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Partition sums for non-local thermodynamic equilibrium applications

Jonathan Fischer, Robert R. Gamache *

Department of Environmental, Earth and Atmospheric Sciences, University of Massachusetts Lowell, Olney Hall-DEFAS, 265 Riverside Street-Room 301B, Lowell, MA 01854-5045, USA

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Abstract

Internal partition functions are calculated for nine molecules, which are abundant in the terrestrial atmosphere and are important in non-local thermodynamic equilibrium processes. Calculations are performed for the most abundant isotopomer and for several molecules for lesser abundant isotopomers as well. The temperature range considered in the study is for applications in the terrestrial atmosphere from 100 to 450 K. The resulting rotational and vibrational partition functions are each fit separately to a polynomial expression, which is third order in temperature. The methods of calculation of the partition functions, the convergence, and the quality of the fits for each isotopomer are discussed. © 2002 Published by Elsevier Science Ltd.

Keywords: Partition sums; Terrestrial atmosphere; Non-local thermodynamic equilibrium

1. Introduction

When a system is in local thermodynamic equilibrium (LTE), the relative populations of the upper and lower states of a vibrational–rotational transition are determined by the Boltzmann distribution, evaluated at the local kinetic temperature. However, at high altitudes, collisional energy exchange under conditions of lower atmospheric pressure, coupled with radiative and chemical pumping and radiative losses can cause the internal energy populations to deviate from the Boltzmann distribution. The partition of population is then characterized by a temperature that is different from the local kinetic temperature. In effect, this causes a system to exhibit an effective rotational temperature different from its effective vibrational temperature.

Several different radiative transfer models [1–4] have been developed to perform non-local thermodynamic equilibrium (NLTE) studies in planetary atmospheres. These models are important, both

* Corresponding author. Tel.: +1-978-934-3904.
E-mail address: robert_gamache@uml.edu (R.R. Gamache).

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for remote sensing applications and for understanding middle-upper atmosphere energetics. A recent analysis of incorporating NLTE corrections into radiative transfer models has shown that such corrections can affect a 30% difference in calculated radiance at an altitude of 130 km [5]. In order to apply these codes the rotational and vibrational partition functions are needed for molecules that are not in LTE. In this paper, partition functions for use in NLTE calculations for the terrestrial atmosphere are presented. It should be noted that in the literature, the terms partition function and partition sum are synonymous.

2. Total internal partition sums

The total internal partition sum (TIPS) of a molecule is defined as a direct sum over all states, s, of the factor $e^{-hcE_s/kT}$. In this expression, h is the Planck constant, c is the speed of light, k is the Boltzmann constant, T is the temperature in K and E_s is the total energy of state s in wavenumber units, including electronic, vibrational, rotational and any other quantized motion. This expression can be simplified by accounting for degenerate states with the following formula:

$$Q(T) = d_i \sum_s d_s e^{-hcE_s/kT}, \tag{1}$$

where d_s accounts for state dependent degeneracy factors and d_i accounts for state independent degeneracy factors. Examples of state dependent degeneracy factors are the $2J+1$ degenerate states of total angular momentum J in the absence of an electric field or the coupling of rotational and nuclear wavefunctions due to the symmetry of a molecule such as ozone ($^{16}O_3$), which using the rotational band as an example gives one-fold degeneracy for even rotational states and causes odd rotational states not to exist. An example of a state independent degeneracy factor is the product, $\Pi(2I_i+1)$, where I_i is the nuclear spin of each atom, present in a molecule where identical atoms are not exchanged by rotations, which leave the symmetry of the molecule intact, such as $HD^{16}O$.

For NLTE applications the rotational and vibrational partition sums must be done separately since the effective temperature of each is different. The calculation of the rotational partition sum for a molecule requires that the ground state energy levels and degeneracy factors be known for the isotopomer in question. As the energy of state s increases, the exponential in Eq. (1) approaches zero, and the partition sum can be truncated with no loss of accuracy. The state at which truncation can occur without loss of accuracy is dependent on temperature, as kT divides the energy of the state. An accurate calculation of the partition sum by direct summation can only be made by summing over energy levels until the exponential factor no longer contributes significantly to $Q(T)$. This can readily be determined by plotting $Q(T)$ versus energy and noting the point beyond which $Q(T)$ remains constant as additional energies are summed over. At this point, the calculation of the partition sum is said to have converged. This is demonstrated in Fig. 1 for $^{16}O_3$. Note that the partition sum has converged up to roughly 1500 K after which it is clear that the addition of higher energies in the sum would change $Q(T)$.

