Total internal partition sums for the HITRAN2020 database

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ABSTRACT

Total internal partition sums (TIPS) are reported for the 181 isotopologues of 57 molecules important in planetary atmospheres. Molecules 1 to 55, with the exception of #34 atomic oxygen, are taken from the HITRAN2020 list, and for some molecules additional isotopologues are considered. Molecules 56 and 57 are C_3H_4, CH_3, respectively. New to TIPS are the calculations for $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$, $^{14}N^{16}O$, $^{15}N^{16}O$, $^{14}N^{18}O$, $^{16}O^{32}S^{18}O$, $^{33}S^{16}O_2$, $^{15}N^{16}O_2$, ^{18}OH, ^{16}OD, $^{35}Cl^{16}O$, $^{37}Cl^{16}O$, $^{16}O^{13}C^{34}S$, $^{32}S^{19}F_6$, $^{12}C_2H_5D$, $^{12}C_2H_3D$, $^{12}C^{19}F_4$, $^{12}CH_3^{19}F$, $^{70}GeH_4$, $^{72}GeH_4$, $^{73}GeH_4$, $^{74}GeH_4$, $^{76}GeH_4$, $^{12}CH_3^{127}I$, $^{13}CH_3^{127}I$, and $^{14}N^{19}F_3$. In addition, all the molecules/isotopologues that were not recalculated for TIPS2017 (Gamache et al., JQSRT 203, 70, 2017) have been recalculated using the 2014 CODATA physical constants. The TIPS are determined by various methods, generally from 1 to 5000 K. These data are provided with HITRAN2020 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) are a very useful quantity in chemistry and physics. 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 [1]. Given a number density of molecules, the TIPS can be used to determine the population of molecules as a function of quantum state. These population factors are needed to determine the intensity of ro-vibrational transitions. The expressions that show the relationships between the intensity of a spectral line and the square of the transition moment, the Einstein-*A* coefficient, or the oscillator strength [2] all contain the partition sum.

When applying radiative-transfer (RT) models to study planetary atmospheres, there is a set of input parameters needed for the models, which includes the line position, lower-state energy, intensity at a reference temperature, the line shape parameters for the atmospheric pressure regimes. These parameters can be found in molecular spectroscopic databases such as HITRAN [3,4] or GEISA [5]. Because planetary atmospheres are not isothermal, the temperature dependence of these parameters must be known. The temperature dependence of both line shape parameters, the half-width and the line shift, was derived by Gamache and Vispoel [6]. While HITRAN has adopted the Gamache and Vispoel model, most of the data for the half-widths are the old power law form, $\gamma(T) = \gamma(T_{ref}) \left[\frac{T_{ref}}{T}\right]^n$ and few data are presented for the line shift. For the line intensity, S, for a transition $f \leftarrow i$ the dependence on temperature is given by

$$S_{f \leftarrow i}(T) = S_{f \leftarrow i}(T_{ref}) \frac{Q(R_{ref})}{Q(T)} \frac{e^{-hcE''/kT}}{e^{-hcE''/kT_{ref}}} \frac{\left[1 - e^{-hc\omega_{f \leftarrow i}/kT}\right]}{\left[1 - e^{-hc\omega_{f \leftarrow i}/kT_{ref}}\right]} \quad (1)$$

where $Q(T)$ is the total internal partition sum, h and $\underline{k}$ are the Planck and Boltzmann constants, c is the speed of light, hcE'' is the lower state energy, and $\omega_{f \leftarrow i}$ is the wavenumber of the transition. Thus, these expressions allow the parameters on HITRAN or GEISA to be propagated to other temperatures.

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For high temperature applications such as stellar atmospheres, Sauval and Tatum [7] calculated partition functions for roughly 300 diatomic molecules over a temperature range of 1000 to 9000 K. Irwin [8] refined the work of Sauval and Tatum for H_2 and CO and later [9] calculated partition functions for 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 [10]. In 2016, Barklem and Collet [11] determined partition functions and dissociation equilibrium constants for 291 diatomic molecules for temperatures in the range from near absolute zero to 10 000 K.

This work is an update and an extension of previous studies [12–19] that calculated TIPS for the molecules and isotopologues present on the HITRAN databases [3,4,20–25] and for astrophysical applications. In 1990 Gamache et al. [12] presented TIPS for the 11 closed shell linear molecules and their isotopologues in HITRAN86 [20]. The Q(T) data were given by polynomial expansions in two temperature ranges: 70–400 and 400–2005 K and a logarithmic expansion that allowed extrapolation to 3000 K. This work was extended [13] to include all molecular/isotopologue species on HITRAN92 [21] and three additional molecular/isotopologue species from HITRAN96 [22]. The Q(T) data were made for temperatures from 70 to 3005 K. The data were divided into three temperature regions and each region fit by a 3rd order polynomial. In 2002, Fischer and Gamache made TIPS calculations for 5 molecules (16 isotopologues) abundant in Planetary atmospheres [15]. They also made partition sum calculations for Non-Local Thermodynamic Equilibrium (NLTE) applications [16]. Using the same temperature ranges as the previous study [15], they used 4th order polynomials to fit the data. Fischer et al. [17] calculated TIPS for the 40 molecules and 95 isotopologues/isotopomers present on the HITRAN2000 database [23]. They also added an additional 13 lesser abundant isotopologues/isotopomers of ozone and carbon dioxide. The calculations were done from 70-3000K, however, now the data were recalled using a Lagrange 4-point interpolation scheme. In 2011, Laraia et al. [18] determined TIPS for 14 molecules (33 isotopologues) needed to support planetary remote sensing. The molecules of this study are now part of HITRAN2020. Finally, in 2017 new calculations were made for 24 molecules (73 isotopologues) in the HITRAN2016 database [19]. All of the calculations represented an improvement over previous calculations, many using *ab initio* energy levels to do direct summations of Q(T). In fact, in all of the above studies the methods of calculating *Q(T)* were improved upon from earlier studies.

There are many other examples of high-quality partition sums in the literature, i.e. partition sums that use accurate energy values and are converged at the temperatures reported. Some recent examples include work on MgH by Szidarovszky and Császár [26], on $H_2{}^{16}O$ by Furtenbacher et al. [27], and on three isotopologues of D_2O by Simkó et al. [28].

It should be noted that when one scans the literature, the terms partition function and partition sum are often interchanged. Here, the standard chemistry notation, *Q(T)*, is adopted for the total internal partition sum as a function of temperature *T*. The total partition function is assumed to be the product of the internal and the translational partition functions.

In this work, the total internal partition sums are calculated for a number of molecules and isotopologues new to the HITRAN database and some improvements to previous calculations, they are: $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$, $^{14}N^{16}O$, $^{15}N^{16}O$, and $^{14}N^{18}O$, $^{16}O^{32}S^{18}O$, $^{33}S^{16}O_2$, $^{15}N^{16}O_2$, ^{18}OH, ^{16}OD, $^{35}Cl^{16}O$, $^{37}Cl^{16}O$, $^{16}O^{13}C^{34}S$, $^{32}S^{19}F_6$, $^{12}C_2H_5D$, $^{12}C_2H_3D$, $^{12}C^{19}F_4$, $^{12}CH_3^{19}F$, $^{70}GeH_4$, $^{72}GeH_4$, $^{73}GeH_4$, $^{74}GeH_4$, $^{76}GeH_4$, $^{12}CH_3^{127}I$, $^{13}CH_3^{127}I$, and $^{14}N^{19}F_3$. These new calculations used the 2014 Codata values of the fundamental physical constants [29]. However, the data for a number of the molecules/isotopologues on the 2017 version of TIPS came

from previous work [13,18] that used older values of the physical constants. The TIPS have been recalculated for all of these molecules/isotopologues using the 2014 Codata values to provide consistent values for all molecules/isotopologues. In the new calculations the maximum temperature was set to 5000 K, with some exceptions, and the calculations made in 1 K steps starting at 1 K. In this work, the calculations of the TIPS do not consider unbound states. Recall of the data is possible using either a FORTRAN standalone program (TIPS_2021_v1p0.for), a blockdata subroutine code (BD_TIPS_2021_v1p0.for), or a Python code (TIPS_2021_v1p0.py).

Section 2 describes the calculation of total internal partition sums and is primarily intended for those new to these calculations. These methods have been presented in previous publications [15–19] so only a quick overview is presented with appropriate references given. Section 3 describes the methods used to calculate Q(T) for each molecule/isotopologue of this work. The codes to quickly recall the Q(T) values are presented in Section 4 and, finally, Section 5 summarizes the work.

2. Determining the total internal partition sum

Every isotopologue of a molecule has a unique set of quantum energy states, F_s. The total internal partition sum is given by summing the factor $e^{-hcF_s/kT}$ over all states *s* of the isotopologue. Here hcF_s is the total energy (electronic, vibrational, rotational, and any other quantized motion) of state *s*. F_s is the term value [30] and has units of cm^{-1}. When energy states are degenerate, the sum need only be done once multiplied by the degeneracy factor, of which some are state dependent; i.e. it depends on the quantum numbers of the state, d_s, or state independent; i.e. it is a factor given for the molecule, d_i. Given these factors, $Q(T)$, can be written as

$$Q_{elec, vib, rot, tors, etc.}(T) = d_i \sum_{all\ states\ s} d_s\ e^{-hcF_s/kT}. \qquad (2)$$

The d_s factors are generally composed of two components. The first is the rotational and total angular momentum degeneracy factor and is given in terms of the quantum numbers: $(2J+1)$ or $(2F+1)$. When molecules have symmetry such that identical atoms can be interchanged by a symmetry operation, e.g. CH_4 or H_2O, only certain products of rotational and nuclear wavefunctions yield the proper symmetry for the complete wavefunctions. For such cases, even and odd symmetry states have different nuclear spin weight and these values must be factored into Eq. (2) accordingly. The calculation of these nuclear statistical weights depends on whether the nuclei being exchanged have half-integer spins (Fermi systems) or integer spins (Bose systems). For details see Refs. [19] or [30]. Some examples include; for H_2O, the two hydrogen atoms that are interchanged have spin ½ nuclei giving a three-fold degeneracy for the odd states and a one-fold degeneracy for the even states; for $C^{16}O_2$, the two oxygen atoms that are exchanged have spin zero nuclei giving one-fold degeneracy for the even levels and a zero-fold degeneracy for the odd levels (i.e., such levels do not exist).

