$ | 1 | 446 | 9 | $4.9849 \times 10^3$ | 165 | 14275 | 5000 |
| | $^{14}N^{15}N^{16}O$ | 2 | 456 | 6 | $3.3620 \times 10^3$ | | | 3500 |
| | $^{15}N^{14}N^{16}O$ | 3 | 546 | 6 | $3.4586 \times 10^3$ | | | 3500 |
| | $^{14}N_2^{18}O$ | 4 | 448 | 9 | $5.3147 \times 10^3$ | | | 3500 |
| | $^{14}N_2^{17}O$ | 5 | 447 | 54 | $3.0972 \times 10^4$ | | | 3500 |
| 5 | $^{12}C^{16}O$ | 1 | 26 | 1 | $1.0742 \times 10^2$ | 150 | 119658.44 | 9000 |
| | $^{13}C^{16}O$ | 2 | 36 | 2 | $2.2469 \times 10^2$ | 150 | 88787.98 | 9000 |
| | $^{12}C^{18}O$ | 3 | 28 | 1 | $1.1277 \times 10^2$ | 150 | 88660.52 | 9000 |
| | $^{12}C^{17}O$ | 4 | 27 | 6 | $6.6117 \times 10^2$ | 150 | 89433.11 | 9000 |
| | $^{13}C^{18}O$ | 5 | 38 | 2 | $2.3644 \times 10^2$ | 150 | 87060.40 | 9000 |
| | $^{13}C^{17}O$ | 6 | 37 | 12 | $1.3847 \times 10^3$ | 150 | 87886.89 | 9000 |
| | $^{14}C^{16}O$ | 7 | 46 | 1 | $1.1693 \times 10^2$ | 150 | 87435.55 | 9000 |
| | $^{14}C^{18}O$ | 8 | 48 | 1 | $1.2331 \times 10^2$ | 150 | 85610.49 | 9000 |
| | $^{14}C^{17}O$ | 9 | 47 | 6 | $7.2137 \times 10^2$ | 150 | 86482.69 | 9000 |
| 6 | $^{12}CH_4$ | 1 | 211 | 1 | $5.9048 \times 10^2$ | | | 3500 |
| | $^{13}CH_4$ | 2 | 311 | 2 | $1.1808 \times 10^3$ | | | 3500 |
| | $^{12}CH_3D$ | 3 | 212 | 3 | $4.7955 \times 10^3$ | | | 3500 |
| | $^{13}CH_3D$ | 4 | 312 | 6 | $9.5992 \times 10^3$ | | | 4500 |
| 7 | $^{16}O_2$ | 1 | 66 | 1 | $2.1573 \times 10^2$ | 40 | 40748 | 7500 |
| | $^{16}O^{18}O$ | 2 | 68 | 1 | $4.5523 \times 10^2$ | 99 | 45869 | 7500 |
| | $^{16}O^{17}O$ | 3 | 67 | 6 | $2.6581 \times 10^3$ | 101 | 46430 | 7500 |
| | $^{18}O^{18}O$ | 4 | 88 | 1 | $2.4232 \times 10^2$ | 99 | 44989 | 7500 |
| | $^{18}O^{17}O$ | 5 | 87 | 6 | $2.8191 \times 10^3$ | 101 | 45738 | 7500 |
| | $^{17}O^{17}O$ | 6 | 77 | 1 | $8.2238 \times 10^3$ | 104 | 46338 | 7500 |
| 8 | $^{14}N^{16}O$ | 1 | 46 | 3 | $1.1421 \times 10^3$ | | | 3500 |
| | $^{15}N^{16}O$ | 2 | 56 | 2 | $7.8926 \times 10^2$ | | | 3500 |

**Table 1** (continued)

| Molecule # | Formula | ISO# | AFGL code | $g_i$ | Q(296 K) | $J_{max}$ | $F_{max}$ cm$^{-1}$ | $T_{max}$ K |
|---|---|---|---|---|---|---|---|---|
| | $^{14}N^{18}O$ | 3 | 48 | 3 | $1.2044 \times 10^3$ | | | 3500 |
| 9 | $^{32}S^{16}O_2$ | 1 | 626 | 1 | $6.3403 \times 10^3$ | | | 3500 |
| | $^{34}S^{16}O_2$ | 2 | 646 | 1 | $6.3690 \times 10^3$ | | | 3500 |
| 10 | $^{14}N^{16}O_2$ | 1 | 646 | 3 | $1.3577 \times 10^4$ | | | 3500 |
| 11 | $^{14}NH_3$ | 1 | 4111 | 3 | $1.7252 \times 10^3$ | 23 | 35332 | 6000 |
| | $^{15}NH_3$ | 2 | 5111 | 2 | $1.1533 \times 10^3$ | 18 | 29851 | 6000 |
| 12 | $H^{14}N^{16}O_3$ | 1 | 146 | 6 | $2.1393 \times 10^5$ | | | 3500 |
| | $H^{15}N^{16}O_3$ | 2 | 156 | 4 | $1.4313 \times 10^5$ | | | 3500 |
| 13 | $^{16}OH$ | 1 | 61 | 2 | $8.0348 \times 10^1$ | 68.5 | 538367 | 9000 |
| | $^{18}OH$ | 2 | 81 | 2 | $8.0882 \times 10^1$ | | | 3500 |
| | $^{16}OD$ | 3 | 62 | 3 | $2.0932 \times 10^2$ | | | 3500 |
| 14 | $H^{19}F$ | 1 | 19 | 4 | $4.1469 \times 10^1$ | 51 | 52766 | 6000 |
| | $D^{19}F$ | 2 | 29 | 6 | $1.1591 \times 10^2$ | 80 | 56107 | 6000 |
| 15 | $H^{35}Cl$ | 1 | 15 | 8 | $1.6065 \times 10^2$ | 79 | 47780 | 6000 |
| | $H^{37}Cl$ | 2 | 17 | 8 | $1.6089 \times 10^2$ | 81 | 49220 | 6000 |
| | $D^{35}Cl$ | 3 | 25 | 12 | $4.6278 \times 10^2$ | 81 | 38630 | 6000 |
| | $D^{37}Cl$ | 4 | 27 | 12 | $4.6413 \times 10^2$ | 41 | 21912 | 4000 |
| 16 | $H^{79}Br$ | 1 | 19 | 8 | $2.0017 \times 10^2$ | 81 | 41794 | 6000 |
| | $H^{81}Br$ | 2 | 11 | 8 | $2.0023 \times 10^2$ | 100 | 38915 | 6000 |
| | $D^{79}Br$ | 3 | 29 | 12 | $5.8640 \times 10^2$ | 119 | 44434 | 6000 |
| | $D^{81}Br$ | 4 | 21 | 12 | $5.8676 \times 10^2$ | 81 | 41786 | 6000 |
| 17 | $H^{127}I$ | 1 | 17 | 12 | $3.8899 \times 10^2$ | 85 | 36450 | 6000 |
| | $D^{127}I$ | 2 | 27 | 18 | $1.1471 \times 10^3$ | 121 | 37144 | 6000 |
| 18 | $^{35}Cl^{16}O$ | 1 | 56 | 4 | $3.2746 \times 10^3$ | | | 3500 |
| | $^{37}Cl^{16}O$ | 2 | 76 | 4 | $3.3323 \times 10^3$ | | | 3500 |
| 19 | $^{16}O^{12}C^{32}S$ | 1 | 622 | 1 | $1.2210 \times 10^3$ | | | 3500 |
| | $^{16}O^{12}C^{34}S$ | 2 | 624 | 1 | $1.2535 \times 10^3$ | | | 3500 |
| | $^{16}O^{13}C^{32}S$ | 3 | 632 | 2 | $2.4841 \times 10^3$ | | | 3500 |
| | $^{16}O^{12}C^{33}S$ | 4 | 623 | 4 | $4.9501 \times 10^3$ | | | 3500 |
| | $^{18}O^{12}C^{32}S$ | 5 | 822 | 1 | $1.3138 \times 10^3$ | | | 3500 |
| 20 | $H_2^{12}C^{16}O$ | 1 | 126 | 1 | $2.8445 \times 10^3$ | | | 3500 |
| | $H_2^{13}C^{16}O$ | 2 | 136 | 2 | $5.8377 \times 10^3$ | | | 3500 |
| | $H_2^{12}C^{18}O$ | 3 | 128 | 1 | $2.9864 \times 10^3$ | | | 3500 |
| 21 | $H^{16}O^{35}Cl$ | 1 | 165 | 8 | $1.9275 \times 10^4$ | | | 3500 |
| | $H^{16}O^{37}Cl$ | 2 | 167 | 8 | $1.9616 \times 10^4$ | | | 3500 |
| 22 | $^{14}N_2$ | 1 | 44 | 1 | $4.6710 \times 10^2$ | 75 | 76465 | 9000 |
| | $^{14}N^{15}N$ | 2 | 45 | 6 | $6.4410 \times 10^2$ | 75 | 75034 | 9000 |
| | $^{15}N_2$ | 3 | 55 | 1 | $2.2230 \times 10^2$ | 75 | 73581 | 9000 |
| 23 | $H^{12}C^{14}N$ | 1 | 124 | 6 | $8.9220 \times 10^2$ | 60 | 18817 | 3500 |
| | $H^{13}C^{14}N$ | 2 | 134 | 12 | $1.8310 \times 10^3$ | 60 | 18817 | 3500 |
| | $H^{12}C^{15}N$ | 3 | 125 | 4 | $6.1528 \times 10^2$ | | | 3500 |
| 24 | $^{12}CH_3^{35}Cl$ | 1 | 215 | 4 | $5.7916 \times 10^4$ | | | 3500 |
| | $^{12}CH_3^{37}Cl$ | 2 | 217 | 4 | $5.8834 \times 10^4$ | | | 3500 |
| 25 | $H_2^{16}O_2$ | 1 | 1661 | 1 | $9.8198 \times 10^3$ | 40 | 27090 | 6000 |
| 26 | $^{12}C_2H_2$ | 1 | 1221 | 1 | $4.1245 \times 10^2$ | 100 | 26386 | 5000 |
| | $H^{12}C^{13}CH$ | 2 | 1231 | 8 | $1.6562 \times 10^3$ | | | 3500 |
| | $H^{12}C^{12}CD$ | 3 | 1222 | 6 | $1.5818 \times 10^3$ | | | 3500 |
| 27 | $^{12}C_2H_6$ | 1 | 1221 | 1 | $7.0883 \times 10^4$ | | | 3500 |
| | $^{12}CH_3^{13}CH_3$ | 2 | 1231 | 2 | $3.6192 \times 10^4$ | | | 3500 |
| 28 | $^{31}PH_3$ | 1 | 1111 | 2 | $3.2494 \times 10^3$ | | | 4500 |
| 29 | $^{12}C^{16}O^{19}F_2$ | 1 | 269 | 1 | $7.0028 \times 10^4$ | | | 3500 |
| | $^{13}C^{16}O^{19}F_2$ | 2 | 369 | 2 | $1.4006 \times 10^5$ | | | 3500 |
| 30 | $^{32}S^{19}F_6$ | 1 | 29 | 1 | $1.6240 \times 10^6$ | | | 3500 |