Often the rotational energy levels of an isotopomer are not known for high-energy states, hence Q_{rot} cannot be computed with high accuracy at elevated temperatures. For such cases, there are a number of analytical formulae [6–15], which can be used, with varying degrees of complexity and

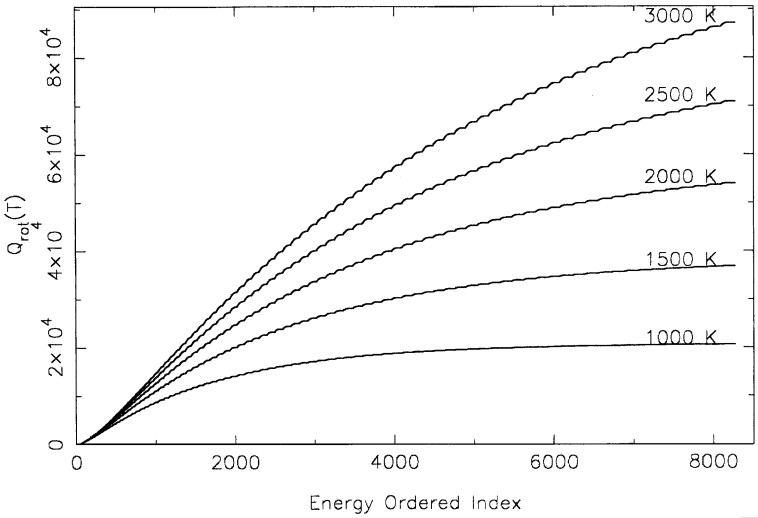

Fig. 1. Convergence of the rotational partition sum of $^{16}O_3$.

accuracy. Such formulae range from the approximate classical formulae, which rely only on the principle moment of inertia, to complicated analytical expressions, utilizing dozens of terms.

The methodology used to calculate the rotational partition functions in this study is as follows. The rotational partition functions were calculated by direct summation to the highest temperature at which $Q(T)$ converged. The rotational partition sums were also calculated by analytical expression and compared with the results obtained by direct summation to ensure agreement. When the direct sum remained convergent over the entire temperature range of the study, it was used for the rotational partition function. However, for species where the direct sum did not remained converged throughout the temperature range of the study, an analytical expression was used to calculate the partition sum throughout the entire temperature range of the study. This is a reasonable approach since in all such cases, the agreement between the analytical expression and the direct sum was quite good at all temperatures for which the direct sum had converged, and the analytical formulae are more valid in the limit of high temperature.

The vibrational partition sums are calculated using the harmonic oscillator approximation (HOA) of Herzberg [6] for all species in this study. This approximation expresses the vibrational partition sum as a product over the fundamental vibrational energies, ω_i of a molecule,

$$Q_{\mathrm{vib}}(T) = \prod \left(\frac{1}{1 - \mathrm{e}^{-hc\omega_i/kT}} \right). \tag{2}$$

Once the partition functions are calculated, it is useful to reduce them to a form that allows for rapid recall. While interpolation provides for a convenient, accurate method of recall, a simple polynomial provides the necessary accuracy for the limited temperature range of this study (100–450 K). The expression used is third order in temperature, requiring the storage of four coefficients for a given partition function,

$$Q(T) = a + bT + cT^2 + dT^3. \tag{3}$$

Tests showed that this third-order expression introduced $<1\%$ error for all species at all temperatures under consideration and did significantly better for most species within the specified temperature range. This temperature range was selected to be of the greatest utility in studying the terrestrial atmosphere.

The vibrational and rotational partition sums were calculated at 5 K steps between 95–455 K. The resulting values were fit to the polynomial expression, Eq. (3), where the coefficients are determined by fitting to the data using a Simplex nonlinear minimization algorithm [16]. This method has previously been shown to be extremely well suited for fitting to partition functions [17,18]. The fitting is based on minimizing the eighth powers of the percentage differences between the polynomial of Eq. (3) and the calculated partition sums. The use of percentage differences reflects the way in which partition functions are used in calculations, as well as the accuracy of the calculations better than absolute differences would. The use of least-eighth powers as a fitting criterion yields almost a minimax fit. A true minimax fit would produce insignificantly smaller maximum differences, but larger average differences in many cases. The resulting coefficients can then be used to calculate the partition sums within the range of the fit.

The methods used to calculate the rotational partition sums, as well as the agreement between the direct sum and the analytical expression and the quality of the polynomial fits are described below. In all cases, the state dependent and state independent factors are accounted for as accurately as possible.