In this work, the state independent factors are explicitly included in the determination of *Q(T)*. However, in the literature, state independent factors are often omitted from partition sum calculations when the application involves a ratio of partition sums. Note, these factors are necessary to relate the partition functions to thermodynamic quantities. The state independent degeneracy factor is given by the product $\prod(2I+1)$, where *I* is the nuclear spin and the product is taken over all nuclei not interchanged by rotations [30]. Thus, when comparing the partition sums from this study to values from the literature, it is sometimes necessary to

multiply by an integer value to obtain agreement due to the omission of the state independent factors.

The method of evaluation of $Q(T)$ depends on the availability of the energy levels and corresponding degeneracy factors for the molecule/isotopologue in question. The ideal situation is to have energy levels up to the dissociation limit of the isotopologue in question. For such cases, a direct sum using Eq. (2) can be done. However, seldom are energy levels available up to the dissociation limit. The question then becomes, given the set of energy levels available, to what temperature can $Q(T)$ accurately be computed. Since, as the energy increases, the exponential factor approaches zero and the sum can be truncated with no loss of accuracy. The work done on TIPS2017 took advantage of the many *ab initio* determinations of ro-vibrational energy levels that allowed direct sums over Eq. (2) to be done. However, there are many molecules/isotopologues for which a full set of energy levels are not available. In addition, there are often additional structures, such as lambda doubling, torsional motion, etc. for which the energy expressions are more complicated. For all cases, the energy is assumed to be additive

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

Taking advantage of the property of the exponential, Eq. (2) can be rewritten

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

which is called the product approximation, PA. Often, Q_{elec} is equal to one and there is no torsional structure. For such a case the product approximation gives

$$Q(T) = Q_{vib} \times Q_{rot} = \sum_{i=0}^{i_{max}} g_{\nu_i} e^{-hc\omega_i/kT} \times \sum_{J=0}^{J_{max}} g_J e^{-hcE_J/kT} \quad (5)$$

However, when the molecule under consideration is a linear Bose system caution must be made when applying the product approximation. Consider $^{12}C^{16}O_2$ as an example. The vibrational states are labeled by $\nu_1 \nu_2 l_2 \nu_3$ and when $l_2=0$ only even J levels are allowed (Bose statistics for nuclei with spin equal zero being exchanged). When $l_2>0$ all J levels are allowed. The sum over states can be rewritten as

$$Q(T) = \left(\sum_{\substack{all\ vib\ states \\ with\ \ell_2=0}} g\, e^{-E_\nu/kT} \right) \left(\sum_{\substack{J=0 \\ even\ only}} g_j e^{-E_r/kT} \right)$$
$$+ \left(\sum_{\substack{all\ vib\ states \\ with\ \ell_2>0}} g\, e^{-E_\nu/kT} \right) \left(\sum_{\substack{J=0 \\ even\ and\ odd}}^{J_{max}} g_j e^{-E_r/kT} \right) \quad (6)$$

Or equivalently

$$Q(T) = Q_{vib}^{\ell_2=0}(T) \times Q_{rot}(J\ even) + Q_{vib}^{\ell_2>0}(T) \times Q_{rot}(all\ J) \quad (7)$$

which can be called the double product approximation, DPA.

For $^{12}C^{16}O_2$ sufficient *ab initio* term values exist to converge the TIPS to 5000 K, thus allowing a comparison between the PA and the DPA. Fig. 1 shows the TIPS determined by direct summation of Eq. (2) (red dashed-line), the TIPS determined by the double product approximation blue (solid line with + symbols), Eq. (6), and the TIPS determined by the product approximation (black dot-dashed line), Eq. (5) versus temperature. The PA underestimates the TIPS by ~50% at high temperatures, but even at low temperatures the differences grow quickly: ~1% at 200 K, 4% at 300 K, 13% at 500 K.

When it is not possible to do a direct sum over energies, Eq. (4) reduces the problem to computing the electronic, vibrational, rotational, ... partition sums. There are various approximations that can be used to compute each. Generally, Q_{elec} is one,
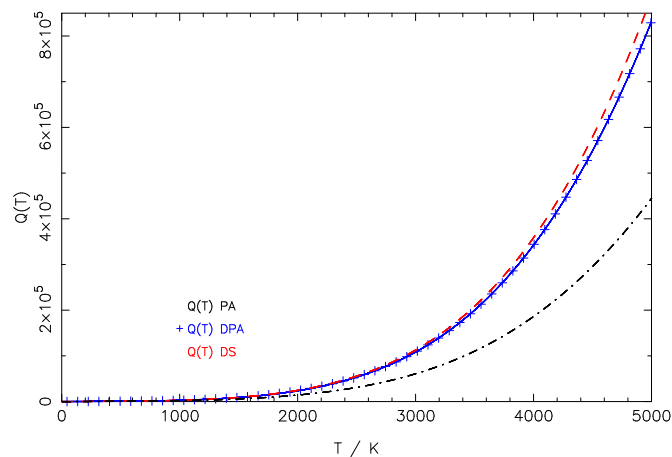

Fig. 1. The $Q(T)$ determined by a direct sum, Eq. (2), over *ab initio* term values (red dashed curve), $Q(T)$ determined by the double product approximation Eq. (6) (blue curve with + symbols) and $Q(T)$ determined by the product approximation Eq. (5) (black dot-dashed curve) for $^{12}C^{16}O_2$ versus temperature in K.

however, for a number of molecules sums over electronic states must be done, such as NO or O_2. For Q_{vib} the harmonic oscillator approximation (HOA) of Herzberg is often used [30] or the inclusion of anharmonic corrections [19]. There are a number of analytical representations for Q_{rot} [31–34] that are given in terms of the rotational constants. See Ref. [19] for the expressions of these quantities.

3. Calculations

Table 1 lists for the molecules/isotopologues shown below the molecule number, isotopologue number, the original HITRAN isotopologue (AFGL) code, state-independent degeneracy, $Q(296\ K)$, and maximum temperature of the calculation. For molecule/isotopologues that have not changed from TIPS_2017, a short description of the method of calculations is presented, complete details can be found in the original paper [19].

3.1. Water vapor

The $Q(T)$ values for the nine isotopologues of H_2O shown in Table 1 are from Ref. [19]. For all isotopologues, the method of calculation was direct sums over *ab initio* term values, which were calculated to high J values to ensure convergence of the partition sums at all temperatures.

3.2. Carbon dioxide

The $Q(T)$ values for the thirteen isotopologues of CO_2 shown in Table 1 are from Ref. [19]. The calculations were made by direct summation using the *ab initio* energy levels form the work of Huang et al. [35–37] and are converged for all reported temperatures.

3.3. Ozone

In a quest towards the sub-percent uncertainty of the intensities of ozone lines across multiple spectral regions, the quality of the partition sums becomes particularly important. In a recent study by Birk et al. [38] it was found that the partition sums of the $^{16}O_3$ isotopologue at 296K differ from those in the JPL catalogue [39] and S&MPO database [40] by about 0.3%. The partition some in S&MPO are considered to be most accurate as they are obtained

Table 1

Molecule number, chemical formula, isotopologue number (ISO#), AFGL code, state independent degeneracy factor (g_i), $Q(296\ K)$, and T_{max} in K.