**Table 1** *(continued)*

| Molecule # | Formula | ISO# | AFGL code | $g_i$ | Q(296 K) | $J_{max}$ | $F_{max}$ cm$^{-1}$ | $T_{max}$ K |
|---|---|---|---|---|---|---|---|---|
| 31 | $H_2{}^{32}S$ | 1 | 121 | 1 | $5.0579 \times 10^2$ | | | 4000 |
| | $H_2{}^{34}S$ | 2 | 141 | 1 | $5.0435 \times 10^2$ | | | 3500 |
| | $H_2{}^{33}S$ | 3 | 131 | 4 | $2.0149 \times 10^3$ | | | 3500 |
| 32 | $H^{12}C^{16}O^{16}OH$ | 1 | 126 | 4 | $3.9133 \times 10^4$ | | | 3500 |
| 33 | $H^{16}O_2$ | 1 | 166 | 2 | $4.3004 \times 10^3$ | | | 3500 |
| 35 | ${}^{35}Cl^{16}O^{14}N^{16}O_2$ | 1 | 5646 | 12 | $4.7888 \times 10^6$ | | | 3500 |
| | ${}^{37}Cl^{16}O^{14}N^{16}O_2$ | 2 | 7646 | 12 | $4.9107 \times 10^6$ | | | 3500 |
| 36 | ${}^{14}N^{16}O^+$ | 1 | 46 | 3 | $3.1169 \times 10^2$ | | | 3500 |
| 37 | $H^{16}O^{79}Br$ | 1 | 169 | 8 | $2.8339 \times 10^4$ | | | 3500 |
| | $H^{16}O^{81}Br$ | 2 | 161 | 8 | $2.8238 \times 10^4$ | | | 3500 |
| 38 | ${}^{12}C_2H_4$ | 1 | 221 | 1 | $1.1042 \times 10^4$ | | | 3500 |
| | ${}^{12}CH_2{}^{13}CH_2$ | 2 | 231 | 2 | $4.5197 \times 10^4$ | | | 3500 |
| 39 | ${}^{12}CH_3{}^{16}OH$ | 1 | 2161 | 1 | $7.0570 \times 10^4$ | | | 3500 |
| 40 | ${}^{12}CH_3{}^{79}Br$ | 1 | 219 | 4 | $8.3052 \times 10^4$ | | | 3500 |
| | ${}^{12}CH_3{}^{81}Br$ | 2 | 211 | 4 | $8.3395 \times 10^4$ | | | 3500 |
| 41 | ${}^{12}CH_3{}^{12}C^{14}N$ | 1 | 2124 | 3 | $8.8672 \times 10^4$ | | | 3500 |
| | ${}^{13}CH_3{}^{12}C^{14}N$ | 2 | 3124 | 6 | $1.8366 \times 10^5$ | | | 3500 |
| | ${}^{12}CH_3{}^{13}C^{14}N$ | 3 | 2134 | 6 | $1.8096 \times 10^5$ | | | 3500 |
| | ${}^{13}CH_3{}^{13}C^{14}N$ | 4 | 3134 | 12 | $3.7416 \times 10^5$ | | | 3500 |
| 43 | ${}^{12}C_4H_2$ | 1 | 2211 | 1 | $9.8190 \times 10^3$ | | | 3500 |
| 44 | $H^{12}C_3{}^{14}N$ | 1 | 12224 | 6 | $2.4787 \times 10^4$ | | | 3500 |
| | $H^{12}C_3{}^{15}N$ | 2 | 12225 | 12 | $1.7036 \times 10^4$ | | | 3500 |
| | $H^{12}C^{12}C^{13}C^{14}N$ | 3 | 12234 | 12 | $4.9887 \times 10^4$ | | | 3500 |
| | $H^{12}C^{13}C^{12}C^{14}N$ | 4 | 12324 | 12 | $4.9718 \times 10^4$ | | | 3500 |
| | $H^{13}C^{12}C^{12}C^{14}N$ | 5 | 13224 | 4 | $5.1541 \times 10^4$ | | | 3500 |
| | $D^{12}C^{12}C^{12}C^{14}N$ | 6 | 22224 | 9 | $4.5918 \times 10^4$ | | | 3500 |
| 45 | $H_2$ | 1 | 11 | 1 | $7.6712$ | 31 | 36126 | 6000 |
| | $HD$ | 2 | 12 | 6 | $2.9874 \times 10^1$ | 36 | 36405 | 6000 |
| 46 | ${}^{12}C^{32}S$ | 1 | 22 | 1 | $2.5362 \times 10^2$ | | | 3500 |
| | ${}^{12}C^{34}S$ | 2 | 24 | 1 | $2.5777 \times 10^2$ | | | 3500 |
| | ${}^{13}C^{32}S$ | 3 | 32 | 2 | $5.3750 \times 10^2$ | | | 3500 |
| | ${}^{12}C^{33}S$ | 4 | 23 | 4 | $1.0230 \times 10^3$ | | | 3500 |
| 47 | ${}^{32}S^{16}O_3$ | 1 | 26 | 1 | $7.7833 \times 10^3$ | | | 3500 |
| 48 | ${}^{14}N^{12}C^{12}C^{14}N$ | 1 | 4224 | 1 | $1.5582 \times 10^4$ | | | 3500 |
| | ${}^{15}N^{12}C^{12}C^{15}N$ | 2 | 5225 | 1 | $7.3650 \times 10^3$ | | | 3500 |
| 49 | ${}^{12}C^{16}O^{35}Cl_2$ | 1 | 2655 | 1 | $1.4800 \times 10^6$ | | | 5000 |
| | ${}^{12}C^{16}O^{35}Cl^{37}Cl$ | 2 | 2657 | 16 | $3.0435 \times 10^6$ | | | 5000 |
| 50 | ${}^{32}S^{16}O$ | 1 | 26 | 1 | $8.4304 \times 10^2$ | | | 3500 |
| | ${}^{34}S^{16}O$ | 2 | 46 | 1 | $8.5988 \times 10^2$ | | | 3500 |
| | ${}^{32}S^{18}O$ | 3 | 28 | 1 | $9.1068 \times 10^2$ | | | 3500 |
| 51 | ${}^{12}C_3H_4$ | 1 | 1221 | 2 | $7.4897 \times 10^4$ | | | 3500 |
| 52 | ${}^{12}CH_3$ | 1 | 2111 | 1 | $6.3488 \times 10^2$ | | | 3500 |
| 53 | ${}^{32}S\ {}^{12}C^{32}S$ | 1 | 222 | 1 | $1.3526 \times 10^3$ | | | 3500 |
| | ${}^{32}S\ {}^{12}C^{34}S$ | 2 | 224 | 1 | $2.7980 \times 10^3$ | | | 3500 |
| | ${}^{32}S\ {}^{12}C^{33}S$ | 3 | 223 | 4 | $1.1007 \times 10^4$ | | | 3500 |
| | ${}^{32}S\ {}^{13}C^{32}S$ | 4 | 232 | 2 | $2.7397 \times 10^3$ | | | 3500 |

adequate for convergence at 3500 K so new calculations were performed. The potential energy surface (PES) used for the computation of $H_2{}^{18}O$ and $H_2{}^{17}O$ energy levels was constructed from the fitted $H_2{}^{16}O$ PES [33]. The PES contains two parts a) a mass independent part (Born-Oppenheimer (BO) surface, including a relativistic correction surface) and b) the part dependent on nuclear mass (diagonal Born-Oppenheimer correction, DBOC). Only the first part of the potential was fitted to the experimental $H_2{}^{16}O$ term values in the 0–25,000 cm$^{-1}$ range – common for both isotopologues. The second part was specific for each isotopologue
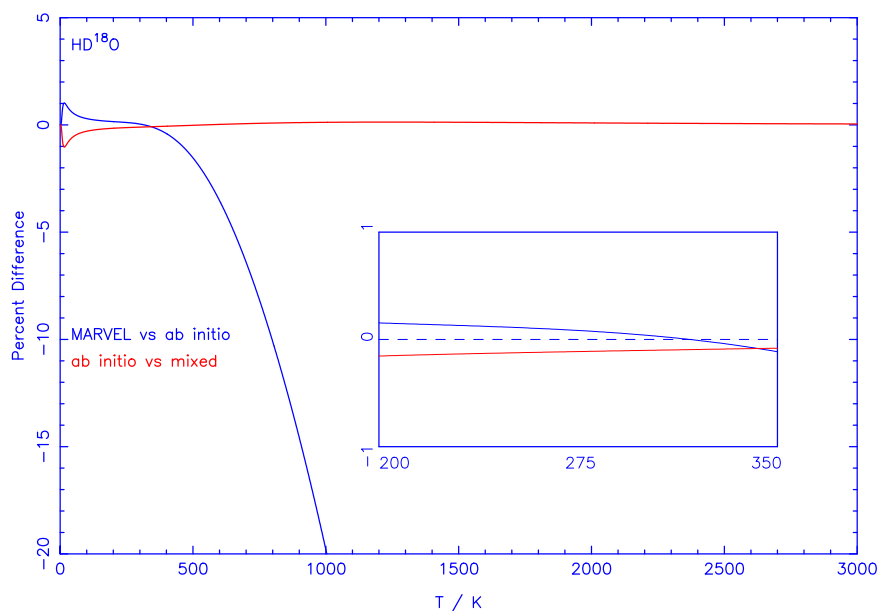
**Fig. 3.** The percent difference between $Q(T)$ determined with purely MARVEL term values and $Q(T)$ determined with *ab initio* term values (blue curve) and $Q(T)$ determined with mixed term values and $Q(T)$ determined with *ab initio* energies (red curve) HD$^{18}$O versus temperature in K. The insert gives an expanded view of the data in the temperature range of Earth's atmosphere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[34]. The experimental term values of $H_2{}^{17}O$ and $H_2{}^{18}O$ are known to only about 17,000 cm$^{-1}$ [35] in comparison with term values to about 41,000 cm$^{-1}$ for the main isotopologue [36]. The fitted PES describe experimental rovibrational levels of $H_2{}^{17}O$ and $H_2{}^{18}O$ with accuracy better than 0.1 cm$^{-1}$ and will predict unknown experimental levels in the range up to $J=30$ and term value up to 30,000 cm$^{-1}$ with accuracy better than 1 cm$^{-1}$. The latter assumption was partly confirmed by comparing the predictions with half a dozen $H_2{}^{18}O$ levels measured by Makarov et al. [37] around of 27,500 cm$^{-1}$. Nuclear motion calculations were performed with the DVR3D program suite [38]. The calculations used 28 radial points and 44 angular points with the final matrix of 2500. The final calculations go to $J=50$ and are complete to $\sim$55,000 cm$^{-1}$, see Table 1 for details. A set of term values was constructed using MARVEL term values where possible and other levels used the *ab initio* values. TIPS were calculated by direct summation with the *ab initio* term values, with MARVEL term values, and mixed term values. The data show the MARVEL and *ab initio* $Q(T)$ values agree at low temperature (reflecting the accuracy of the low $J$ *ab initio* energies) and the purely MARVEL TIPS begin to diverge at $\sim$500 K.