3. Calculation of partition sums

3.1. H_2O

Six isotopomers of water were considered in this study; $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, $HD^{18}O$. Q_{vib} was calculated using the vibrational energies of Ref. [19]. For the $HD^{17}O$ and $HD^{18}O$ isotopomers, the v_2 fundamental was estimated from HITRAN 2000 [20] v_1 and v_3 used the values for the $HD^{16}O$ species. For the direct sum of the $H_2{}^{16}O$ species, the rotational energy levels of Coudert [21] were used. For the lesser abundant isotopomers, rotational energy levels came from diagonalizing the Watson Hamiltonian [22], using the constants of Flaud and Camy-Peyret [23] for the $H_2{}^{17}O$, $H_2{}^{18}O$ and $HD^{16}O$ species and Toth [24] for the $HD^{17}O$ and $HD^{18}O$ species. For the $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$ and $HD^{16}O$ isotopomers, the direct sum converged over the entire area of interest and was therefore used for the rotational partition sum. For the $HD^{17}O$ and $HD^{18}O$ species, the direct sum only converged to about 75 K, so the analytical expression of Watson [25] was used. The difference between the direct sum and the analytical expression was about 5.6% at 75 K for both of these species. The absolute error of the polynomial fits never exceeds 0.15% for the rotational partition sums and 0.02% for the vibrational partition sums. Fig. 2 shows the percent error for the rotational partition function fit for the principal isotopomer. The state independent statistical factors are 1, 1, 6, 6, 36 and 6 for $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{17}O$ and $HD^{18}O$, respectively. The coupling of rotational motion with nuclear wavefunctions gives rise to state dependent degeneracies for all the nondeuterated species. These degeneracies are three-fold for the odd J levels and one-fold for the even J levels. No such degeneracies exist in the deuterated species.

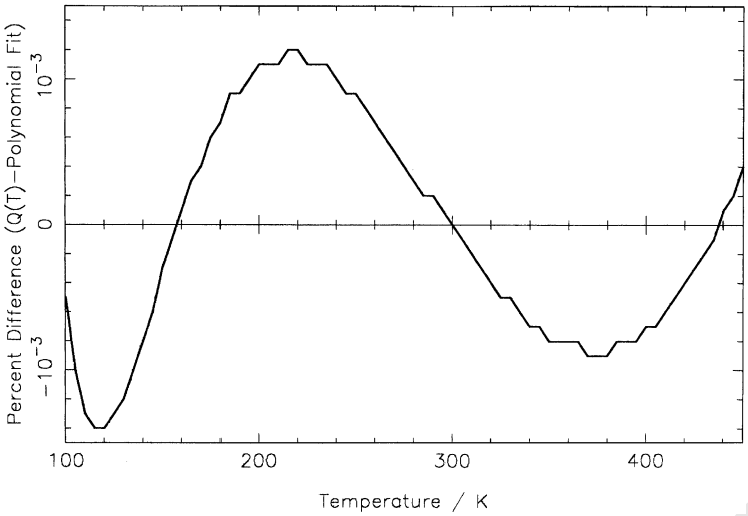

Fig. 2. Percent error, [$Q(T)$-polynomial fit]/$Q(T)$, versus temperature for $H_2{}^{16}O$.

The product of the values for $Q_{rot}(T)$ and $Q_{vib}(T)$ compare well with total internal partition sums found in the literature. For example, Ref. [26] gives the value for the total internal partition sum at 300 K as 178.12 for the $H_2{}^{16}O$ isotopomer, while this work gives the product of $Q_{rot}(T)$ and $Q_{vib}(T)$ as $179.35 \times 1.0004 = 179.44$. Likewise, Ref. [27] gives a value of 174.6 for the TIPS at 296 K for the $H_2{}^{16}O$ isotopomer, while this work gives $175.80 \times 1.0004 = 175.87$.