Molecule #	Formula	ISO#	AFGL code	g_i	$Q(296\ K)$	T_{max} K
1	$H_2^{16}O$	1	161	1	1.7458×10^2	5000
	$H_2^{18}O$	2	181	1	1.7605×10^2	5000
	$H_2^{17}O$	3	171	6	1.0521×10^3	5000
	$HD^{16}O$	4	162	6	8.6474×10^2	5000
	$HD^{18}O$	5	182	6	8.7557×10^2	5000
	$HD^{17}O$	6	172	36	5.2268×10^3	5000
	$D_2^{16}O$	7	262	1	1.0278×10^3	6000
	$D_2^{18}O$	8	282	1	1.0434×10^3	6000
	$D_2^{17}O$	9	272	6	6.2160×10^3	6000
2	$^{12}C^{16}O_2$	1	626	1	2.8609×10^2	5000
	$^{13}C^{16}O_2$	2	636	2	5.7664×10^2	5000
	$^{16}O^{12}C^{18}O$	3	628	1	6.0781×10^2	3500
	$^{16}O^{12}C^{17}O$	4	627	6	3.5426×10^3	3500
	$^{16}O^{13}C^{18}O$	5	638	2	1.2255×10^3	3500
	$^{16}O^{13}C^{17}O$	6	637	12	7.1413×10^3	3500
	$^{12}C^{18}O_2$	7	828	1	3.2342×10^2	5000
	$^{17}O^{12}C^{18}O$	8	827	6	3.7666×10^3	3500
	$^{12}C^{17}O_2$	9	727	1	1.0972×10^4	5000
	$^{13}C^{18}O_2$	0	838	2	6.5224×10^2	5000
	$^{18}O^{13}C^{17}O$	11	837	12	7.5950×10^3	3500
	$^{13}C^{17}O_2$	12	737	2	2.2120×10^4	5000
	$^{14}C^{16}O_2$	13	646	1	2.9048×10^2	5000
3	$^{16}O_3$	1	666	1	3.4750×10^3	1000
	$^{16}O^{16}O^{18}O$	2	668	1	7.5846×10^3	1000
	$^{16}O^{18}O^{16}O$	3	686	1	3.7030×10^3	1000
	$^{16}O^{16}O^{17}O$	4	667	6	4.4044×10^4	1000
	$^{16}O^{17}O^{16}O$	5	676	6	2.1742×10^4	1000
	$^{18}O^{18}O^{16}O$	6	886	1	7.9376×10^3	1000
	$^{18}O^{16}O^{18}O$	7	868	1	4.0703×10^3	1000
	$^{16}O^{17}O^{18}O$	8	678	6	4.6563×10^4	1000
	$^{17}O^{16}O^{18}O$	9	768	6	4.7135×10^4	1000
	$^{17}O^{18}O^{16}O$	10	786	6	4.6074×10^4	1000
	$^{17}O^{17}O^{16}O$	11	776	36	2.7051×10^5	1000
	$^{17}O^{16}O^{17}O$	12	767	1	1.3704×10^5	1000
	$^{18}O_3$	13	888	1	4.2647×10^3	1000
	$^{18}O^{18}O^{17}O$	14	887	6	4.9325×10^4	1000
	$^{18}O^{17}O^{18}O$	15	878	6	2.5005×10^4	1000
	$^{17}O^{17}O^{18}O$	16	778	36	2.8147×10^5	1000
	$^{17}O^{18}O^{17}O$	17	787	1	1.4342×10^5	1000
	$^{17}O_3$	18	777	6	8.4189×10^5	1000
4	$^{14}N_2^{16}O$	1	446	9	4.9849×10^3	5000
	$^{14}N^{15}N^{16}O$	2	456	6	3.3616×10^3	5000
	$^{15}N^{14}N^{16}O$	3	546	6	3.4580×10^3	5000
	$^{14}N_2^{18}O$	4	448	9	5.3135×10^3	5000
	$^{14}N_2^{17}O$	5	447	54	3.0966×10^4	5000
5	$^{12}C^{16}O$	1	26	1	1.0742×10^2	9000
	$^{13}C^{16}O$	2	36	2	2.2469×10^2	9000
	$^{12}C^{18}O$	3	28	1	1.1277×10^2	9000
	$^{12}C^{17}O$	4	27	6	6.6117×10^2	9000
	$^{13}C^{18}O$	5	38	2	2.3644×10^2	9000
	$^{13}C^{17}O$	6	37	12	1.3847×10^3	9000
	$^{14}C^{16}O$	7	46	1	1.1693×10^2	9000
	$^{14}C^{18}O$	8	48	1	1.2331×10^2	9000
	$^{14}C^{17}O$	9	47	6	7.2137×10^2	9000
6	$^{12}CH_4$	1	211	1	5.9053×10^2	2500
	$^{13}CH_4$	2	311	2	1.1811×10^3	2500
	$^{12}CH_3D$	3	212	3	4.7947×10^3	2500
	$^{13}CH_3D$	4	312	6	9.6010×10^3	2500
7	$^{16}O_2$	1	66	1	2.1573×10^2	7500
	$^{16}O^{18}O$	2	68	1	4.5523×10^2	7500
	$^{16}O^{17}O$	3	67	6	2.6581×10^3	7500
	$^{18}O^{18}O$	4	88	1	2.4232×10^2	7500
	$^{18}O^{17}O$	5	87	6	2.8191×10^3	7500
	$^{17}O^{17}O$	6	77	1	8.2238×10^3	7500
8	$^{14}N^{16}O$	1	46	3	1.1411×10^3	5000
	$^{15}N^{16}O$	2	56	2	7.8831×10^2	5000
	$^{14}N^{18}O$	3	48	3	1.1825×10^3	5000
9	$^{32}S^{16}O_2$	1	626	1	6.3391×10^3	5000
	$^{34}S^{16}O_2$	2	646	1	6.3678×10^3	5000
	$^{33}S^{16}O_2$	3	636	4	2.5607×10^4	5000
	$^{16}O\ ^{32}S^{18}O$	4	628	1	1.3681×10^4	5000
10	$^{14}N^{16}O_2$	1	646	3	1.3575×10^4	1000
	$^{15}N^{16}O_2$	2	656	2	9.2929×10^3	1000

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Table 1 (*continued*)

Molecule #	Formula	ISO#	AFGL code	g_i	Q(296 K)	T_{max} K
11	$^{14}NH_3$	1	4111	3	1.7252×10^3	6000
	$^{15}NH_3$	2	5111	2	1.1533×10^3	6000
12	$H^{14}N^{16}O_3$	1	146	6	2.1393×10^5	3500
	$H^{15}N^{16}O_3$	2	156	4	1.4313×10^5	3500
13	^{16}OH	1	61	2	8.0348×10^1	9000
	^{18}OH	2	81	2	8.0881×10^1	5000
	^{16}OD	3	62	3	2.0931×10^2	5000
14	$H^{19}F$	1	19	4	4.1469×10^1	6000
	$D^{19}F$	2	29	6	1.1591×10^2	6000
15	$H^{35}Cl$	1	15	8	1.6065×10^2	6000
	$H^{37}Cl$	2	17	8	1.6089×10^2	6000
	$D^{35}Cl$	3	25	12	4.6278×10^2	6000
	$D^{37}Cl$	4	27	12	4.6413×10^2	6000
16	$H^{79}Br$	1	19	8	2.0017×10^2	6000
	$H^{81}Br$	2	11	8	2.0023×10^2	6000
	$D^{79}Br$	3	29	12	5.8640×10^2	6000
	$D^{81}Br$	4	21	12	5.8676×10^2	6000
17	$H^{127}I$	1	17	12	3.8899×10^2	6000
	$D^{127}I$	2	27	18	1.1471×10^3	6000
18	$^{35}Cl^{16}O$	1	56	4	3.2918×10^3	5000
	$^{37}Cl^{16}O$	2	76	4	3.3492×10^3	5000
19	$^{16}O^{12}C^{32}S$	1	622	1	1.2207×10^3	5000
	$^{16}O^{12}C^{34}S$	2	624	1	1.2531×10^3	5000
	$^{16}O^{13}C^{32}S$	3	632	2	2.4835×10^3	5000
	$^{16}O^{12}C^{33}S$	4	623	4	4.9487×10^3	5000
	$^{18}O^{12}C^{32}S$	5	822	1	1.3134×10^3	5000
	$^{16}O^{13}C^{34}S$	6	634	2	2.5465×10^3	5000
20	$H_2^{12}C^{16}O$	1	126	1	2.8445×10^3	3500
	$H_2^{13}C^{16}O$	2	136	2	5.8368×10^3	5000
	$H_2^{12}C^{18}O$	3	128	1	2.9860×10^3	5000
21	$H^{16}O^{35}Cl$	1	165	8	1.9272×10^4	5000
	$H^{16}O^{37}Cl$	2	167	8	1.9613×10^4	5000
22	$^{14}N_2$	1	44	1	4.6710×10^2	9000
	$^{14}N^{15}N$	2	45	6	6.4410×10^2	9000
	$^{15}N_2$	3	55	1	2.2230×10^2	9000
23	$H^{12}C^{14}N$	1	124	6	8.9220×10^2	3500
	$H^{13}C^{14}N$	2	134	12	1.8310×10^3	3500
	$H^{12}C^{15}N$	3	125	4	6.1528×10^2	3500
24	$^{12}CH_3^{35}Cl$	1	215	4	5.7915×10^4	5000
	$^{12}CH_3^{37}Cl$	2	217	4	5.8832×10^4	5000
25	$H_2^{16}O_2$	1	1661	1	9.8480×10^3	6000
26	$^{12}C_2H_2$	1	1221	1	4.1245×10^2	5000
	$H^{12}C^{13}CH$	2	1231	8	1.6557×10^3	5000
	$H^{12}C^{12}CD$	3	1222	6	1.5937×10^3	5000
27	$^{12}C_2H_6$	1	1221	1	7.0873×10^4	5000
	$^{12}CH_3^{13}CH_3$	2	1231	2	3.6183×10^4	5000
	$H_3^{12}C_2H_2D$	3	1222	12	3.9266×10^5	5000
28	$^{31}PH_3$	1	1111	2	3.2494×10^3	4500
29	$^{12}C^{16}O^{19}F_2$	1	269	1	7.0028×10^4	3500
	$^{13}C^{16}O^{19}F_2$	2	369	2	1.4006×10^5	3500
30	$^{32}S^{19}F_6$	1	29	1	1.6110×10^6	5000
31	$H_2^{32}S$	1	121	1	5.0579×10^2	4000
	$H_2^{34}S$	2	141	1	5.0428×10^2	5000
	$H_2^{33}S$	3	131	4	2.0147×10^3	5000
32	$H^{12}C^{16}O^{16}OH$	1	126	4	3.9124×10^4	5000
33	$H^{16}O_2$	1	166	2	4.2998×10^3	5000
35	$^{35}Cl^{16}O^{14}N^{16}O_2$	1	5646	12	4.7864×10^6	5000
	$^{37}Cl^{16}O^{14}N^{16}O_2$	2	7646	12	4.9082×10^6	5000
36	$^{14}N^{16}O^+$	1	46	3	3.1166×10^2	5000
37	$H^{16}O^{79}Br$	1	169	8	2.8335×10^4	5000
	$H^{16}O^{81}Br$	2	161	8	2.8233×10^4	5000
38	$^{12}C_2H_4$	1	112211	1	1.1040×10^4	5000
	$^{12}CH_2^{13}CH_2$	2	112311	2	4.5189×10^4	5000
	$^{12}CH_2^{13}CHD$	3	112212	24	8.2452×10^4	5000
39	$^{12}CH_3^{16}OH$	1	2161	1	7.0570×10^4	3500
40	$^{12}CH_3^{79}Br$	1	219	4	8.3049×10^4	5000
	$^{12}CH_3^{81}Br$	2	211	4	8.3392×10^4	5000
41	$^{12}CH_3^{12}C^{14}N$	1	2124	3	8.8659×10^4	5000
	$^{13}CH_3^{12}C^{14}N$	2	3124	6	1.8363×10^5	5000
	$^{12}CH_3^{13}C^{14}N$	3	2134	6	1.8093×10^5	5000
	$^{13}CH_3^{13}C^{14}N$	4	3134	12	3.7410×10^5	5000
42	$^{12}C^{19}F_4$	1	29	1	1.2686×10^5	5000.
43	$^{12}C_4H_2$	1	2211	1	9.8215×10^3	5000