For HD$^{16}$O, the term values were taken from Voronin et al. [39]. The calculations go to $J=50$ and the term values are complete to 29,665 cm$^{-1}$. A mixed term value set was made. TIPS were calculated by direct summation using the 3 term value sets (*ab initio*, MARVEL, and mixed). The MARVEL and *ab initio* $Q(T)$ values agree at low temperature and the MARVEL TIPS begin to diverge: -0.143% at $\sim$1000 K, -10% at 2000 K, -47% at 3000 K. The TIPS from this study agree with the UCL data [40], which are reported for 32 temperatures between 1 and 6000 K .

For HD$^{18}$O and HD$^{17}$O, new calculations were performed in order to get $Q(T)$ that are converged up to high temperatures. The calculation of HD$^{18}$O and HD$^{17}$O levels were done with the use of the *ab initio* PES of Polyansky et al. [41]. A high-accuracy *ab initio* BO potential energy surface for the water molecule is combined with relativistic, adiabatic, quantum electrodynamics, and non-adiabatic corrections. The *ab initio* calculation reproduces about 200 known band origins of seven isotopologues of water in the range up to 15,000 cm$^{-1}$ with an accuracy of about 0.1 cm$^{-1}$. This accuracy smoothly deteriorates to several wavenumbers at the energies 25,000–30,000 cm$^{-1}$, as could be seen from comparing theoretical levels with the experimental ones of the $H_2{}^{16}O$

and HD$^{16}$O isotopologues [32,42]. Nuclear motion calculations were performed with the DVR3D program suite [38].

The TIPS were calculated using the *ab initio*, the MARVEL, and the mixed *ab initio*-MARVEL term values. Fig. 3 presents the percent difference between $Q(T)$ determined with MARVEL term values and $Q(T)$ determined with *ab initio* term values (blue curve) and $Q(T)$ determined with mixed term values and $Q(T)$ determined with *ab initio* term values (red curve) for HD$^{18}$O versus temperature. The insert gives an expanded view of the data in the temperature range of Earth's atmosphere. Here, because there are differences between the MARVEL and *ab initio* term values for low energy states, differences of order 1% are seen at low temperatures. The MARVEL term values are only complete to $\sim$1590 and 867 cm$^{-1}$ for HD$^{18}$O and HD$^{17}$O, respectively. The MARVEL TIPS values begin to diverge around 350 and 200 K for these isotopologues. The *ab initio* term values go to $J=30$ and $\sim$42,000 cm$^{-1}$ and are complete to $\sim$32,500 cm$^{-1}$ for these isotopologues. Fig. 4 shows $Q(T)$ for HD$^{18}$O as a function of the term value, $F$, in wavenumbers for temperature values: 1000, 2000, 3000, 3500, 4000, 4500, and 5000 K. The figure shows that the TIPS have converged up to 4500 K.

The doubly-deuterated isotopologues of water, $D_2{}^{16}O$, $D_2{}^{18}O$, and $D_2{}^{17}O$, used the *ab initio* term values reported in Simkó et al. [24]. The calculations go to $J=98$ and are complete to $\sim$42,000 cm$^{-1}$ for all isotopologues. Where possible the MARVEL term values were used to replace the *ab initio* term values. Convergence tests were done and the TIPS are converged to 6000 K. The TIPS for $D_2{}^{16}O$ agree with the UCL data, which are reported for 22 temperatures between 1 and 1000 K.

In Table 2 are listed the molecule number and isotopologue number (ISO#), and the percent difference TIPS_2017 – TIPS_2011 at 100, 296, 1000, and 2500 K for molecule/isotopologues that have been recalculated in this work. For the isotopologues of water vapor the differences are not large except at higher temperatures. Note, the improved calculations done here allow the TIPS to be determined at higher temperatures than what was done in 2011. Also, the TIPS are now presented for three isotopologues of $D_2O$.

### 3.2. Carbon dioxide

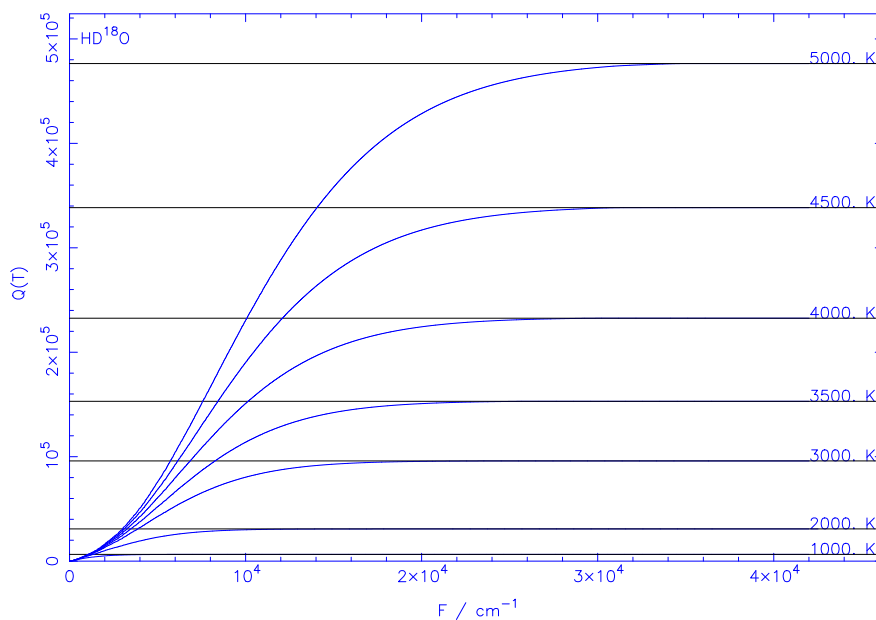The 13 isotopologues of $CO_2$ listed in Table 1 were considered in

**Fig. 4.** $Q(T)$ for HD$^{18}$O versus the term value, $F$, in wavenumbers for the following T values: 1000, 2000, 3000, 3500, 4000, 4500, and 5000 K.

this work. The term values for all isotopologues are from the *ab initio* calculations of Huang et al. [43–45], which go to $J=150$. The maximum term values are listed in Table 1. First the total internal partition sums were calculated using the *ab initio* term values. These values were compared with the carbon dioxide spectroscopic databank (CDSD) partition functions [46]. Note, the CDSD TIPS are reported only to 1000 K. What is observed is very good agreement for the isotopologues $^{12}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{16}O_2$, $^{13}C^{18}O_2$, $^{13}C^{17}O_2$, $^{16}O^{12}C^{17}O$. CDSD does not report the isotopologue $^{14}C^{16}O_2$. For the other isotopologues small differences in energy between CDSD and *ab initio* values lead to several percent difference in $Q(T)$ at low temperatures. Fig. 5 shows the percent difference between the CDSD and *ab initio* $Q(T)$ versus temperature for the $^{16}O$ $^{12}C^{18}O$ isotopologue. To correct this problem, the *ab initio* term values for the isotopologues $^{16}O^{12}C^{18}O$, $^{16}O^{13}C^{18}O$, $^{16}O^{13}C^{17}O$, $^{18}O^{12}C^{17}O$, $^{12}C^{17}O_2$, and $^{18}O^{13}C^{17}O$ were replaced from 0 to just over 600 cm$^{-1}$ using the CDSD values. The TIPS were run again and the results show excellent agreement with the CDSD $Q(T)$ throughout the CDSD temperature range (1–1000 K).

The TIPS for the symmetric isotopologues (inversion symmetry), $^{12}C^{16}O_2$, $^{12}C^{18}O_2$, $^{13}C^{16}O_2$, etc. are converged to about 4500 K and those for the isotopologues that are not symmetric, $^{16}O^{12}C^{18}O$, $^{16}O$ $^{12}C^{17}O$, etc. are converged to ~3000 K. The difference is easily explained by looking at the $F_{max}$ values listed in Table 1. The symmetric isotopologue term values are complete to around 30,000 cm$^{-1}$ and the non-symmetric isotopologues are complete to about half that value. The final TIPS calculations were made to 5000 K for the symmetric isotopologues and to 3500 K for the non-symmetric isotopologues.

Table 3 lists the total internal partition sums at 210, 410, 610, 810, and 1010 K for twelve isotopologues of CO$_2$ from this work, the CDSD values [46], and from the work of Cerezo et al. [47]. There is reasonably good agreement up to 610 K but the maximum energy for each isotopologue used in Ref. [47] is too low to ensure convergence past about 750 K. This fact is confirmed by data presented in Table 3. Comparing Q(296 K) for $^{12}C^{16}O_2$ with the CDSD value and the UCL value [48] gives 0.0014 and -0.29 percent differences, respectively.

Looking at Table 2 shows that for the temperature range of TIPS_2011 the improvements using the *ab initio* energies are small. However, the use of the *ab initio* energies allows convergence to higher temperatures than TIPS_2011.

### 3.3. Ozone

Total internal partition sums are provided for the following 18 isotopologues of ozone: $^{16}O_3$, $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{16}O^{17}O$, $^{16}O^{17}O^{16}O$, $^{18}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{16}O^{17}O^{18}O$, $^{17}O^{16}O^{18}O$, $^{17}O^{18}O^{16}O$, $^{17}O^{17}O^{16}O$, $^{17}O^{16}O^{17}O$, $^{18}O_3$, $^{18}O^{18}O^{17}O$, $^{18}O^{17}O^{18}O$, $^{17}O^{17}O^{18}O$, $^{17}O^{18}O^{17}O$, and $^{17}O_3$. The TIPS are from Fischer et al. [16] and are reported to 3500 K for all isotopologues.