3.2. CO_2

Nine isotopomers of carbon dioxide were considered in this study; $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, $^{12}C^{16}O^{17}O$, $^{13}C^{16}O^{18}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{18}O_2$, $^{12}C^{17}O^{18}O$, and $^{12}C^{17}O_2$. The vibrational partition sums were calculated using the vibrational energies of Wattson [28] for the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$ species and Chedin and Teffo [29] for the remaining species. The rotational partition sums calculated by direct summation converged over the entire temperature of interest for all species of CO_2. For the $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{16}O^{18}O$ isotopomers, the constants of Rothman et al. [30] were used to generate energy levels. For the remaining species, the constants of Chedin and Teffo [29] were used. The absolute error of the polynomial fits never exceeded 0.15% for the vibrational partition sums and 0.02% for the rotational partition sums. The state independent degeneracy factors are 1, 2, 1, 6, 2, 12, 1, 6 and 1 for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{18}O$, $^{12}C^{16}O^{17}O$, $^{13}C^{16}O^{18}O$, $^{13}C^{16}O^{17}O$, $^{12}C^{18}O_2$, $^{12}C^{17}O^{18}O$, and $^{12}C^{17}O_2$, respectively. Additionally, the coupling of rotational motion with nuclear wavefunctions gives rise to state dependent degeneracies for the $^{2}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$ species. These degeneracies for the $^{2}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O_2$ species are 1 for the even states and 0 for the odd J states. The degeneracies are 21-fold on the odd levels and 15-fold on the even levels for the $^{12}C^{17}O_2$ species.

Our values of the total internal partition sum ($Q_{rot} \times Q_{vib}$) at 300 K are compared with those of Gray and Young [31] in Table 1. The agreement is very good noting that the values from Ref. [31] omit the state independent factor due to nuclear spins, resulting in the values being too small by

Table 1
Comparison of total internal partition sums from this work with those of Ref. [31] for isotopomers of CO_2 at 300 K

Isotopomer	Q_{tot} Ref. [31]	Q_{tot} this work	d_I
$^{16}O^{12}C^{16}O$	291.05	291.90	1
$^{16}O^{13}C^{16}O$	293.40	588.57	2
$^{16}O^{12}C^{18}O$	618.41	620.08	2
$^{16}O^{12}C^{17}O$	600.65	3614.30	6
$^{16}O^{13}C^{18}O$	623.58	1250.77	2

Table 2
Comparison of total internal partition sums for isotopomers of O_3 at 296 K with literature values

Isotopomer	Q_{tot} (296 K)[a]	Q_{tot} (296 K)[b]	Ref.
$^{16}O^{16}C^{16}O$	3483.71	3473	[38]
$^{16}O^{16}C^{18}O$	7465.67	7358	[34]
$^{16}O^{18}C^{16}O$	3647.08	3599	[33]
$^{16}O^{17}C^{16}O$	21404.96	3543	[35]
$^{17}O^{16}C^{17}O$	134794.40	7159	[35]

[a] This work.
[b] Other work.

a factor of 2 for the $^{16}O^{13}C^{16}O$ and $^{16}O^{13}C^{18}O$ isotopomers due to the omission of the $\frac{1}{2}$ spin of Carbon-13 and too small by a factor of 6 for the $^{16}O^{12}C^{17}O$ isotopomer due to the omission of the $\frac{5}{2}$ spin of Oxygen-17.

3.3. O_3

Eighteen isotopomers of ozone were considered in this study; $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{16}O^{17}O$, $^{16}O^{17}O^{16}O$, $^{18}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{16}O^{17}O^{18}O$, $^{16}O^{18}O^{17}O$, $^{17}O^{16}O^{18}O$, $^{17}O^{17}O^{16}O$, $^{17}O^{16}O^{17}O$, $^{18}O^{18}O^{18}O$, $^{18}O^{18}O^{17}O$, $^{18}O^{17}O^{18}O$, $^{17}O^{17}O^{18}O$, $^{17}O^{18}O^{17}O$, and $^{17}O^{17}O^{17}O$. The vibrational partition sums were calculated using the vibrational energies from Refs. [19,32–34] for the $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ isotopomers, the energies from Refs. [35,36] for the $^{16}O^{16}O^{17}O$ and $^{16}O^{17}O^{16}O$ isotopomers and the energies from Ref. [37] for all other isotopomers. Rotational energy levels for the direct sum were calculated by diagonalizing the Watson Hamiltonian constants of Flaud [38] for the $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ isotopomers. The direct sum rotational partition function converged throughout the temperature range of interest for the $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$ and $^{16}O^{18}O^{16}O$ species. For all other species, Watson's analytical expression [25] was used, using the Hamiltonian constants of Refs. [35,37,38]. Comparisons between the direct sum and the analytical expression were performed for the $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$ and species. The difference between the two methods never exceeded 0.42% within the temperature range of this study. The absolute error of the polynomial fits never exceeded 0.16% for the rotational partition sums or 0.14% for the vibrational partition sums. The state independent degeneracy factors are 1 for the $^{16}O^{16}O^{16}O$, $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{18}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{17}O^{16}O^{17}O$, $^{18}O^{18}O^{18}O$, and $^{17}O^{18}O^{17}O$ isotopomers, 6 for the $^{16}O^{16}O^{17}O$, $^{16}O^{17}O^{16}O$, $^{18}O^{18}O^{17}O$, $^{18}O^{17}O^{18}O$, $^{16}O^{17}O^{18}O$, $^{16}O^{18}O^{17}O$, $^{17}O^{16}O^{18}O$ and $^{17}O^{17}O^{17}O$ isotopomers and 36 for the $^{17}O^{17}O^{16}O$ and $^{17}O^{17}O^{18}O$ isotopomers. Additionally, the coupling of rotational motion with nuclear wavefunctions gives rise to state dependent degeneracies for certain species. For the $^{16}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{17}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{18}O^{18}O^{18}O$ and $^{18}O^{17}O^{18}O$ species, these degeneracies are 1-fold for the even J levels and 0 for the odd J levels. For the $^{17}O^{16}O^{17}O$, $^{17}O^{18}O^{17}O$ and $^{17}O^{17}O^{17}O$ isotopomers, these degeneracies are 21-fold for the odd J levels and 15-fold for the even J levels. The total internal partition sums from this work are compared with literature values for five isotopomers in Table 2. The data agree considering that the values from Ref. [35] do not include the state independent degeneracy factor which is 6 due to