Table 1 (*continued*)

Molecule #	Formula	ISO#	AFGL code	g_i	Q(296 K)	T_{max} K
44	$H^{12}C_3^{14}N$	1	12224	6	2.4711×10^4	5000
	$H^{12}C_3^{15}N$	2	12225	12	1.7040×10^4	5000
	$H^{12}C^{12}C^{13}C^{14}N$	3	12234	12	4.9897×10^4	5000
	$H^{12}C^{13}C^{12}C^{14}N$	4	12324	12	4.9728×10^4	5000
	$H^{13}C^{12}C^{12}C^{14}N$	5	13224	4	5.1552×10^4	5000
	$D^{12}C^{12}C^{12}C^{14}N$	6	22224	9	4.5928×10^4	5000
45	H_2	1	11	1	7.6712	6000
	HD	2	12	6	2.9874×10^1	6000
46	$^{12}C^{32}S$	1	22	1	2.5318×10^2	5000
	$^{12}C^{34}S$	2	24	1	2.5774×10^2	5000
	$^{13}C^{32}S$	3	32	2	5.3745×10^2	5000
	$^{12}C^{33}S$	4	23	4	1.0229×10^3	5000
47	$^{32}S^{16}O_3$	1	26	1	7.7833×10^3	3500
48	$^{14}N^{12}C^{12}C^{14}N$	1	4224	1	1.5585×10^4	5000
	$^{15}N^{12}C^{12}C^{15}N$	2	5225	1	7.3662×10^3	5000
49	$^{12}C^{16}O^{35}Cl_2$	1	2655	1	1.4800×10^6	5000
	$^{12}C^{16}O^{35}Cl^{37}Cl$	2	2657	16	3.0435×10^6	5000
50	$^{32}S^{16}O$	1	26	1	8.4288×10^2	3500
	$^{34}S^{16}O$	2	46	1	8.5973×10^2	3500
	$^{32}S^{18}O$	3	28	1	9.1052×10^2	3500
51	$^{12}CH_3^{19}F$	1	219	2	1.4707×10^4	5000
52	$^{74}GeH_4$	1	7411	1	1.6341×10^3	5000
	$^{72}GeH_4$	2	7211	1	1.6340×10^3	5000
	$^{70}GeH_4$	3	7011	1	1.6340×10^3	5000
	$^{73}GeH_4$	4	7311	10	1.6341×10^4	5000
	$^{76}GeH_4$	5	7611	1	1.6341×10^3	5000
53	$^{32}S\ ^{12}C^{32}S$	1	222	1	1.7187×10^3	5000
	$^{32}S\ ^{12}C^{34}S$	2	224	1	2.7975×10^3	5000
	$^{32}S\ ^{12}C^{33}S$	3	223	4	1.1009×10^4	5000
	$^{32}S\ ^{13}C^{32}S$	4	232	2	3.5614×10^3	5000
54	$^{12}CH_3^{127}I$	1	217	6	1.6427×10^5	5000
	$^{13}CH_3^{127}I$	2	317	12	3.4936×10^5	5000
55	$^{14}N^{19}F_3$	1	49	3	3.4773×10^5	5000
56	$^{12}C_3H_4$	1	1221	2	7.4879×10^4	5000
57	$^{12}CH_3$	1	2111	1	6.6865×10^2	5000

through direct summation of the most complete set of *ab initio* energy levels. The computation of partition sums for ozone is problematic due to a number of factors: a) a low dissociation threshold, D_0; b) important contributions of metastable levels above D_0 which depend on their lifetime; c) severe convergence issues for high T; d) three potential wells due to Jahn-Teller effect, which implies singularities in rotational constants at linear configurations when nuclear are vibrating among these wells; and e) the inclusion of bound state vib-rot levels of excited electronic states with spin effects for the triplet states. Because of these issues, the partition sums are limited here to a maximum temperature of 1000 K.

For the principal isotopologue, $^{16}O_3$, the TIPS values have been determined by a direct summation [41] using a combination of experimental rovibrational levels for low and medium energies [42] and global variational calculations [43] accounting for dense patterns of levels near the dissociation threshold [44] using ab initio potential energy surface of Tyuterev et al. [45]. The details of the direct sum calculations will be reported elsewhere [41]. For the other 17 isotopologues of ozone shown in Table 1, total internal partition sums were recalculated using the 2014 Codata constants. The Q_{vib} values were determined using the harmonic oscillator approximation [30] and the Q_{rot} values were determined using the analytical expression of Watson [34] with the latest vibrational and rotational constants from the S&MPO database [40]. Calculations were made from 1-1000 K.

3.4. Nitrous oxide

The $Q(T)$ values for the $^{14}N_2^{16}O$ isotopologue is from Ref. [19], which was a direct sum using the data of Tashkun et al. [46]. Those for the $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N_2^{18}O$, and $^{14}N_2^{17}O$ isotopologues

were recalculated using the 2014 Codata constants and the vibrational and rotational constants of Toth [47]. The HOA was used to calculate Q_{vib} and McDowell formula for linear molecules [31] was used for Q_{rot}.

3.5. Carbon monoxide

The $Q(T)$ values for the nine isotopologues of CO shown in Table 1 are from Ref. [19]. The partition sum calculations were made by direct summation over the energy levels of Li et al. [48], which includes all levels to $v=41$ and $J=150$. The $Q(T)$ data were reported to 9000 K.

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 data for all isotopologues were calculated using the 2014 Codata constants and the calculations were made from 1-2500 K. The calculations of TIPS included both direct sums over *ab initio term values* and the product approximation as described below.

Because of the structure of the vibrational states of methane and its isotopologues, the classical vibrational partition sum only provides reasonable results at low temperatures. For example, considering Q_{vib} for $^{12}CH_4$ at 296 K, the difference between a direct sum and the classical harmonic oscillator approximation is ~0.1%, however by 700 K, the difference is ~7% and it increases to ~75% at 2500 K. Therefore, calculations were made for the $G(\nu_1, \nu_2, \nu_3, \nu_4)$ values $(J=0)$ for $^{12}CH_4$ and $^{13}CH_4$ and $G(\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6)$ for $^{12}CH_3D$ and $^{13}CH_3D$. For these molecules the normal mode representation is a good choice providing an adequate description of the nuclear motions. The normal mode kinetic energy

operator was built in the frame of the Eckart-Watson (EW) formalism [49]. The curvilinear potential energy surface (PES) reported by Nikitin et al. [50] was transformed and Taylor-expanded in mass-dependent normal mode coordinates Q adapted to the T_d and C_{3v} point groups. Both the kinetic and potential parts have been expanded at order 14 in Q and reduced at order 7 using the technique described by Rey et al. [51]. To account for symmetry, the use of the irreducible tensor operator technique was used to build the EW Hamiltonian and ro-vibrational basis functions following Refs. [52,53] while energy levels were computed by variational method.

The J=0 vibrational problem was first solved using a direct product of harmonic oscillator functions where a "pruned" vibrational basis was considered by selecting a limited number of functions through the criterion

$$F(n) = \sum_{i=1}^{M} k_i v_i \leq n. \tag{8}$$

with M=4 for T_d species and M=6 for C_{3V} species. Here, $v_i=0,...,n$ and k_i are weighting coefficients. For this work, n=16 and k_i = {1.1; 1; 1.1; 1} for $^{12}CH_4$ and $^{13}CH_4$ and n=14 and k_i = {1.2; 1.1; 1; 1.2; 1; 1} for $^{12}CH_3D$ and $^{13}CH_3D$, resulting in 52062, 47028, 99041, 145354 and 150382 functions for the symmetry blocks {A1, A2, E, F1, F2} and 70552, 65855 and 136374 functions for the symmetry blocks {A1, A2, E}, respectively. The use of such basis sets represents an improvement of previous results [53,54]. Contrary to the effective polyad models, variational calculations require the diagonalization of very large matrices for J>0, even for computing pure rotational energy levels. To this end, a set of vibrational reduced eigenfunctions obtained from the projection technique [51] was introduced to drastically reduce dimensionality of the full problem, making thus calculations feasible even for high J values. From this analysis $G(v_1, v_2, v_3, v_4)$ for $^{12}CH_4$ and $^{13}CH_4$ and $G(v_1, v_2, v_3, v_4, v_5, v_6)$ for $^{12}CH_3D$ and $^{13}CH_3D$ were determined with a cutoff in vibrational energy at 134 152, 121 261, 68 871, and 121 260 cm^{-1}, respectively. These vibrational energies were used to determine $Q_{vib}(T)$ for the four isotopologues of methane.