### 3.4. Nitrous oxide

TIPS are given for 5 isotopologues of nitrous oxide: $^{14}N_2^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N_2^{18}O$, and $^{14}N_2^{17}O$. The principal isotopologue, $^{14}N_2^{16}O$, uses the data of Tashkun et al. [49]. From the supplementary line list, quantum numbers and term values were extracted, giving 143,096 states. The data are complete to 11,344 cm$^{-1}$ and go as high as ~14,275 cm$^{-1}$. Fig. 6 shows $Q(T)$ versus $F$ for $T=1000$, 2000, 3000, 4000, 5000, and 6000 K. The figure shows the TIPS are converged upto ~4000 K. The TIPS are reported to 5000 K; however, users should realize that at 5000 K the uncertainty may be several percent. Table 2 shows a -9% difference between TIPS_2017 and TIPS_2011 at 2500 K indicating the improvement at higher temperatures.

The isotopologues $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N_2^{18}O$, and $^{14}N_2^{17}O$ use the TIPS from Fischer et al. [16], which are reported to 3500 K.

### 3.5. Carbon monoxide

The nine isotopologues of CO reported here are from the work of Li et al. [50]. The calculations were made for $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, $^{13}C^{18}O$, $^{13}C^{17}O$, $^{14}C^{16}O$, $^{14}C^{18}O$, and $^{14}C^{17}O$ in the electronic ground state with $\nu \leq 41$ and $J \leq 150$. The term values are complete to 85,600 cm$^{-1}$ or higher and the TIPS are converged to 9000 K for each isotopologue. The final TIPS are reported to 9000 K; see Ref. [50] for details. While Table 2 shows little difference between the TIPS_2017 and TIPS_2011 results, the new calculations have allowed the TIPS to be determined to 9000 K for each isotopologue.

### 3.6. Methane

Total internal partition sums are reported for the $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, and $^{13}CH_3D$ isotopologues of methane. The $Q(T)$ data for the

**Table 2**
Molecule number (MOL), isotopologue number (ISO#), percent difference (PD) TIPS_2017-TIPS_2011 at 100, 296, 1000, and 2500 K for molecule/isotopologues that have been recalculated in this work.

| MOL | ISO# | PD(100K) | PD(296K) | PD(1000K) | PD(2500K) |
|---|---|---|---|---|---|
| 1 | 1 | 0.3515 | -0.0333 | -0.4697 | -0.8250 |
| 1 | 2 | 2.7963 | 0.5322 | -0.1926 | -2.3800 |
| 1 | 3 | 2.8112 | 0.3962 | -0.2834 | -2.3461 |
| 1 | 4 | 3.4565 | 0.6622 | -0.3344 | -0.0644 |
| 1 | 5 | 0.0140 | 0.0438 | -0.1728 | -1.9053 |
| 1 | 6 | 0.0089 | 0.1229 | 0.2363 | -2.7051 |
| 2 | 1 | -0.1082 | -0.2956 | 0.2293 | 1.1611 |
| 2 | 2 | -0.1079 | -0.3067 | -0.1944 | 0.3255 |
| 2 | 3 | -0.1035 | -0.2747 | 0.6965 | 1.3697 |
| 2 | 4 | -0.1092 | -0.2845 | 0.4559 | 0.9915 |
| 2 | 5 | -0.1086 | -0.2924 | 0.1305 | 0.2629 |
| 2 | 6 | -0.1083 | -0.3026 | -0.0411 | 0.0329 |
| 2 | 7 | -0.1057 | -0.2445 | 1.2934 | 2.7046 |
| 2 | 8 | -0.1001 | -0.2590 | 0.9951 | 1.8050 |
| 2 | 9 | -0.1064 | -0.2704 | 0.7189 | 1.8904 |
| 2 | 10 | -0.1005 | -0.2325 | 0.9831 | 2.0704 |
| 2 | 11 | -0.1054 | -0.2666 | 0.5484 | 0.9175 |
| 4 | 1 | -0.1070 | -0.3380 | -0.6272 | -9.1219 |
| 5 | 1 | 0.3377 | 0.1495 | -0.4972 | -1.3732 |
| 5 | 2 | 0.3311 | 0.1358 | -0.5060 | -1.3660 |
| 5 | 3 | 0.3293 | 0.1356 | -0.5048 | -1.3681 |
| 5 | 4 | 0.3302 | 0.1422 | -0.4990 | -1.3693 |
| 5 | 5 | 0.3195 | 0.1250 | -0.5132 | -1.3631 |
| 5 | 6 | 0.3230 | 0.1324 | 0.0239 | 0.4317 |
| 6 | 1 | 0.0144 | -0.0069 | -0.0293 | -29.3002 |
| 7 | 1 | -0.0186 | -0.0203 | -3.0794 | -34.1502 |
| 7 | 2 | 1.9374 | 0.6428 | 0.3704 | 1.1137 |
| 7 | 3 | 83.6639 | 83.4437 | 83.3942 | 83.5161 |
| 11 | 1 | 0.0012 | -0.0020 | 2.1400 | -0.0548 |
| 11 | 2 | 0.0546 | 0.0528 | -1.6130 | -45.7731 |
| 12 | 1 | 0.0015 | -0.0875 | -0.3391 | -0.4765 |
| 13 | 1 | -0.0281 | -0.0171 | 0.0172 | 0.8492 |
| 13 | 2 | 0.0134 | -0.0001 | -0.0005 | 0.0001 |
| 13 | 3 | 0.0068 | 0.0032 | 0.0000 | -0.0007 |
| 14 | 1 | 0.0051 | 0.0065 | 0.0299 | 0.0784 |
| 15 | 1 | -0.0015 | -0.0053 | -0.0006 | -0.0037 |
| 15 | 2 | -0.0014 | -0.0006 | -0.0017 | 0.0026 |
| 16 | 1 | -0.0015 | -0.0028 | -0.0016 | -0.0040 |
| 16 | 2 | 0.0000 | -0.0028 | -0.0001 | -0.0040 |
| 17 | 1 | 0.0008 | -0.0018 | -0.0004 | -0.0495 |
| 22 | 1 | 0.3541 | 0.2403 | -0.1383 | -0.6741 |
| 23 | 1 | -0.1163 | -0.3467 | -1.0911 | 0.4282 |
| 23 | 2 | -0.2117 | -0.5101 | -1.0842 | 1.4781 |
| 23 | 3 | -0.8340 | -0.9960 | 3.8605 | 4.8491 |
| 25 | 1 | 0.1027 | 0.2863 | -13.1611 | -130.1650 |
| 26 | 1 | -0.1121 | -0.3836 | -1.9538 | -14.5110 |
| 28 | 1 | 0.0093 | 0.0256 | 1.0164 | 3.9380 |
| 29 | 1 | 0.0008 | -0.0231 | -0.0650 | -0.0946 |
| 31 | 1 | 0.1876 | 0.5373 | 1.6113 | 5.2136 |
| 45 | 1 | 0.0500 | -0.0163 | -0.0196 | -0.0233 |
| 45 | 2 | 0.0039 | -0.0182 | -0.0194 | -0.0234 |

principal isotopologue are from the work of Nikitin et al. [51]. They estimate a number of high-energy contributions to the partition sums to improve the accuracy, which they estimate to be 1–2% at 2000 K. Their calculations consider temperatures up to 3000 K. They have also made an estimate for the temperature range 3001–3500 K [52]. Table 2 shows little difference between TIPS_2017 and TIPS_2011 values at the lower temperatures, but a -29% difference at 2500 K.

The TIPS for $^{13}CH_4$ are from the work of Fischer et al. [16] and use the product approximation with the analytical approximation of McDowell [29] for $Q_{rot}$. However, the analytical model does not give reliable $Q(T)$ values at low temperatures. To correct for this fact, energies for $^{13}CH_4$ were extracted from HITRAN2012 and $Q(T)$ determined by direct sum. The direct sum values of $Q(T)$ were used from 1–25 K and the product approximation values from 26–3500 K. The TIPS for $^{12}CH_3D$ are from the work of Laraia et al. [17]. The TIPS for $^{13}CH_3D$ were recalculated up to 4500 K using the vibrational fundamentals of Nikitin et al. [53] for $Q_{vib}$ and the $Q_{rot}$ of Laraia et al. [17].

The TIPS are reported up to 3500 K for $CH_4$, $^{13}CH_4$, and $^{13}CH_3D$, and up to 4500 K for $^{12}CH_3D$.

### 3.7. Oxygen molecule

Six isotopologues of the oxygen molecule were considered in this work: $^{16}O_2$, $^{16}O^{18}O$, $^{16}O^{17}O$, $^{18}O^{18}O$, $^{18}O^{17}O$, $^{17}O^{17}O$. The term values were determined using an isotopically-invariant Dunham fit of $O_2$ with newly reported literature transitions [54] for the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states. As shown in Table 1, the term values are calculated up to 40,000–46,000 $cm^{-1}$ and are complete to roughly 39,000 $cm^{-1}$. The TIPS converge to 7500 K for all isotopologues. Table 2 shows little difference between TIPS_2017 and TIPS_2011 results for $^{16}O_2$ and $^{16}O^{18}O$ until 2500 K. For the $^{16}O^{17}O$ isotopologue, there was a zero point error in the TIPS_2011 results that was corrected in 2014. This error is shown in the table.

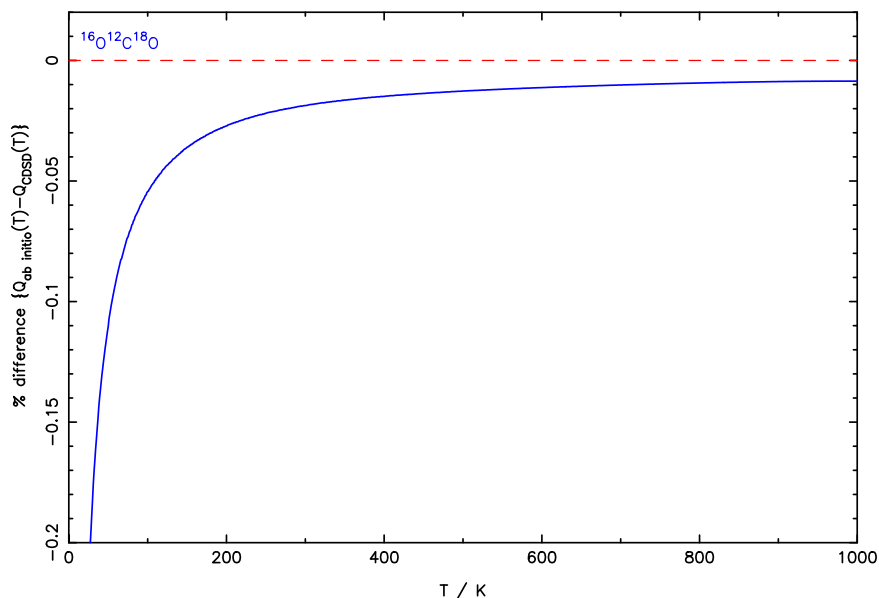**Fig. 5.** The percent difference between the CDSD and *ab initio* $Q(T)$ versus temperature for the $^{16}O\,^{12}C\,^{18}O$ isotopologue.