the $\frac{5}{2}$ nuclear spin of oxygen-17 for the $^{16}O^{17}O^{16}O$ species and the state dependent weights for the $^{17}O^{16}O^{17}O$ isotopomer.

3.4. N_2O

Five isotopomers of N_2O were considered in this study; $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$, $^{14}N^{14}N^{17}O$. The vibrational partition sums were calculated using the vibrational energy levels of Ref. [19]. The rotational partition sum was calculated by direct sum for the principal species ($^{14}N^{14}N^{16}O$), using the energy levels calculated from the molecular constants of Toth [39]. For all other species, McDowell's analytical expression [7] was used, with the constants of [39]. The absolute error of the polynomial fits never exceeds 0.24% for the rotational partition sums and 0.15% for the vibrational partition sums. The state independent statistical factors are 9, 6, 6, 9 and 54 for the $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$ and $^{14}N^{14}N^{17}O$ isotopomers, respectively. The value obtained for the total internal partition function of the $^{14}N^{14}N^{16}O$ species at 300 K in this study was 5094.40. This compares favorably (0.3%) with the value 564.1 from Ref. [40] which omits the state independent factor of 9.

3.5. CO

Six isotopomers of CO were considered in this study: $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, $^{13}C^{18}O$ and $^{13}C^{17}O$. The vibrational partition sums were calculated using the vibrational energies of Guelachvili et al. [41]. For the $^{13}C^{17}O$ species, the vibrational energy of the principal species was used. For all species except $^{13}C^{17}O$, the rotational partition sum was calculated by a direct sum. The rotational energy levels were calculated using the Dunham constants of Ref. [41] with the constants of Tipping [42]. For the $^{13}C^{17}O$ species, the rotational partition sum was calculated using the analytical expression of McDowell [7] with the constants of Ref. [41]. The absolute error of the polynomial fits never exceeded 0.02% for the rotational partition sums or 0.05% for the vibrational partition sums. The state independent statistical factors are 1, 2, 1, 6, 2 and 12 for the $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$, $^{13}C^{18}O$ and $^{13}C^{17}O$ species, respectively. The value obtained for Q_{rot} in this study for the $^{12}C^{16}O$ isotopomer at 300 K is 108.88, which agrees with the value of 108.78 from Ref. [26].

3.6. CH_4

Three isotopomers of methane were considered in this study: $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$. The vibrational partition functions were calculated using the energies of Norton and Rinsland [43]. The rotational partition functions were calculated using McDowell's analytical expressions [8,9], with the constants of Tarrago et al. [44] for the $^{12}CH_4$ species, Dang-Nhu et al. [45] for the $^{13}CH_4$ species and Tarrago et al. [46] for the $^{12}CH_3D$ species. The absolute error of the polynomial fits never exceeded 0.16% for the rotational partition sums and 0.04% for the vibrational partition sums. The state independent statistical factors are 1, 2 and 3 for the $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ species, respectively.

The rotational partition sums at 300 K obtained from this study are 598.65, 1197.22, and 4841.36 for the $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ species, respectively. These values agree with those of Ref. [47], 598.639, 598.600, and 1613.817. Note that Ref. [47] omits the state independent factor of 2 (nuclear

spin factor of Carbon-13) for $^{13}CH_4$ and the state independent factor of 3 (nuclear spin factor of deuterium) for $^{12}CH_3D$.