For the principal isotopologue, $^{12}CH_4$, Q(T) was first determined by direct sum over *ab initio* term values, which were calculated for levels up to J=67 and are complete to ~15,000 cm^{-1}. These partition sums are converged to ~1300 K. Next, the rotational *term values* for $^{12}CH_4$ were calculated for states with J=0 to 80 from an effective Hamiltonian calculation of the ground vibrational state. These *term values* are complete to 30, 424 cm^{-1} and were used to compute the direct sum for Q_{rot}, which are converged at all temperatures. The Q_{vib} values were determined by a direct sum over G_v values as described above. The final Q(T) data for $^{12}CH_4$ are the direct sum values up to 1300 K and the product approximation values from 1301 to 2500 K.

Because the *term values* for $^{13}CH_4$ are almost identical to those for $^{12}CH_4$, the TIPS for $^{13}CH_4$ were determined by multiplying the $^{12}CH_4$ TIPS by 2 to account for the spin of ^{13}C. These values were compared to the product approximation Q(T), where Q_{rot} was determined using the rotational constants of Dang-Nhu et al. [55] in McDowell's analytical formula [33] and Q_{vib} as determined above, and the results are identical at high T. Note that the corresponding TIPS are in a much better agreement with the temperature dependence of Q(T) obtained by Nikitin et al. [56] using the PES of [52] and the contact transformation method [57] compared to other Q(T) values available in the literature. The comparison with Nikitin et al. [56] shows 0.01% difference at 300 K and 0.02% difference at 1000 K.

For the two deuterated isotopologues, the analytical formula of McDowell [32] was used to compute Q_{rot} with the rotational constants of Tarrago et al. [58] for $^{12}CH_3D$ and those of Ulenikov

et al. [59] for $^{13}CH_3D$. The final Q(T) for the two deuterated isotopologues were determined via the product approximation, Q_{rot}(analytical)* Q_{vib}(direct sum).

3.7. Oxygen molecule

The Q(T) values for the six isotopologues of O_2 shown in Table 1 are from Ref. [19]. The calculations were made by direct summation over a set of *term values* complete to ~39 000 cm^{-1} [60] for all isotopologues. The TIPS converge to 7500 K for all isotopologues.

3.8. Nitric oxide

The TIPS for $^{14}N^{16}O$, $^{15}N^{16}O$, and $^{14}N^{18}O$ were calculated via the product approximation using the 2014 Codata constants. Rotational *term values* were taken from an update to the HITEMP database [61] and are from the work of Hargraves et al. [62]. The *term values* were determined up to J=184.5, F=185.5; J=99.5, F=100.5; and J=99.5, F=100.5 and are complete to 51423, 15747, and 15747 cm^{-1}, respectively. These *term values* were used to compute Q_{rot} by direct sum. The vibrational term values are 1876.0765 cm^{-1}, 1843.02092 cm^{-1}, and 1827.38716 cm^{-1}, respectively, and were used to compute Q_{vib} via the HOA. The calculations were made from 1 to 5000 K and are converged at all temperatures.

3.9. Sulfur dioxide

The TIPS for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ were recalculated by the product approximation using the 2014 Codata constants. Q_{rot} was computed using Watson's analytical model with rotational constants from Pine [63] and Q_{vib} used the vibrational term values of Lafferty et al. [64] in the harmonic oscillator approximation. Two new isotopologues were considered; $^{16}O^{32}S^{18}O$ and $^{33}S^{16}O_2$. For $^{16}O^{32}S^{18}O$ the rotational constants and the v_1 and v_3 vibrational energies are from Ulenikov et al. [65]. The v_2 vibrational energy was scaled from the $^{32}S^{16}O_2$ value using the average ratio of the v_1 and v_3 vibrational energies: e.g. $v_1(^{16}O^{32}S^{18}O)/v_1(^{32}S^{16}O_2)$. The rotational constants and the v_2 vibrational energy are from Blake et al. [66]. The v_1 and v_3 vibrational energies were scaled from the $^{32}S^{16}O_2$ values using the ratio $v_2(^{33}S^{16}O_2)/v_2(^{32}S^{16}O_2)$. The calculations were made from 1–5000 K.

3.10. Nitrogen dioxide

The TIPS for $^{14}N^{16}O_2$ were recalculated via the product approximation using the 2014 Codata constants from 1 – 1000 K. The rotational constants were taken from Perrin et al. [67] and used in Watson's analytical formula. The vibrational term values are from Norton and Rinsland [68] and were used in Herzberg's HOA.

3.11. Ammonia

The Q(T) values for the two isotopologues of NH_3 shown in Table 1 are from Ref. [19]. The TIPS were calculated by direct summation over the *ab initio* energies of Yurchenko et al. [69,70] and are converged to 6000 K.

3.12. Nitric acid

The Q(T) values for the two isotopologues of HNO_3 shown in Table 1 are from Ref. [19]. The TIPS were calculated via the product approximation where Q_{rot} was determined by Watson's analytical formula [34] and Q_{vib} was determined via the Harmonic oscillator approximation of Herzberg.
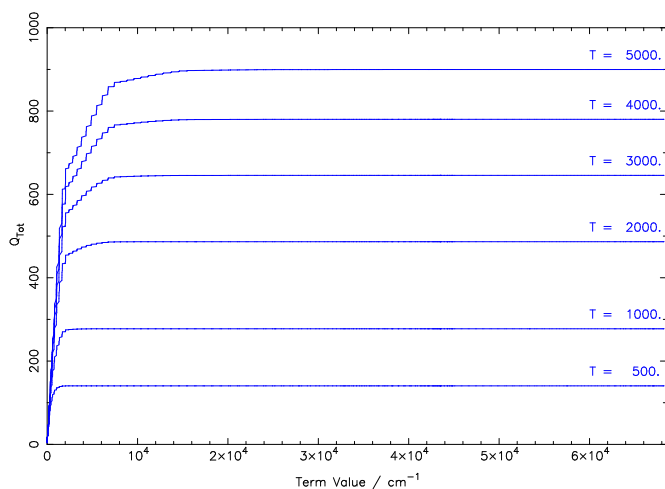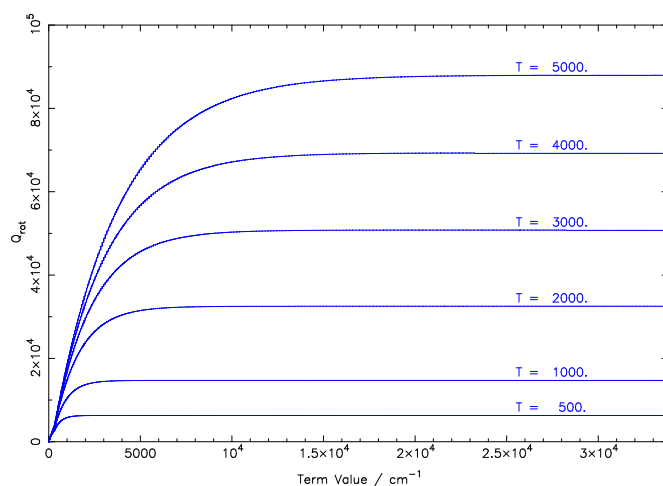
Fig. 2. $Q(T)$ for ^{18}OH determined by direct summation of Eq. (2) versus the *term value* in wavenumbers for T values: 500, 1000, 2000, 3000, 4000, and 5000 K. The saw tooth structure at low term value is due to the structure of the energy; groups of 4 near identical term values for the $^2\Pi_{3/2} \pm$ states for the states with $F = J\pm0$.

3.13. Hydroxyl radical

The $Q(T)$ values for the ^{16}OH isotopologues of OH shown in Table 1 are from Ref. [19]. These were determined from a direct summation over the *term values* of Brooke et al. [71] and are converged to 9000 K. For the ^{18}OH and ^{16}OD isotopologues, the rotational term values for the $^2\Pi_{1/2}$, $^2\Pi_{3/2}$, and $^2\Sigma_{1/2}$, states were calculated using the formalism of Beaudet and Poynter [72] which includes the fine structure interaction and lambda doubling. This procedure generated energies complete to 42 000 cm^{-1} for ^{18}OH, and 39 000 cm^{-1} for ^{16}OD. Rotational and vibrational partition sums were calculated using the 2014 Codata constants from 1-5000 K. The total internal partition sums were determined by the product approximation. Fig. 2 shows Q_{rot} for ^{18}OH versus the term value in cm^{-1} at T=500, 1000, 2000, 3000, 4000, and 5000 K demonstration convergence. The saw tooth structure at low term value is due to the structure of the energy; groups of 4 near identical term values for the $^2\Pi_{3/2} \pm$ states for the states with $F = J\pm0$. The data for the ^{16}OD isotopologue shows similar convergence.

3.14. Hydrogen fluoride

The $Q(T)$ values for H^{19}F and D^{19}F are from Ref. [19]. The TIPS were determined by direct summation over the *term values* of Li et al. [73] giving results that are converged to 6000 K.