**Table 3**
Total internal partition sums at 210, 410, 610, 810, and 1010 K for twelve isotopologues of $CO_2$ for this work, TIPS_2011, CDSD-296, and from the work of Cerezo et al.

| | This work | TIPS_2011 | CDSD | Cerezo et al. | This work | TIPS_2011 | CDSD | Cerezo et al. |
|---|---|---|---|---|---|---|---|---|
| | | $^{12}C^{16}O_2$ | | | | $^{13}C^{16}O_2$ | | |
| 210 | 191.167 | 191.60 | 191.169 | 191.12 | 383.418 | 384.29 | 383.421 | 383.33 |
| 410 | 451.432 | 452.80 | 451.441 | 451.18 | 916.148 | 919.43 | 916.164 | 915.63 |
| 610 | 906.772 | 908.25 | 906.797 | 906.09 | 1858.50 | 1864.9 | 1858.54 | 1857.1 |
| 810 | 1676.48 | 1675.9 | 1676.53 | 1674.9 | 3462.20 | 3471.8 | 3462.28 | 3458.9 |
| 1010 | 2914.36 | 2907.4 | NA | 2910.1 | 6055.24 | 6066.8 | NA | 6046.2 |
| | | $^{16}O^{12}C^{18}O$ | | | | $^{16}O^{12}C^{17}O$ | | |
| 210 | 405.502 | 406.40 | 405.507 | 405.43 | 2365.22 | 2370.5 | 2365.22 | 2364.8 |
| 410 | 961.784 | 964.02 | 961.837 | 961.45 | 5598.19 | 5613.2 | 5598.29 | 5596.1 |
| 610 | 1942.59 | 1941.6 | 1942.731 | 1941.5 | 11,277.2 | 11,284. | 11,277.5 | 11,271 |
| 810 | 3609.70 | 3595.6 | 3609.974 | 3606.9 | 20,904.6 | 20,861. | 20,905.2 | 20,887 |
| 1010 | 6301.65 | 6256.8 | NA | 6293.2 | 36,420.6 | 36,250. | NA | 36,371 |
| | | $^{16}O^{13}C^{18}O$ | | | | $^{16}O^{13}C^{17}O$ | | |
| 210 | 813.440 | 815.28 | 813.462 | 813.31 | 4744.16 | 4755.0 | 4744.24 | 4755.0 |
| 410 | 1952.77 | 1958.8 | 1952.90 | 1954.1 | 11,363.3 | 11,402. | 11,364.0 | 11,402 |
| 610 | 3984.04 | 3991.8 | 3984.37 | 3981.9 | 23,120.0 | 23,184. | 23,121.6 | 23,184 |
| 810 | 7460.42 | 7462.6 | 7461.03 | 7454.6 | 43,186.6 | 43,256. | 43,189.7 | 43,256 |
| 1010 | 13,104.6 | 13,086. | NA | 13,086 | 75,702.7 | 75,729. | NA | 75,729 |
| | | $^{18}O^{12}C^{18}O$ | | | | $^{18}O^{12}C^{17}O$ | | |
| 210 | 215.413 | 215.88 | 215.408 | 215.35 | 2510.71 | 2516.2 | 2510.74 | 2364.8 |
| 410 | 513.322 | 513.97 | 513.318 | 513.03 | 5969.47 | 5980.2 | 5969.76 | 5596.1 |
| 610 | 1042.80 | 1039.3 | 1042.80 | 1042.0 | 12,093.2 | 12,070. | 12,094.0 | 11,271 |
| 810 | 1947.82 | 1931.2 | 1947.83 | 1945.9 | 22,532.4 | 22,393. | 22,533.9 | 20,887 |
| 1010 | 3415.12 | 3370.2 | NA | 3410.0 | 39,425.0 | 39,025. | NA | 36,371 |
| | | $^{18}O^{13}C^{18}O$ | | | | $^{18}O^{13}C^{17}O$ | | |
| 210 | 432.161 | 433.05 | 432.150 | 432.04 | 5036.71 | 5047.7 | 5036.78 | 5035.8 |
| 410 | 1042.63 | 1044.1 | 1042.630 | 1042.0 | 12,122.5 | 12,150. | 12,123.2 | 12,118 |
| 610 | 2139.9 | 2135.1 | 2139.900 | 2138.2 | 24,808.8 | 24,807. | 24,810.7 | 24,795 |
| 810 | 4028.46 | 4003.1 | 4028.533 | 4024.5 | 46,585.4 | 46,449. | 46,589.1 | 46,548 |
| 1010 | 7107.52 | 7036.4 | NA | 7096.8 | 82,018.9 | 81,558. | NA | 81,907 |
| | | $^{17}O^{12}C^{17}O$ | | | | $^{17}O^{13}C^{17}O$ | | |
| 210 | 7319.05 | 7335.3 | 7319.14 | 7317.8 | 14,681.7 | NA | 14,681.8 | 14,679 |
| 410 | 17,364.0 | 17,403. | 17,364.8 | 17,358 | 35,254.6 | NA | 35,256.1 | 35,243 |
| 610 | 35,081.8 | 35,060. | 35,083.5 | 35,063 | 71,947.8 | NA | 71,951.4 | 71,909 |
| 810 | 65,205.6 | 64,938. | 65,208.5 | 65,154 | 134,763. | NA | 134,769. | 134,655 |
| 1010 | 113,857. | 113,020. | NA | 113,703 | 236,769. | NA | NA | 236,445 |

## 3.8. Nitric oxide

Total internal partition sums are provided for $^{14}N^{16}O$, $^{15}N^{16}O$, and $^{14}N^{18}O$ from the work of Fischer et al. [16], which used the product approximation with $Q_{vib}$ from the harmonic approximation [25] and $Q_{rot}$ from McDowell's formula [27]. In Ref. [16] the partition sums were reported from 70–3000 K. Here, the temperature range starts at 1 K where the analytical formula does not give reliable results. The TIPS were calculated by direct sums using term values that include spin-orbit, lambda doubling and hyperfine interactions complete to $\sim$9000 cm$^{-1}$ and the direct sum values were used at low temperatures. The point where the data changes from direct sum values to
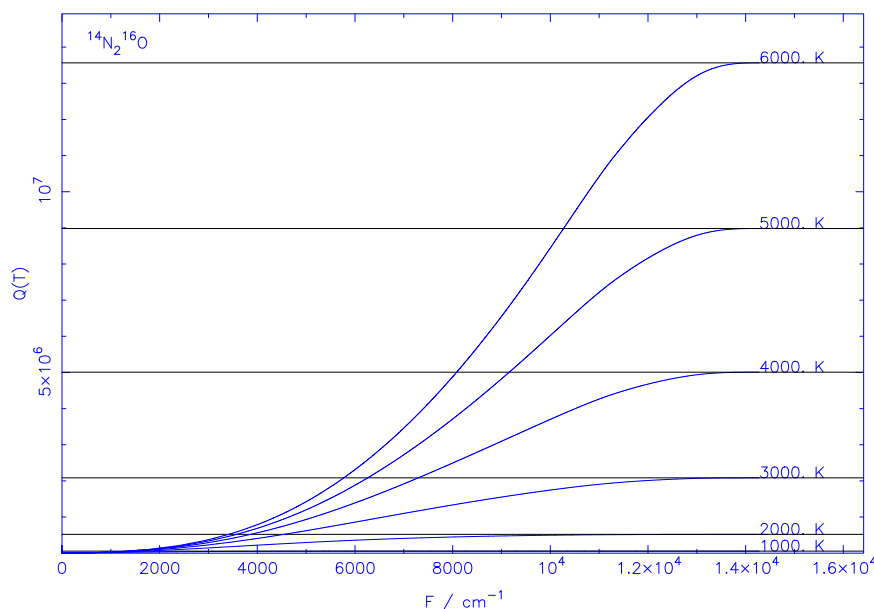
**Fig. 6.** $Q(T)$ for $^{14}N_2^{16}O$ versus $F$ in wavenumbers for $T=1000, 2000, 3000, 4000, 5000,$ and $6000$ K.

product approximation values is where the two have the best agreement (lowest percent difference). These values are 109, 105, and 106 K for $^{14}N^{16}O$, $^{15}N^{16}O$, and $^{14}N^{18}O$, respectively. The TIPS are reported to 3500 K for each isotopologue.

### 3.9. Sulfur dioxide

The TIPS for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ are from the work of Fischer et al. [16], which used the product approximation with Watson's asymmetric rotor analytical formula [30] for $Q_{rot}$. A low-temperature correction from 1–67 K was made for $^{32}S^{16}O_2$ using the UCL-Ames data [55], which goes to 1000 K. The TIPS are reported to 3500 K.

### 3.10. Nitrogen dioxide

The TIPS for $^{14}N^{16}O_2$ are taken from Fischer et al. [16], which used the product approximation with Watson's asymmetric rotor analytical formula [30] for $Q_{rot}$. The TIPS are reported to 3500 K with no low temperature corrections needed.

### 3.11. Ammonia

Two isotopologues of ammonia were considered in this work: $^{14}NH_3$ and $^{15}NH_3$. The term values for $^{14}NH_3$ are from Yurchenko et al. [56] and those for $^{15}NH_3$ are from Yurchenko et al. [57]. The term values are complete to 35,332 and 29,851 cm$^{-1}$ for the $^{14}NH_3$ and $^{15}NH_3$ isotopologues, respectively. These term values were used to compute the TIPS by direct summation. The TIPS calculated here agree with the values given by Yurchenko et al. [56] and Yurchenko et al. [57], which are reported to 1600 and 2000 K, respectively. The TIPS are converged to 6000 K. Table 2 shows that for the $^{14}NH_3$ isotopologue there is little difference at the temperatures of the TIPS_2011 study. However, the new calculations allow convergence to much higher temperatures. For the $^{15}NH_3$ isotopologue there is a noticeable difference in the TIPS at 2500 K.