3.7. NO

Three species of NO were considered in this study: $^{14}N^{16}O$, $^{14}N^{18}O$, $^{15}N^{16}O$. The vibrational partition sums were calculated using the vibrational energies of Amiot et al. [48]. The molecular constants of Amiot et al. [48] and Meerts [49] were used to calculate energy for the e and f levels of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. These energies were used to calculate direct sums for each of the species. The absolute error of the polynomial fits never exceeded 0.29% for the rotational partition sums or 0.02% for the vibrational partition sums. The state independent statistical factors are 3, 3 and 2 for the $^{14}N^{16}O$, $^{14}N^{18}O$, $^{15}N^{16}O$ isotopomers, respectively. The value obtained for the rotational partition function of $^{14}N^{16}O$, 1151.13, compares well with the value from the JPL Catalogue [26], 1159.46.

3.8. NO_2

One species of NO_2 was considered in this study: $^{14}N^{16}O_2$. The vibrational partition sum was calculated using the vibrational energies of Ref. [43]. The direct sum rotational partition function was evaluated using energy levels calculated by the formalism of Perrin et al. [50], including electron spin rotation and hyperfine Fermi-contact resonances. The direct sum converged to about 150 K. The analytical formula of Watson [25] was implemented, with an additional factor of 2 to account for the spin–rotation interaction. Between 10 and 150 K, the greatest difference between the analytical formula and the direct sum was 0.36%. The analytical formula was used throughout the temperature range. The absolute error of the polynomial fits never exceeded 0.16% for the rotational partition sums or 0.10% for the vibrational partition sums. The state independent statistical factor is equal to 3.

The total internal partition function at 296 K determined here is 13577.48, which is in excellent agreement with the value of Perrin et al., 13617.9.

3.9. OH

Three species of the hydroxyl radical were considered in this study: ^{16}OH, ^{18}OH and ^{16}OD. The vibrational partition sum was calculated using the vibrational fundamentals of Ref. [51]. The rotational partition functions were calculated by direct summation. The calculation of energy levels followed the development of Beaudet and Poynter [51], which includes the fine structure interaction and lambda doubling. The energies were calculated for the $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ and $^2\Sigma_{1/2}$ states. The absolute error of the polynomial fits never exceeded 0.27% for the rotational partition sums and 0.02% for the vibrational partition sums. The state independent statistical factors are 2, 2 and 3 for ^{16}OH, ^{18}OH and ^{16}OD, respectively. Q_{rot} for ^{16}OH at 296 K from this work, 81.51, can be compared with the value of Ref. [26], 81.49 and [52], 40.75, noting that Ref. [52], neglects hyperfine structure hence their value of Q_{rot} must be multiplied by 2.