3.15. Hydrogen chloride

The $Q(T)$ values for H^{35}Cl, H^{37}Cl, D^{35}Cl, and D^{37}Cl are from Ref. [19]. The TIPS for these isotopologues of HCl were determined by direct summation over the *term values* of Li et al. [73] giving results that are converged to 6000 K.

3.16. Hydrogen bromide

The $Q(T)$ values for the four isotopologues of HBr shown in Table 1 are from Ref. [19]. They were also determined by direct summation over the *term values* of Li et al. [73] giving results that are converged to 6000 K.

Fig. 3. $Q(T)$ for ^{18}OH determined by direct summation of Eq. (2) versus the *term value* in wavenumbers for T values: 500, 1000, 2000, 3000, 4000, and 5000 K.

3.17. Hydrogen iodide

The $Q(T)$ values for H^{127}I and D^{127}I are from Ref. [19]. The last of the hydrogen halides, HI, the TIPS were also determined by direct summation over the *term values* of Li et al. [73] giving results that are converged to 6000 K.

3.18. Chlorine monoxide

The TIPS reported for ^{35}Cl^{16}O and ^{37}Cl^{16}O were determined via the product approximation. The ground vibrational state term values for ClO, an inverted doublet in Hund's case (a), were computed for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states using the formalism of Endo et al. [74] with the constants of Cohen et al. [75]. *Term value* calculations were made to J=249.5 (F=251) and are complete to 33 800 and 33 323 cm^{-1} for ^{35}Cl^{16}O and ^{37}Cl^{16}O, respectively. These *term values* were used to compute Q_{rot} by direct summation. Q_{vib} were computed with ν_1=841.6 cm^{-1} (^{35}Cl^{16}O) and ν_1=837.2 cm^{-1} (^{37}Cl^{16}O). The $Q(T)$ values were determined from 1-5000 K. Note, all partition sums were determined using the 2014 Codata constants. Fig. 3 shows Q_{rot} for ^{35}Cl^{16}O versus the term value in cm^{-1} for the temperatures 500, 1000, 2000, 3000, 4000, and 5000 K. The last 900 *term values* of a sorted list of 3990 values only change Q(5000 K) by 0.33 % demonstrating rotational partition sums are converged.

3.19. Carbonyl sulfide

Previous editions of HITRAN had five isotopologues of carbonyl sulfide: ^{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. HITRAN2020 has data for the ^{16}O^{13}C^{34}S isotopologue. All isotopologues were calculated by the product approximation with the 2014 Codata constants at temperatures from 1-5000 K. The rotational constants for the first five isotopologues are from Maki [76] and those for ^{16}O^{13}C^{34}S are from Burenin et al. [77]. The vibrational constants are from Refs. [68,78,79].

3.20. Formaldehyde

Three isotopologues of formaldehyde were considered in this work: H$_2$^{12}C^{16}O, H$_2$^{13}C^{16}O, and H$_2$^{12}C^{18}O. The calculations of Q_{vib} and Q_{rot} were done from 1-5000 K using the 2014 Codata constants. The rotational constants are from Winnewisser et al. [80] and the vibrational fundamentals are from Norton and Rinsland [68]. The product approximation was used to determine the total internal partition sum.

3.21. Hypochlorous acid

The total internal partition sums for $H^{16}O^{35}Cl$ and $H^{16}O^{37}Cl$ were calculated using the product approximation. The Q_{rot} values were recalculated using the rotational constants of Lovas [81]. The calculation of Q_{vib} used the vibrational frequencies of Norton and Rinsland [68]. The partition sum calculations used the 2014 Codata constants and are reported from 1-5000 K.

3.22. Nitrogen molecule

The $Q(T)$ values for the three isotopologues of nitrogen shown in Table 1 are from Ref. [19]. The partition sums were calculated by direct summation over a rather complete set of *term values* from the work of Le Roy et al. [82], giving values converged to 9000 K.

3.23. Hydrogen cyanide

The $Q(T)$ values for the three isotopologues of hydrogen cyanide, $H^{12}C^{14}N$, $H^{13}C^{14}N$, and $H^{12}C^{15}N$ are from Ref. [19]. The TIPS were determined by a combination of direct summation over the *ab initio term values* of Harris et al. [83,84] from 1-1000 K and via the product approximation from 1001-3500 K, where Q_{vib} was determined by direct summation and Q_{rot} was determined using the analytical formula of McDowell [31].

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 recalculated using the 2014 Codata constants. The TIPS were determined from 1-5000 K via the product approximation. The Q_{rot} values were determined using the constants of Di Lauro and Alamichel [85] in the analytical expression of McDowell [32]. The Q_{vib} values were determined by the HOA using the vibrational frequencies of Norton and Rinsland [68].

3.25. Hydrogen peroxide

The $Q(T)$ values for the $H_2^{16}O_2$ isotopologue shown in Table 1 are from Ref. [19]. The TIPS were determined by direct summation over the *ab initio term values* of Al-Refaie et al. [86] allowing convergence to 6000 K.

3.26. Acetylene

The $Q(T)$ values for the $^{12}C_2H_2$ isotopologue are from Ref. [19], which was a direct summation using the *term values* of Amyay et al. [87]. For the $H^{12}C^{13}CH$ and $H^{12}C^{12}CD$ isotopologues the TIPS were recalculated via the product approximation. The calculation of Q_{rot} used the rotational constants from Refs. [88] and [89] and the Q_{vib} HOA calculations used the vibrational frequencies from NIST tables (http://webbook.nist.gov) and Ref. [89] for $H^{12}C^{13}CH$ and $H^{12}C^{12}CD$, respectively. The calculations were done from 1-5000 K using the 2014 Codata constants.

3.27. Ethane

The TIPS for $^{12}C_2H_6$ and $^{12}CH_3^{13}CH_3$ were recalculated via the product approximation using the 2014 Codata constants. Q_{rot} values were computed using McDowell's analytical formula [32] and the rotational constants of Duncan et al. [90]. Q_{vib} was computed using the HOA and the vibrational frequencies of Norton and Rinsland [68]. The TIPS were determined for a new isotopologue, $^{12}C_2H_5D$, using the rotational constants of Daly et al. [91] in Watson's analytical formula. Q_{vib} values were determined with

Table 2
Vibrational normal mode wavenumbers in cm^{-1} for $^{32}S^{19}F_6$.

State	Wavenumber in cm^{-1}	Degeneracy	Ref.
ν_1	774.545540(66)	1	[95]
ν_2	643.373626(43)	2	[95]
ν_3	948.1025121(21)	3	[95]
ν_4	614.98196(15)	3	[97]
ν_5	524.027934(93)	3	[98]
ν_6	347.736707(35)	3	[99]

the ν_1, ν_2, ν_3, ν_4, ν_{12}, ν_{13}, ν_{14} vibrational fundamentals from Doney et al. [92]; the ν_5, ν_6, ν_7, ν_8, ν_{10}, ν_{15} vibrational fundamentals from Kondo and Saeki [93]; and the ν_9, ν_{11}, ν_{16}, ν_{17}, ν_{18} from Daly et al. [91]. Daly et al. report the partition sums at a few temperatures from 9.375 to 300 K. In their calculations they only consider the tortional degeneracy, g_t=4. The calculations made here also include the state-independent degeneracy factor: $(2I_H+1)^{2*}(2I_{12C}+1)^{2*}(2I_D+1) = 12$. Thus, taking ratios of our computed Q(T) values to those of Daly et al. give a ratio of 12. The final TIPS go from 1-5000 K.

3.28. Phosphine

The $Q(T)$ values for phosphine, $^{31}PH_3$ are from Ref. [19], where a direct summation on *term values* form the work of Sousa-Silva et al. [94]. The TIPS were converged and reported to 4500 K

3.29. Carbonyl fluoride

The total internal partition sums for the two isotopologues of carbonyl fluoride shown in Table 1 are from Ref. [19]. The TIPS were determined using the product approximation with Q_{vib} via the HOA and Q_{rot} via Watson's analytical formula.

3.30. Sulfur hexafluoride

The total internal partition sums for $^{32}S^{19}F_6$ were computed by Q_{vib} x Q_{rot}, where the rotational partition sum was evaluated by analytical formula [33] using the constants of Faye et al. [95] The vibrational partition sums were computed using the HOA with the following vibrational state frequencies listed in Table 2. All calculations used the 2014 Codata constants and considered temperature from 1 to 5000 K. The Q(296 K) value determined here agrees has a 0.2% difference compared with the *ab initio* determined value of Rey et al. [96].

3.31. Hydrogen sulfide

The $Q(T)$ values for the $H_2^{32}S$ isotopologue are from Ref. [19]. The TIPS for the $H_2^{34}S$ and $H_2^{33}S$ isotopologues were recalculated by the product approximation. The rotational partition sums used the analytical formula of Watson [34] with the constants of Flaud et al. [100]. The Q_{vib} calculations used the HOA with the constants of Norton and Rinsland [68]. The partition sum calculations were from 1-5000 K and used the 2014 Codata constants.

3.32. Formic acid

The TIPS for $H^{12}C^{16}O^{16}OH$ were computed via Q_{vib} x Q_{rot}, where the rotational partition sum was evaluated by analytical formula of Watson [34] with the constants of Willemot [101]. Q_{vib} values were determined using the HOA with the constants of Norton and Rinsland [68]. Both calculations were done over the range 1-5000 K and used the 2014 Codata constants.