### 3.12. Nitric acid

The TIPS were calculated for the $H^{14}N^{16}O_3$ and $H^{15}N^{16}O_3$ isotopologues of nitric acid. The calculations used the product approximation with $Q_{vib}$ coming from the harmonic approximation and $Q_{rot}$

from the analytical formula of Watson [30]. For the $H^{14}N^{16}O_3$ isotopologue the rotational constants are from Perrin et al. [58] and the vibrational fundamentals are from Perrin [59], which includes the $\nu_9$ torsion state. The rotational constants for the $H^{15}N^{16}O_3$ isotopologue are from Perrin et al. [60]. The vibrational fundamentals for $H^{15}N^{16}O_3$ are as follows: $\nu_1$ through $\nu_4$ were taken from the NIST webbook [61], $\nu_5$ was taken from Perrin et al. [60], and $\nu_6$ through $\nu_9$ (torsion) was from the work of Petkie et al. [62]. Pavlyuchko et al. [63] report TIPS values from 1 to 500 K for $H^{14}N^{16}O_3$ from direct summation over *ab initio* term values. The agreement between the TIPS determined in this work and Pavlyuchko et al. is good, the maximum difference is 1%. The TIPS from this work are reported for temperatures from 1 to 3500 K in 1 K steps. There are small differences between the TIPS_2017 and TIPS_2011 results as shown in Table 2. However, the calculations done here are an improvement as $T$ increases due to a more complete term value set.

### 3.13. Hydroxyl radical

New calculations of $Q(T)$ were made for the $^{16}OH$ isotopologue of OH. The term values are taken from Brooke et al. [64]. Their calculations go to rotational quantum number $J_{max}=68.5$ with a term value of $F(J_{max})=53,836.6$ cm$^{-1}$. The TIPS were calculated by direct summation over these energy states and are considered to be converged up to 9000 K.

The TIPS for the $^{18}OH$ and $^{16}OD$ isotopologues are from Fischer et al. [16]. Their calculations used the product approximation; no low temperature correction was needed.

The final TIPS are reported up to 9000, 3500, and 3500 K for the $^{16}OH$, $^{18}OH$ and $^{16}OD$ isotopologues, respectively.

For the principal isotopologue, Table 2 shows little differences between TIPS_2017 and TIPS_2011 for the temperatures of the 2011 study. However, the use of the *ab initio* term values in the direct sum allow the TIPS to be converged to 9000 K.

### 3.14. Hydrogen fluoride

TIPS were calculated for $H^{19}F$ and $D^{19}F$ by direct summation using the term values reported by Li et al. [65]. The term values are complete to 24,262 and 18,486 with $F_{max}$ values of 52,766 and 56,107 cm$^{-1}$ for $H^{19}F$ and $D^{19}F$, respectively. Convergence plots show the TIPS are accurate to 6000 K, which is the temperature to which they are reported.
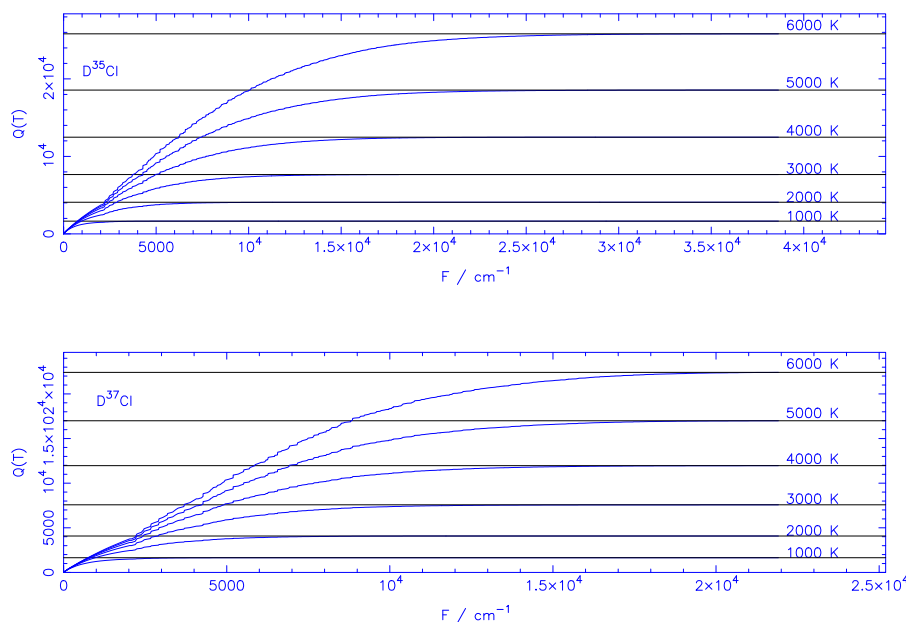
**Fig. 7.** $Q(T)$ for $D^{35}Cl$ and $D^{37}Cl$ versus $F$ in wavenumbers for T between 1000 and 6000 K in 1000 K steps.

Little difference is observed between the TIPS_2017 and TIPS_2011 values (Table 2) but the new calculations allow converged TIPS to 6000 K.

### 3.15. Hydrogen chloride

Four isotopologues of hydrogen chloride were considered in this work: $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, $D^{37}Cl$. The total internal partition sums were calculated by direct summation using the term values of Li et al. [65]. The term values, $E/hc$, in wavenumbers are calculated to ($F_{max}$, $F_{complete}$) values of (47,780, 20,196), (49,220, 20,184), (38,630, 15,239), and (21,912, 15,219) for $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, $D^{37}Cl$, respectively. Clearly for the $D^{37}Cl$ isotopologue the calculations were done up to substantially smaller energy levels than for the other three isotopologues. This is due to the fact that the original goal of Li et al. was to calculate partition sums only up to 3000 K. When it was decided to recalculate partition sums up to the energies required for converged calculations up to 6000 K, the $D^{37}Cl$ isotopologue was unintentionally forgotten. As a result, the first three isotopologues are converged to 6000 K. Fig. 7 shows the convergence plots, $Q(T)$ versus term value, for $D^{35}Cl$ and $D^{37}Cl$ from 1000 to 6000 K in 1000 K steps. While it is clear that $D^{35}Cl$ is converged to 6000 K (top panel), for $D^{37}Cl$ the similar convergence is at 4000 K (bottom panel). The TIPS are reported up to 6000 K for $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and up to 4000 K for $D^{37}Cl$.

Table 2 shows that the TIPS_2017 and TIPS_2011 values agree well at the temperatures of the 2011 study, but the new calculations generate TIPS that are converged to 6000 K.

### 3.16. Hydrogen bromide

For hydrogen bromide, $Q(T)$ values are calculated by direct summation using the term values of Li et al. [65] for four isotopologues: $H^{79}Br$, $H^{81}Br$, $D^{79}Br$, $D^{81}Br$. The $F_{max}$ and $F_{complete}$ term values in cm$^{-1}$ are (41,795, 21,435), (41,786, 17,909), (38,915, 13,433), and (44,435, 13,430) for $H^{79}Br$, $H^{81}Br$, $D^{79}Br$, $D^{81}Br$, respectively. The resulting TIPS are converged to 6000 K and they are reported to this temperature.

Table 2 demonstrates that little difference is observed between the TIPS_2017 and TIPS_2011 values, but the new calculations generate TIPS that are converged to 6000 K.

### 3.17. Hydrogen iodide

Two isotopologues of hydrogen iodide, $H^{127}I$ and $D^{127}I$, were considered here. The TIPS were calculated by direct summation over the term values of Li et al. [65], which have ($F_{max}$, $F_{complete}$) term values, in cm$^{-1}$, of (36,450, 12,154) and (37,144, 8990) for $H^{127}I$ and $D^{127}I$, respectively. Plots suggest that the TIPS are converged to 6000 K. However, with the $F_{complete}$ values shown above caution should be used above 4000 K where the uncertainties could be several percent. The final TIPS data are reported to 6000 K.

The TIPS_2017 and TIPS_2011 values agree well for the temperatures of the 2011 study, see Table 2, but the new calculations generate TIPS that are converged to 6000 K.

### 3.18. Chlorine monoxide

The TIPS reported for $^{35}Cl^{16}O$ and $^{37}Cl^{16}O$ are from Fischer et al. [16]. Fischer et al. calculated $Q(T)$ by the product approximation. Because chlorine monoxide has spin-orbit, lambda doubling and hyperfine interactions, an analytical formula, based on the linear molecule formula of McDowell [27] was developed, see Ref. [16] for details. The final $Q(T)$ are reported to 3500 K.

### 3.19. Carbonyl sulfide

The five isotopologues of carbonyl sulfide reported here, $^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$, $^{16}O^{13}C^{32}S$, $^{16}O^{12}C^{33}S$, and $^{18}O^{12}C^{32}S$, are from the product approximation calculations of Fischer et al. [16]. The TIPS are reported to 3500 K.

### 3.20. Formaldehyde

Data are reported for three isotopologues of formaldehyde: $H_2^{12}C^{16}O$, $H_2^{13}C^{16}O$, and $H_2^{12}C^{18}O$. The data are from Fischer et al. [16] and go to 3500 K. For the $H_2^{12}C^{16}O$ isotopologue term values are available from the *ab initio* calculations of Al-Refaie et al. [66]. Using these data, $Q(T)$ can be evaluated by direct summation. However, the resulting TIPS are not converged to 3500 K. The direct sums calculated in this work agree with the $Q(T)$ data of Al-Refaie et al. Comparing the direct sum $Q(T)$s to those from the product approximation results of Fischer et al. shows a minimum
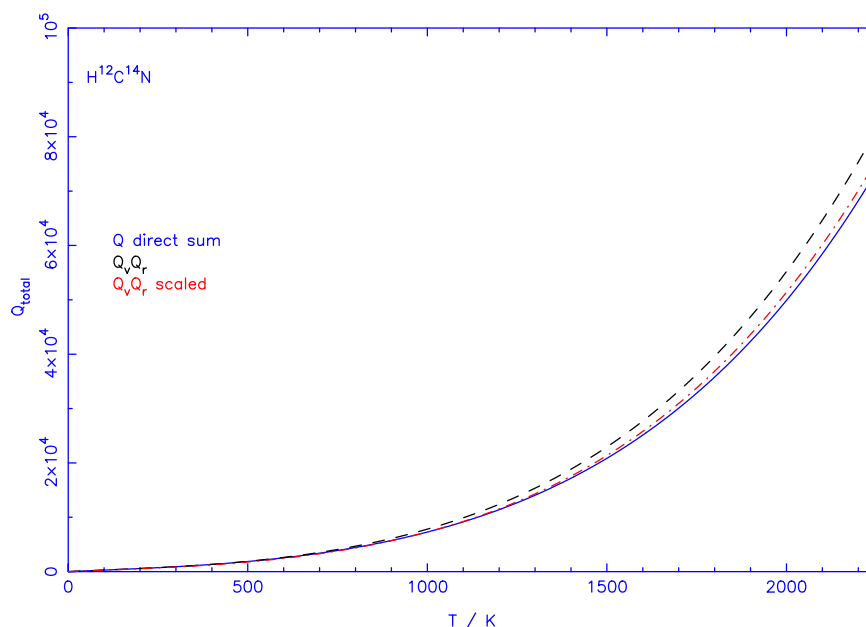
**Fig. 8.** $Q(T)$ from the direct sum (blue solid line), $Q(T)$ from $Q_{vib} \times Q_{rot\ McDowell}$ (black dashed line), and $Q(T)$ from $Q_{vib} \times Q_{rot\ scaled\ McDowell}$ (red dash-dot line) versus temperature in K for the $H^{12}C^{14}N$ isotopologue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

difference at 632 K. So for $H_2^{12}C^{16}O$ the direct sum values are used up to 632 K and from 633–3500 the values from Fischer et al. are used. The final TIPS are reported to 3500 K.