Table 3
Polynomial constants for rotational partition sums

Species	a	b	c	d
$H_2{}^{16}O$	-4.9589	2.8147×10^{-1}	1.2848×10^{-3}	-5.8343×10^{-7}
$H_2{}^{18}O$	-4.9589	2.8147×10^{-1}	1.2848×10^{-3}	-5.8343×10^{-7}
$H_2{}^{17}O$	-2.9625×10^{1}	1.6822	7.6781×10^{-3}	-3.4865×10^{-6}
$HD^{16}O$	-2.5676×10^{1}	1.3745	6.3618×10^{-3}	-2.8991×10^{-6}
$HD^{18}O$	-2.6018×10^{1}	1.3915	6.4422×10^{-3}	-2.9359×10^{-6}
$HD^{17}O$	-1.5513×10^{2}	8.3008	3.8425×10^{-2}	-1.7511×10^{-5}
$^{16}O^{12}C^{16}O$	1.6708×10^{-1}	8.9065×10^{-1}	1.0000×10^{-5}	1.0901×10^{-12}
$^{16}O^{13}C^{16}O$	3.3417×10^{-1}	1.7812	1.9997×10^{-5}	1.1721×10^{-12}
$^{16}O^{12}C^{18}O$	3.3411×10^{-1}	1.8879	2.1192×10^{-5}	7.1375×10^{-12}
$^{16}O^{12}C^{17}O$	2.0048	1.1015×10^{1}	1.2444×10^{-4}	3.5048×10^{-11}
$^{16}O^{13}C^{18}O$	6.6820×10^{-1}	3.7759	4.2377×10^{-5}	1.2864×10^{-11}
$^{16}O^{13}C^{17}O$	4.0095	2.2031×10^{1}	2.4705×10^{-4}	6.8948×10^{-11}
$^{18}O^{12}C^{18}O$	1.6702×10^{-1}	1.0021	1.1248×10^{-5}	5.0684×10^{-12}
$^{17}O^{12}C^{18}O$	2.0043	1.1684×10^{1}	1.3096×10^{-4}	5.1947×10^{-11}
$^{17}O^{12}C^{17}O$	6.0138	3.4074×10^{1}	3.8251×10^{-4}	1.1807×10^{-10}
$^{16}O^{16}O^{16}O$	-1.0882×10^{2}	5.2319	2.4982×10^{-2}	-1.1471×10^{-5}
$^{16}O^{16}O^{18}O$	-2.3242×10^{2}	1.1171×10^{1}	5.3349×10^{-2}	-2.4498×10^{-5}
$^{16}O^{18}O^{16}O$	-1.1357×10^{2}	5.4601	2.6072×10^{-2}	-1.1972×10^{-5}
$^{16}O^{16}O^{17}O$	-1.3512×10^{3}	6.4955×10^{1}	3.1017×10^{-1}	-1.4243×10^{-4}
$^{16}O^{17}O^{16}O$	-6.6755×10^{2}	3.2096×10^{1}	1.5326×10^{-1}	-7.0373×10^{-5}
$^{18}O^{18}O^{16}O$	-2.4276×10^{2}	1.1668×10^{1}	5.5719×10^{-2}	-2.5586×10^{-5}
$^{18}O^{16}O^{18}O$	-1.2427×10^{2}	5.9713	2.8519×10^{-2}	-1.3096×10^{-5}
$^{16}O^{17}O^{18}O$	-1.4264×10^{3}	6.8559×10^{1}	3.2741×10^{-1}	-1.5034×10^{-4}
$^{16}O^{18}O^{17}O$	-1.4107×10^{3}	6.7815×10^{1}	3.2384×10^{-1}	-1.4870×10^{-4}
$^{17}O^{16}O^{18}O$	-1.4440×10^{3}	6.9393×10^{1}	3.3141×10^{-1}	-1.5218×10^{-4}
$^{17}O^{17}O^{16}O$	-8.2908×10^{3}	3.9855×10^{2}	1.9032	-8.7394×10^{-4}
$^{17}O^{16}O^{17}O$	-4.1960×10^{3}	2.0168×10^{2}	9.6312×10^{-1}	-4.4226×10^{-4}
$^{18}O^{18}O^{18}O$	-1.2988×10^{2}	6.2405	2.9805×10^{-2}	-1.3687×10^{-5}
$^{18}O^{18}O^{17}O$	-1.5077×10^{3}	7.2452×10^{1}	3.4602×10^{-1}	-1.5889×10^{-4}
$^{18}O^{17}O^{18}O$	-7.6294×10^{2}	3.6658×10^{1}	1.7508×10^{-1}	-8.0399×10^{-5}
$^{17}O^{17}O^{18}O$	-8.8635×10^{3}	4.2594×10^{2}	2.0342	-9.3412×10^{-4}
$^{17}O^{18}O^{17}O$	-4.3824×10^{3}	2.1063×10^{2}	1.0059	-4.6189×10^{-4}
$^{17}O^{17}O^{17}O$	-2.5751×10^{4}	1.2377×10^{3}	5.9105	-2.7141×10^{-3}
$^{14}N^{14}N^{16}O$	3.9847×10^{1}	8.1159	-2.1754×10^{-3}	2.2637×10^{-5}
$^{14}N^{15}N^{16}O$	2.0050	9.9541	1.1354×10^{-4}	4.8260×10^{-11}
$^{15}N^{14}N^{16}O$	2.0048	1.0301×10^{1}	1.1746×10^{-4}	5.0698×10^{-11}
$^{14}N^{14}N^{18}O$	3.0070	1.5815×10^{1}	1.8051×10^{-4}	1.2112×10^{-10}
$^{14}N^{14}N^{17}O$	1.8043×10^{1}	9.2299×10^{1}	1.0529×10^{-3}	5.1969×10^{-10}
$^{12}C^{16}O$	3.3737×10^{-1}	3.6156×10^{-1}	9.1570×10^{-7}	-7.5455×10^{-11}
$^{13}C^{16}O$	6.7434×10^{-1}	7.5639×10^{-1}	1.8989×10^{-6}	-1.4272×10^{-10}
$^{12}C^{18}O$	3.3716×10^{-1}	3.7964×10^{-1}	9.5167×10^{-7}	-6.8683×10^{-11}
$^{12}C^{17}O$	2.0234	2.2256	5.6019×10^{-6}	-4.3383×10^{-10}
$^{13}C^{18}O$	6.7393×10^{-1}	7.9605×10^{-1}	1.9825×10^{-6}	-1.3639×10^{-10}
$^{13}C^{17}O$	4.0454	4.6408	3.6191×10^{-3}	-1.0571×10^{-9}
$^{12}CH_4$	-1.8312×10^{1}	9.3325×10^{-1}	4.3490×10^{-3}	-2.0147×10^{-6}
$^{13}CH_4$	-3.6622×10^{1}	1.8664	8.6974×10^{-3}	-4.0291×10^{-6}
$12CH_3D$	-1.4977×10^{2}	7.5332	3.5251×10^{-2}	-1.6341×10^{-5}
$^{14}N^{16}O$	-3.5215×10^{1}	2.7383	5.6720×10^{-3}	-5.3671×10^{-6}
$^{15}N^{16}O$	-2.1715×10^{1}	1.8926	3.9182×10^{-3}	-3.7069×10^{-6}
$^{14}N^{18}O$	-3.7147×10^{1}	2.8869	5.9844×10^{-3}	-5.6624×10^{-6}
$^{14}N^{16}O_2$	-4.3332×10^{2}	2.0816×10^{1}	9.8876×10^{-2}	-4.6097×10^{-5}
^{16}OH	7.7363	1.7152×10^{-1}	3.4886×10^{-4}	-3.3504×10^{-7}
^{18}OH	7.6867	1.7321×10^{-1}	3.4997×10^{-4}	-3.3611×10^{-7}
^{16}OD	8.3072	4.5959×10^{-1}	9.9174×10^{-4}	-9.2504×10^{-7}