3.33. Hydroperoxyl radical

TIPS were recalculated for the $H^{16}O_2$ isotopologue via the product approximation. Q_{rot} values were determined via the analytical formula of Watson [34] using the constants of Charo and DeLucia [102]. Because HO_2 is an open shell molecule, Q_{rot} was multiplied by a factor of 2 to account for the F splitting. Q_{vib} values were determined using the HOA with the constants of Ref. [68]. The calculations were made from 1 to 5000 K using the 2014 Codata constants.

3.34. Oxygen atom

No data are reported for the oxygen atom.

3.35. Chlorine nitrate

TIPS were computed for two isotopologues of chlorine nitrate: $^{35}Cl^{16}O^{14}N^{16}O_2$ and $^{37}Cl^{16}O^{14}N^{16}O_2$. The rotational partition sums used Watson's analytical formula [34] with the constants of Carten and Lovejoy [103]. The Q_{vib} values come from a HOA calculation using the constants of Norton and Rinsland [68]. Both calculations used the 2014 Codata constants. The final $Q(T)$ values are reported from 1-5000 K.

3.36. Nitric oxide cation

The TIPS for $^{14}N^{16}O^+$ ion (also known as the nitrosonium ion) were recalculated by the product approximation with rotational and vibrational constants taken from von Esse [104]. Q_{rot} values were determined using McDowell analytical formula and Q_{vib} values were from the HOA; both calculations ranged from 1 to 5000 K and used the 2014 Codata constants.

3.37. Hypobromous acid

The TIPS for two isotopologues of hypobromous acid, $H^{16}O^{79}Br$ and $H^{16}O^{81}Br$, were recalculated using the product approximation. The rotational $Q(T)$ values were determined using Watson analytical formula and the vibrational $Q(T)$ values were determined via the HOA. Both calculations used the molecular constants of Cohen [105], the 2014 Codata constants, and were done for temperatures from 1 to 5000 K.

3.38. Ethylene

The TIPS for $^{12}C_2H_4$ and $^{12}CH_2^{13}CH_2$ were recalculated from 1-5000 K using the 2014 Codata constants. The rotational constants are from Tan et al. [106] and [107], respectively, and used in Watson's analytical formula. The vibrational frequencies are from the work of Georges et al. [108] for $^{12}C_2H_4$, from Duncan et al. [109,110] for $^{12}CH_2^{13}CH_2$ and were used to calculate Q_{vib} via the HOA. New to HITRAN is the $^{12}C_2H_3D$ isotopologue. Watson's formula was used for Q_{rot} with the constants of Herbin *et al.* [111] and Q_{vib} calculated using the HOA with the vibrational constants of Viglaska et al. [112]. The 296 K partition sums calculated in this work are in a good agreement with the *ab initio* direct sum results of Rey et al. [113] for $^{12}C_2H_4$, the difference being of 0.4% .

3.39. Methanol

The $Q(T)$ values for the $^{12}CH_3^{16}OH$ isotopologue shown in Table 1 are from Ref. [19]. They were determined via the product approximation where Q_{vib} was determined using the vibrational energies from the Virtual Planetary Laboratory of the University of Washington [114], which includes the torsional state and the rotational constants of De Lucia et al. [115]in the analytical formula of Watson.

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 recalculated from 1-5000 K using the 2014 Codata constants. The rotational partition sums of both isotopologues were computed using the symmetric-top analytical formula of McDowell [32]. The vibrational partition sums were computed using the HOA of Herzberg with the vibrational frequencies from Refs. [116–119].

3.41. Methyl cyanide (IUPAC name: acetonitrile)

The TIPS for four isotopologues of methyl cyanide were recalculated via the product approximation from 1-5000 K using the 2014 Codata constants: $^{12}CH_3^{12}C^{14}N$, $^{13}CH_3^{12}C^{14}N$, $^{12}CH_3^{13}C^{14}N$, and $^{13}CH_3^{13}C^{14}N$. The rotational constants for the principal isotopologue are from Simeckova et al. [120] and those for the other three isotopologues are from Boucher et al. [121]. These constants were used in McDowell's symmetric-top analytical formula. The vibrational frequencies were taken from Refs. [122–125] and used to compute Q_{vib} via the HOA.

3.42. Carbon tetrafluoride

While $^{12}C^{19}F_4$ has been on the HITRAN database for some time, the TIPS were not reported. Here the TIPS have been calculated via the product approximation from 1-5000 K using the 2014 Codata constants. The rotational and vibrational constants are from Carlos et al. [126]. The rotational partition sums were calculated using McDowell's spherical-top formula and the vibrational partition sums were calculated via Herzberg's HOA. The TIPS value at 296 K determined in this work agrees well, 0.2% difference, with the *ab initio* results of Rey et al. [51].

3.43. Diacetylene

The total internal partition sums for the $^{12}C_4H_2$ isotopologue of diacetylene (1,3-butadiyne) were recalculated from 1-5000 K using the 2014 Codata constants. The linear molecule analytical formula of McDowell [31] was used with the rotational constants of Arie and Johns [127]. The vibrational partition sums were calculated via Herzberg's HOA using the vibrational frequencies from Refs. [127–133]. The TIPS were formed by Q_{vib} x Q_{rot}.

3.44. Cyanoacetylene

The 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 recalculated from 1-5000 K using the 2014 Codata constants. The rotational partition sums used the analytical formula of McDowell [31] with the constants of Lafferty and Lovas [134]. Using the vibrational frequencies from Refs. [130,135–140] the vibrational partition sums were calculated using the HOA. The TIPS were formed using the product approximation.

3.45. Hydrogen molecule

The $Q(T)$ values for H_2 and HD are from Ref. [19] where direct sums were made over the *term values* of Piszczatowski et al. [141] for H_2 and from Pachucki et al. [142] for HD. The TIPS were reported to 6000 K.

3.46. Carbon monosulfide

The 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 recalculated using the product approximation from 1 to 5000 K using the 2014 Codata constants. The rotational partition sums were computed via McDowell's linear molecule analytical formula using the constants of Burkholder et al. [143]. The vibrational frequencies were also taken from Burkholder et al. to compute the vibrational partition sums.

3.47. Sulfur trioxide

The $Q(T)$ values for $^{32}S^{16}O_3$ are from Ref. [19] where a direct sum was made using the *term values* from the work of Underwood et al. [144], which converged to 650 K. $Q(T)$ values were also computed via the product approximation using the rotational and vibrational constants of Maki et al. [145]. The final TIPS are from a direct sum from 1-650 K and the product approximation from 651-3500 K.

3.48. Cyanogen

The TIPS for two symmetric isotopologues of cyanogen, $^{14}N^{12}C^{12}C^{14}N$ and $^{15}N^{12}C^{12}C^{15}N$, were recalculated from 1-5000 K by the product approximation using the 2014 Codata constants. The Q_{rot} values were computed using McDowell's linear molecule analytical formula with the constants of Maki [146]. The vibrational partition sums were computed via the HOA using the frequencies from Grecu et al. [147].

3.49. Phosgene

The $Q(T)$ values for the $^{12}C^{16}O^{35}Cl_2$ and $^{12}C^{16}O^{35}Cl^{37}Cl$ isotopologues of phosgene are from Ref. [19]. The TIPS were determined from 1-5000 K via the product approximation using the rotational constants of Tchana et al. [148] and the vibrational energies for ν_1 and ν_5 from Tchana et al. [148] and ν_2, ν_3, and ν_4 from the NIST webbook (http://webbook.nist.gov).

3.50. Sulfur monoxide

Sulfur Monoxide is a new HITRAN molecule, which was assigned number #50 to be consistent with TIPDS_2017 which already contained this molecule. The TIPS for three isotopologues of sulfur monoxide, $^{32}S^{16}O$, $^{34}S^{16}O$, and $^{32}S^{18}O$, were recalculated from 1-5000 K using the 2014 Codata constants. There is no analytical formula for this $X^3\Sigma$ molecule so direct sums of Q_{rot} were determined for each isotopologue. *Term values* were computed for J up to 250 using the constants of Burkholder et al. [143] giving *Term values* to more than 52000 cm^{-1} for each isotopologue, ensuring convergence of the rotational partition sums at all temperatures of the study. The vibrational frequencies are also from of Burkholder *et al.* and were used in the HOA to compute Q_{vib}. The final $Q(T)$ values were determined by Q_{vib}x Q_{rot}.

3.51. Methyl fluoride (IUPAC name fluoromethane)

Methyl fluoride is a new species on the HITRAN database, molecule #51. The TIPS for the $^{12}CH_3^{19}F$ isotopologue were determined from 1-5000 K using the product approximation with the 2014 Codata constants. The rotational constants of Papousek et al. [149] were used to determine the rotational partition sums with McDowell's symmetric-top analytical formula. The vibrational partition sums were computed via the HOA with the constants from the NIST Chemistry Webbook (webbook.nist.gov/chemistry/).

3.52. Germane

Germane is a new species on the HITRAN database, molecule #52. The TIPS were determined from 1-5000 K using the product approximation with the 2014 Codata constants for five isotopologues: $^{70}GeH_4$, $^{72}GeH_4$, $^{73}GeH_4$, $^{74}GeH_4$, $^{76}GeH_4$. The rotational partition sums were calculated using the spherical-top formula of McDowell [33] and the constants of Richard et al. [150]. The vibrational partition sums were calculated via the HOA with the vibrational fundamentals from Refs. [150,151]. The TIPS for $^{74}GeH_4$ are consistent with the direct sum *ab initio* results reported by Nikitin et al. [152] with very small differences of 0.004% and 0.08% at 80 and 298 K.