### 3.21. Hypochlorous acid

The total internal partition sums for $H^{16}O^{35}Cl$ and $H^{16}O^{37}Cl$ were taken from the work of Fischer et al. [16], who used the product approximation with $Q_{vib}$ determined using the harmonic approximation and $Q_{rot}$ using Watson's analytical formula. The final TIPS are reported to 3500 K.

### 3.22. Nitrogen molecule

TIPS are calculated for 3 isotopologues of the nitrogen molecule: $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$. The term values are from the work of Le Roy et al. [67], whose calculations are to $J=75$ and for which the term values ($F_{max}$, $F_{complete}$) in cm$^{-1}$ are (76,465, 57,156), (75,034, 56,307), and (73,581, 55,440) for $^{14}N_2$, $^{14}N^{15}N$, and $^{15}N_2$, respectively. The TIPS are determined by direct summation and the resulting data are converged and reported to 9000 K.

Table 2 shows that the results from TIPS_2017 and TIPS_2011 are similar; however, the new calculations allow the TIPS to be converged to 9000 K.

### 3.23. Hydrogen cyanide

Total internal partition sums were calculated for three hydrogen cyanide isotopologues: $H^{12}C^{14}N$, $H^{13}C^{14}N$, and $H^{12}C^{15}N$, using the product approximation. The vibrational partition sum was determined using anharmonic frequencies determined using the constants of Maki et al. [68]. The resulting vibrational term values go to $G_{v-max}$ of 67,284, 67,509, and 66,190 wavenumbers. For the rotational partition sum, term values are available from the *ab initio* calculations of Harris et al. [69] for $H^{12}C^{14}N$ and from Harris et al. [70] for $H^{13}C^{14}N$. Both calculations go to $J=60$ and are complete to 18,817 cm$^{-1}$, only allowing convergence of the partition sums to around 2250 K.

Rotational partition sums were calculated for the 3 isotopologues using the rotational constants given by Maki [71], the linear molecule analytical formula of McDowell [27], and by direct

summation over the *ab initio* term values for $H^{12}C^{14}N$ and $H^{13}C^{14}N$. Comparing the two sets of partition sums shows good agreement at low temperature but diverges as the temperature increases. In order to get better agreement from the analytical model the rotational constants, B and D, were scaled and the *ab initio* and analytical model results compared until the best agreement was obtained. The final scale values used for B and D were 1.072, 0.5 and 1.078, 0.1 for $H^{12}C^{14}N$ and $H^{13}C^{14}N$, respectively. Fig. 8 shows $Q(T)$ from the direct sum (blue solid line), $Q(T)$ from $Q_{vib} \times Q_{rot\ McDowell}$ (black dashed line), and $Q(T)$ from $Q_{vib} \times Q_{rot\ scaled\ McDowell}$ (red dash-dot line) versus temperature in K for the $H^{12}C^{14}N$ isotopologue. Not evident in this view is that $Q_{vib} \times Q_{rot\ McDowell}$ gives better agreement to about 650 K but then diverges from the direct sum results.

The final TIPS for the $H^{12}C^{14}N$ and $H^{13}C^{14}N$ isotopologues are direct sums, over *ab initio* term values, to 1000 K followed by $Q_{vib-anharmonic} \times Q_{rot\ scaled\ McDowell}$. For the $H^{12}C^{15}N$ isotopologue the TIPS is given by $Q_{vib-anharmonic} \times Q_{rot\ McDowell}$. The TIPS are reported to 3500 K. Table 2 shows a few percent difference between the TIPS_2017 and TIPS_2011 data at the higher temperatures of the 2011 study.

### 3.24. Methyl chloride (IUPAC name: chloromethane)

The total internal partition sums for the $^{12}CH_3^{35}Cl$ and $^{12}CH_3^{37}Cl$ isotopologues of methyl chloride were taken from corrections to the calculations of Fischer [16] using the work of Laraia et al. [17]. The TIPS are determined by $Q_{vib\ harmonic} \times Q_{rot\ analytical}$ and are reported to 3500 K.

### 3.25. Hydrogen peroxide

Total internal partition sums for $H_2^{16}O_2$ were determined by direct summation over the term values of Al-Refaie et al. [72], which are complete to 27,090 cm$^{-1}$. A major improvement is that the data of Al-Refaie et al. includes the torsional states. The resulting TIPS are converged to and reported to 6000 K. Comparison to $Q(296\ K)$ of Al-Refaie et al. shows a – 0.07 percent difference. Table 2 shows a large percent difference (-14.5) between the TIPS_2017 and TIPS_2011 results at 2500 K and the new calculations allow convergence of the TIPS to 6000 K.

### 3.26. Acetylene

For the $^{12}C_2H_2$ isotopologue, $Q(T)$ was determined by a direct sum using the term values calculated by Amyay et al. [73]. Amyay's calculations considered all vibrational states up to 13,000 cm$^{-1}$ and $J$ up to 100, yielding term values up to 26,386 cm$^{-1}$. The TIPS are converged to 5000 K.

For the H$^{12}$C$^{13}$CH and H$^{12}$C$^{12}$CD isotopologues, the $Q(T)$ data of Laraia et al. [17] were used. The data are a merging of direct sum and product approximation data, see Ref. [17] for details. The data are reported to 3500 K.

### 3.27. Ethane

The TIPS for $^{12}C_2H_6$ and $^{12}CH_3^{13}CH_3$ were taken from Fischer et al. [16]. The TIPS are reported to 3500 K.

### 3.28. Phosphine

The total internal partition sums for $^{31}PH_3$ were determined by direct summation over the *ab initio* term values of Sousa-Silva et al. [74]. These term values were calculated to $J=46$ and are complete to 24,879 cm$^{-1}$. The TIPS are converged and reported to 4500 K. Comparing with the TIPS_2011 results, see Table 2, shows a 4% difference at 2500 K. The new data are converged up to 4500 K.

### 3.29. Carbonyl fluoride

Total internal partition sums were calculated for $^{12}C^{16}O^{19}F_2$ and $^{13}C^{16}O^{19}F_2$ using the product approximation. The vibrational partition sum was determined by the harmonic approximation with vibrational fundamentals from Norton and Rinsland [75] for the $^{12}C^{16}O^{19}F_2$ isotopologue. The $^{13}C^{16}O^{19}F_2$ isotopologue uses vibrational fundamentals from Cohen et al. [76] for $\nu_2$, $\nu_3$, $\nu_5$, $\nu_6$ and the $^{12}C^{16}O^{19}F_2$ values for $\nu_1$ and $\nu_4$. The rotational constants are taken from Cohen et al. [76]. The TIPS were calculated to 3500 K. Table 2 shows small differences between the TIPS_2017 and TIPS_2011 values.

### 3.30. Sulfur hexafluoride

The total internal partition sums for $^{32}S^{19}F_6$ are from Fischer et al. [16] and are reported to 3500 K. No low-temperature corrections were made.

### 3.31. Hydrogen sulfide

TIPS were calculated for the H$_2^{32}$S isotopologue by direct summation over the *ab initio* term values of Yurchenko and Tennyson [77]. The term values are complete to 34,636 cm$^{-1}$. The resulting TIPS are converged to 4000 K. Comparing these data with the TIPS_2011 data show a 5% difference at 2500 K, Table 2, with the current results being converged to higher (4000 K) temperature.

The TIPS for the H$_2^{34}$S and H$_2^{33}$S isotopologues are from Fischer et al. [16] and were calculated using the product approximation. Low temperature corrections were made using rotational term values taken from HITRAN2012 [2] for the H$_2^{34}$S and H$_2^{33}$S isotopologues and $Q(T)$ was calculated by direct summation. For both isotopologues the minimum difference between the analytical and direct sum $Q(T)$ was at 10 K. The TIPS for these isotopologues used the direct sum data to 10 K followed by the product approximation values.

The final TIPS are reported to 4000, 3500, and 3500 K for the H$_2^{32}$S, H$_2^{34}$S, and H$_2^{33}$S isotopologues, respectively.

### 3.32. Formic acid

The TIPS for H$^{12}$C$^{16}$O$^{16}$OH were taken from the work of Fischer et al. [16] and are reported to 3500 K. No low-temperature corrections were made to these data.

### 3.33. Hydroperoxyl radical

The data of Fischer et al. [16] with no low temperature corrections were used for H$^{16}O_2$. The data are reported to 3500 K.

### 3.34. Oxygen atom

No data are reported for the oxygen atom.

### 3.35. Chlorine nitrate

TIPS are reported for two isotopologues of chlorine nitrate: $^{35}Cl^{16}O^{14}N^{16}O_2$ and $^{37}Cl^{16}O^{14}N^{16}O_2$. They were taken from the work of Fischer et al. [16] and given to 3500 K with no low-temperature corrections.

### 3.36. Nitric oxide cation

The TIPS for the $^{14}N^{16}O^+$ ion (also known as the nitrosonium ion) are from the work of Fischer et al. [16]. Using ro-vibrational term values taken from HITRAN2012 $Q(T)$ was calculated by direct summation. The final TIPS used the direct sum values to 9 K and the product approximation values from 10–3500 K.

### 3.37. Hypobromous acid

The TIPS for two isotopologues of hypobromous acid, H$^{16}O^{79}$Br and H$^{16}O^{81}$Br, were taken from Fischer et al. [16] with no low-temperature corrections made. The data are reported up to 3500 K.

### 3.38. Ethylene

The TIPS for $^{12}C_2H_4$ and $^{12}CH_2^{13}CH_2$ are from Fischer et al. [16]. No low-temperature corrections were made. The TIPS are reported to 3500 K.

### 3.39. Methanol

The TIPS for the $^{12}CH_3^{16}OH$ isotopologue were calculated by the product approximation. The vibrational partition sum uses the vibrational fundamentals from the Virtual Planetary Laboratory of the University of Washington [78] and include the torsional state. The rotational partition sums use the rotational constants of De Lucia et al. [79] in the analytical formula of Watson. No low-temperature corrections were made. The TIPS are reported to 3500 K.