3.53. Carbon disulfide

Carbon disulfide is a new species on the HITRAN database, molecule #53; however, it was included in TIPS_2017. Note, the symmetric species are Bose particles, so the double product approximation must be used to compute $Q(T)$ analytically. The double product approximation was not used in TIPS_2017, so there are large differences with the TIPS computed here for the symmetric species. Those presented in this work should be used. The TIPS were determined with the 2014 Codata constants from 1-5000 K using the double product approximation for $^{12}C^{32}S_2$, $^{13}C^{32}S_2$, and the product approximation for $^{32}S^{12}C^{34}S_2$, and $^{32}S^{12}C^{33}S_2$. The rotational constants for all four isotopologues are from Karlovets et al. [153] and were used to compute the partition sums via McDowell's linear molecule analytical formula. The G_v values are also from Karlovets et al. [153] for the four isotopologues. Note however, the $G_v(01^10)$ value for $^{32}S^{12}C^{33}S_2$ was estimated from the average ratio $G_v(02^00)/ G_v(01^10)= 0.494$, from the other three isotopologues and the $G_v(02^00)$ value for $^{32}S^{12}C^{33}S_2$.

3.54. Methyl iodide (IUPAC name iodomethane)

Methyl iodide is a new species on the HITRAN database, molecule #54. The TIPS were determined from 1-5000 K using the product approximation with the 2014 Codata constants for two isotopologues: $^{12}CH_3^{127}I$ and $^{13}CH_3^{127}I$. The rotational and vibrational constants for $^{12}CH_3^{127}I$ are from Perrin et al. [154]. For $^{13}CH_3^{127}I$ the rotational constants are from Alanko [155] and the vibrational term values are from Perrin et al. [154], Alanko [155], and some scaled from Alanko's combination band values. The rotational partition sums were determined using McDowell's symmetric-top analytical formula and the vibrational partition sums were computed using the HOA. There is a 6% difference in $Q(296$ K) between $^{12}CH_3^{127}I$ and $^{13}CH_3^{127}I$, which can be compared to a 0.07% difference between $Q(^{12}CH_3D)$ and $Q(^{13}CH_3D)$ at 296 K. To confirm this difference, a variational calculation was performed using a very small basis set up to J=80, $Q(296$ K) computed by the product approximation, and indeed the 6% difference was confirmed.

3.55. Nitrogen trifluoride

The nitrogen trifluoride isotopologue, $^{14}N^{19}F_3$, is a new species on the HITRAN database, molecule #55. NF$_3$ belongs to the C_{3v} point group at the equilibrium configuration and possesses 4 fundamental vibrations: $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$ and $\nu_4(E)$. Since NF$_3$ is a semirigid molecule, the normal mode coordinates were employed to build the Hamiltonian in the Watson formalism [49] using the reduction technique described by Rey et al. [51]. For this work, both the kinetic energy part and the potential energy surface reported by Egorov et al. [156], have been expanded to order 14 in normal coordinates and reduced to order 7. For a full account of symmetry, the use of irreducible tensor operators turned out to
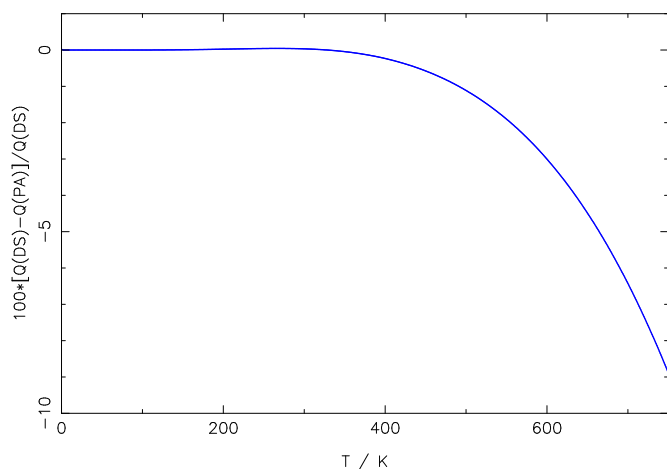
Fig. 4. $Q_{rot}(T)$ for $^{35}Cl^{16}O$ by direct summation of Eq. (2) versus the *term value* in wavenumbers for T values: 500, 1000, 2000, 3000, 4000, and 5000 K.

be an optimal choice [157]. Concerning the computation of energy levels, the J=0 vibrational problem was first solved using a direct product of harmonic oscillator functions, resulting in 6975, 5985 and 12915 functions for the symmetry blocks A_1, A_2 and E, respectively. For J>0, a set of vibrational reduced eigenfunctions obtained from the projection technique [51] was introduced to drastically reduce dimensionality of the full problem, making the calculations feasible even for high J values. For this work, rovibrational term values were computed variationally up to $J_{max}=80$. These term values allow a check of Q(T) data from analytical models.

In the partition sum calculations that follow, the 2014 Codata constants were used. First the TIPS were determined using the term values discussed above. Because the term values are only complete to ~1700 cm^{-1} it is not expected that the resulting partition sums will be converged at high temperatures. Next, the TIPS were calculated from 1-5000 K using the product approximation with Q_{rot} determined using McDowell's symmetric-top formula with the constants of [158] and Q_{vib} determined via the HOA with vibrational constants from Egorov et al. [156]. The comparison of the direct sum and analytical model Q(T)s is shown in Fig. 4, where the percent difference (blue solid line) between the direct summation TIPS, Q(DS) minus the TIPS form the product approximation, Q(PA) is plotted versus temperature from 1-750 K. The results give a 0.034% difference at 296 K, a -1.1% difference at 500 K, and grow rapidly with temperature because Q(DS) is not converged at $J_{max}=80$ for T>350 K. The TIPS from the analytical models are used.

3.56. Propyne

The TIPS for the $^{12}C_3H_4$ isotopologue of propyne were recalculated from 1-5000 K via the PA using the 2014 Codata constants. Using McDowell's analytical formula for symmetric-tops and the constants of Cazzoli and Puzzarini [159] the rotational partition sums were calculated. Using the constants provided by Pracna [160] the vibrational partition sums were calculated via the HOA.

3.57. Methyl radical

The TIPS for the methyl radical, $^{12}CH_3$, were recalculated from 1-5000 K using the 2014 Codata constants. Using the molecular constants of Yamada et al. [161], the energy levels of the methyl radical, a planar symmetric top, were computed for states up to J=50. The terms values are complete to 17, 545 cm^{-1} and were used to compute Q_{rot}. The vibrational partition sums were deter-

mined using the HOA and the following fundamental frequencies: ν_1=3004.43 cm^{-1} [162], ν_2=606.4531 cm^{-1} [161], ν_3=3160.821 cm^{-1} [163], and ν_4=1397 cm^{-1} [164]. The final TIPS were from the product approximation.

4. Rapid recall of the tips

The total internal partition sums will be made available in tabular form for all isotopologues of this study at the HITRAN website (www.hitran.org) and at the website of the corresponding author (http://faculty.uml.edu/Robert_Gamache). To be useful to applications that require the TIPS at various temperatures, codes that make a rapid recall of the TIPS as a function of molecule, isotopologue, and temperature are needed. As discussed above, in earlier works [12–18], a FORTRAN code, e.g., TIPS_2011.for, was made openly available to the scientific community and starting in 2017 a python code [19] was also made available to the community. At the websites listed above, the following codes are available: TIPS_2021_v1p0.for, BD_TIPS_2021_v1p0.for and TIPS_2021_v1p0.py. TIPS_2021_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_2021_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 1-20 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 between the 2 points surrounding the requested temperature is done and that value returned.

For TIPS_2021_v1p0.py, python libraries have been created from the TIPS data. The data are stored similarly to the FORTRAN routines and linear interpolation used. Note, this interpolation method has been shown to have less than 0.001 absolute average percent difference. The library names are "molecule #"_"ISO#".QTpy, where the molecule number and isotopologue number are given in Table 1. For example, the dictionary for the $^{13}C^{16}O_2$ isotopologue of water is 2_2.QTpy. All the dictionaries are stored in a folder labeled /QTpy/. The code, TIPS_2021.py, queries the user for molecule, isotopologue, and temperature; then selects the proper dictionary and extracts Q(T) with a key constructed from the input.

Extracting individual subroutines out of BD_TIPS_2021_v1p0.for allows researchers to create custom codes for applications on 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.

Caution should be used if previous versions of the TIPS codes are to be used with the 2021 versions as some of the molecule numbers have changed to retain compatibility with HITRAN. These can be found by comparing Table 1 from Ref. [19] to Table 1 presented here.

The codes all use the MIT license (see codes for details) and can be downloaded at http://faculty.uml.edu/Robert_Gamache, at www.HITRAN.org or at zenodo.org (10.5281/zenodo.4708099).

5. Summary

Total internal partition sums are presented for all the molecules (55) and isotopologues (179) in the line-by-line portion of the HITRAN2020 database and for additional molecules/isotopologues (C_3H_4 and CH_3) of astrophysical interest. All previous calculations of the TIPS have been updated using *h, k,* and *c* from the 2014 Codata physical constants. New calculations are presented for a number of molecules (13), isotopologues (28) that are either new to HITRAN or for which improvements were possible. 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 supplemental information, at www.HITRAN.org and http://Faculty.uml.edu/Robert_Gamache. Rapid recall of the TIPS can be achieved using the FORTRAN codes TIPS_2021_v1p0.for and BD_TIPS_2021_v1p0.for or using the python code TIPS_2021_v1p0.py, which are available at the web sites listed in section 4.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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