### 3.40. Methyl bromide (IUPAC name: bromomethane)

TIPS for two isotopologues of methyl bromide, $^{12}CH_3^{79}$Br and $^{12}CH_3^{81}$Br, were taken from Laraia et al. [17]. These calculations were made using the product approximation with $Q_{vib}$ from the harmonic approximation and $Q_{rot}$ from McDowell's formula [28]. No low-temperature corrections were made. The TIPS are reported to 3500 K.

### 3.41. Methyl cyanide (IUPAC name: acetonitrile)

Total internal partition sums were taken from the work of Laraia et al. [17] for four isotopologues of methyl cyanide: $^{12}CH_3^{12}C^{14}N$, $^{13}CH_3^{12}C^{14}N$, $^{12}CH_3^{13}C^{14}N$, and $^{13}CH_3^{13}C^{14}N$. No low-temperature corrections were applied to the data. The TIPS are reported to 3500 K.

### 3.42. Carbon tetrafluoride

The TIPS for $^{12}C^{19}F_4$, which are in TIPS_2011.for, were found to have a discontinuity between 600 and 601 K. No TIPS are reported in this work for $CF_4$. They will be made available in the future.

### 3.43. Diacetylene

The total internal partition sums for the $^{12}C_4H_2$ isotopologue of diacetylene (1,3-butadiyne) are from the calculations of Fischer and Gamache [14], which used the product approximation. For details readers should consult Ref. [14]. The TIPS are reported to 3500 K.

### 3.44. Cyanoacetylene

TIPS for 6 isotopologues of cyanoacetylene, $H^{12}C_3^{14}N$, $H^{12}C_3^{15}N$, $H^{12}C^{12}C^{13}C^{14}N$, $H^{12}C^{13}C^{12}C^{14}N$, $H^{13}C^{12}C^{12}C^{14}N$, and $D^{12}C^{12}C^{12}C^{14}N$, were taken from Laraia et al. [17]. They were determined using the product approximation. No low-temperature corrections were applied to the data. The TIPS are reported to 3500 K.

### 3.45. Hydrogen molecule

TIPS for $H_2$ and HD were calculated by direct summation over the term values of Piszczatowski et al. [80] and Pachucki et al. [81], respectively. The term values of Piszczatowski et al. consider states with $\nu = 0$–14 and $J = 0$–31 giving an $F_{max} = 36,126$ cm$^{-1}$ and complete to 35,242 cm$^{-1}$. The term values of Pachucki et al. are for states with $\nu = 0$–17 and $J = 0$–36, with $F_{max} = 36,405$ cm$^{-1}$ and complete to 35,506 cm$^{-1}$. The TIPS are converged and reported to 6000 K. While Table 2 shows little difference between the TIPS_2017 and TIPS_2011 results at the temperatures of the 2011 study, the new calculations give TIPS that are converged to 6000 K.

### 3.46. Carbon monosulfide

TIPS for four isotopologues of carbon monosulfide, $^{12}C^{32}S$, $^{12}C^{34}S$, $^{13}C^{32}S$, and $^{12}C^{33}S$ were taken from the work of Laraia et al. [17]. Laraia et al. applied low-temperature corrections to $Q(T)$. The TIPS are reported to 3500 K.

### 3.47. Sulfur trioxide

*Ab initio* term values are available for $^{32}S^{16}O_3$ from the work of Underwood et al. [82]. The calculations are for $J = 0$ to 129 and have an $F_{max} = 10,000$ cm$^{-1}$, which is too low for the $Q(T)$ to converge for all temperatures. TIPS were determined by direct summation of the *ab initio* term values. TIPS were also calculated by the product approximation. The vibrational partition sums used the harmonic approximation with the fundamentals from Maki et al. [83]. The rotational partition sums were calculated using ground-state term values calculated using the rotational constants of Maki et al. [83]. The total internal partition sum was formed and compared with the direct sum $Q(T)$. The final TIPS used the direct sum values from 1–650 K and the product approximation values from 651–3500 K.

### 3.48. Cyanogen

Two symmetric isotopologues of cyanogen, $^{14}N^{12}C^{12}C^{14}N$ and $^{15}N^{12}C^{12}C^{15}N$, were taken from the work of Fischer and Gamache [14]. Both direct sums and product approximation values of $Q(T)$ were determined. The final TIPS were a merger of the two data sets. The TIPS are reported to 3500 K.

### 3.49. Phosgene

Total internal partition sums were determined for the $^{12}C^{16}O^{35}Cl_2$ and $^{12}C^{16}O^{35}Cl^{37}Cl$ isotopologues of phosgene. First, working with the data of Tchana et al. [84] in the form of a line list provided by Flaud, ro-vibrational term values were extracted. TIPS were determined for both isotopologues. Analysis showed that the TIPS were converged to $\sim 300$ K. Next, using the rotational constants given in Tchana et al. the rotational partition sums were determined. Then vibrational partition sums were determined using the harmonic approximation. For both isotopologues the $\nu_1$ and $\nu_5$ vibrational fundamentals from Tchana et al. [84] and the $\nu_2$, $\nu_3$, $\nu_4$, and $\nu_5$ vibrational fundamentals are from the NIST tables (http://webbook.nist.gov). The product approximation of $Q(T)$ was formed and compared with the direct sum values. Very good agreement is observed between the data determined by the two methods of calculation. The final TIPS values are from the product approximation calculations and are reported to 5000 K.

### 3.50. Sulfur monoxide

TIPS for three isotopologues of sulfur monoxide, $^{32}S^{16}O$, $^{34}S^{16}O$, and $^{32}S^{18}O$, were taken from Laraia et al. [17]. They calculated both direct sum and product approximation $Q(T)$ and their final data are a merger of the two sets of data with direct sum at low temperatures and product approximation data for other temperatures. The TIPS are reported to 3500 K.

### 3.51. Propyne

The TIPS for the $^{12}C_3H_4$ isotopologue of propyne were taken from Laraia et al. [17]. In that work $Q(T)$ was determined by direct summation and product approximation and a low temperature correction was applied to the product approximation data. The TIPS are reported to 3500 K.

### 3.52. Methyl radical

The TIPS for the methyl radical, $^{12}CH_3$, were taken from the work of Laraia et al. [17]. The TIPS were determined by the product approximation where $Q_{vib}$ was calculated using the harmonic approximation and $Q_{rot}$ was determined by direct summation. The TIPS are reported to 3500 K.

### 3.53. Carbon disulfide

The TIPS for four isotopologues of carbon disulfide, $^{32}S^{12}C^{32}S$, $^{32}S^{12}C^{34}S$, $^{32}S^{12}C^{33}S$, and $^{32}S^{13}C^{32}S$, were obtained from Laraia et al. [17]. In that work $Q(T)$ was evaluated by direct sums and by the product approximation to allow low-temperature corrections of the product approximation values. The TIPS are reported to 3500 K.

## 4. Rapid recall of the TIPS

The total internal partition sums are available in tabular form for all isotopologues of this study at the HITRAN website (www.hitran.org) or from the website of the corresponding author (http://faculty.uml.edu/Robert_Gamache). However, to be useful in applications, codes that can make a rapid recall of the TIPS for any isotopologue are needed. In previous works [11–17], a FORTRAN code, e.g., TIPS_2011.for, was made openly available to the scientific community. Earlier versions used a polynomial fit to recall the data, which was later replaced by a Lagrange 3- or 4-point interpolation method with a 25 K step size for recall. From this work two code language options are available. The first code language option is FORTRAN and available are the next versions of TIPS; TIPS_2017_v1p0.for and BD_TIPS_2017_v1p0.for.

TIPS_2017_v1p0.for is a stand-alone program that queries the user for molecule, isotopologue, and temperature and then returns $Q(T)$ for that species. BD_TIPS_2017_v1p0.for is a subroutine version that users can insert into their codes to obtain $Q(T)$ for their applications. These codes store the TIPS from 1 to 20 K in 1 K intervals and then from 22 K to $T_{max}$ in 2 K steps. The algorithms recall the TIPS by first checking if the requested temperature is one of the stored temperatures. If so, the TIPS value is returned, otherwise linear interpolation (not Lagrange 3- or 4-point) between the 2 points surrounding the requested temperature is done and that value returned. Tests of the interpolation scheme were made by calculating the temperatures not stored (i.e., the odd temperatures) and comparing to the calculated $Q(T)$ values; the absolute average percent difference is 0.001.

The second code language choice is a python algorithm, TIPS_2017_v1p0.py. Python libraries have been created from the TIPS data. Note, all temperatures are stored in the dictionaries; linear interpolation is made between the 1 K steps. The library names are "molecule number"_"ISO#".QTpy, where the molecule number and isotopologue number are given in Table 1. For example, the dictionary for the $H_2^{18}O$ isotopologue of water is 1_2. QTpy. All the dictionaries are stored in a folder labeled /QTpy/. The code, TIPS_2017.py, queries the user for molecule, isotopologue, and temperature; then selects the proper dictionary and extracts $Q(T)$ with a key constructed from the user input.

Extracting individual subroutines out of BD_TIPS_2017_v1p0.for allow one to create custom codes for applications to a subset of molecules and isotopologues. Similar routines can be made with the python code by hardwiring the molecule number and isotopologue number into the dictionary definition.

New to the TIPS algorithm is that $T_{max}$ is not fixed for all isotopologues like in previous versions. An array in FORTRAN and a python list are used to store the maximum temperature of the data for each isotopologue. The data are available as Supplementary material and the codes can be downloaded at http://faculty.uml. edu/Robert_Gamache or at www.HITRAN.org.

## 5. Summary

Total internal partition sums are presented for all the molecules and isotopologues in the line-by-line portion of the HITRAN2016 database and for additional molecules and isotopologues of astrophysical interest. Many of the updates are possible due to the availability of accurate *ab initio* rovibrational term values. For a number of the species low-temperature corrections were made by either correcting the *ab initio* values for low term values with measured data or for analytical model data by calculating direct sums over measured data. The TIPS were calculated from 1 K to $T_{max}$, where $T_{max}$ is determined by the convergence of the TIPS for each isotopologue. Tables of the TIPS are available as Supplementary material, at www.HITRAN.org and http://Faculty.uml.edu/Robert_Gamache. Rapid recall of the TIPS can be achieved using the FORTRAN codes TIPS_2017_v1p0.for and BD_TIPS_2017_v1p0.for or using the python code TIPS_2017_v1p0.py, which are available at the above web sites.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jqsrt.2017.03.045.

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