Table 4
Polynomial constants for vibrational partition sums

Species	a	b	c	d
$H_2{}^{16}O$	9.9842×10^{-1}	2.9713×10^{-5}	-1.7345×10^{-7}	3.2366×10^{-10}
$H_2{}^{18}O$	9.9841×10^{-1}	2.9843×10^{-5}	-1.7490×10^{-7}	3.2764×10^{-10}
$H_2{}^{17}O$	9.9841×10^{-1}	2.9836×10^{-5}	-1.7447×10^{-7}	3.2606×10^{-10}
$HD^{16}O$	9.9821×10^{-1}	3.6179×10^{-5}	-2.3230×10^{-7}	4.8406×10^{-10}
$HD^{18}O$	9.9821×10^{-1}	3.6264×10^{-5}	-2.3407×10^{-7}	4.9050×10^{-10}
$HD^{17}O$	9.9821×10^{-1}	3.6224×10^{-5}	-2.3319×10^{-7}	4.8735×10^{-10}
$^{16}O^{12}C^{16}O$	1.0384	-6.4414×10^{-4}	2.6438×10^{-6}	2.1323×10^{-10}
$^{16}O^{13}C^{16}O$	1.0408	-6.9739×10^{-4}	2.9539×10^{-6}	1.0076×10^{-11}
$^{16}O^{12}C^{18}O$	1.0389	-6.5708×10^{-4}	2.7190×10^{-6}	1.7163×10^{-10}
$^{16}O^{12}C^{17}O$	1.0385	-6.4989×10^{-4}	2.6847×10^{-6}	1.8280×10^{-10}
$^{16}O^{13}C^{18}O$	1.0414	-7.0990×10^{-4}	3.0216×10^{-6}	3.4863×10^{-12}
$^{16}O^{13}C^{17}O$	1.0410	-7.0345×10^{-4}	2.9864×10^{-6}	1.1948×10^{-11}
$^{18}O^{12}C^{18}O$	1.0397	-6.7365×10^{-4}	2.8109×10^{-6}	1.1336×10^{-10}
$^{17}O^{12}C^{18}O$	1.0393	-6.6478×10^{-4}	2.7615×10^{-6}	1.4840×10^{-10}
$^{17}O^{12}C^{17}O$	1.0390	-6.5785×10^{-4}	2.7232×10^{-6}	1.6976×10^{-10}
$^{16}O^{16}O^{16}O$	1.0198	-2.8986×10^{-4}	8.3514×10^{-7}	1.5130×10^{-9}
$^{16}O^{16}O^{18}O$	1.0213	-3.1931×10^{-4}	9.8160×10^{-7}	1.4407×10^{-9}
$^{16}O^{18}O^{16}O$	1.0215	-3.1701×10^{-4}	9.3195×10^{-7}	1.5468×10^{-9}
$^{16}O^{16}O^{17}O$	1.0208	-3.0728×10^{-4}	9.1502×10^{-7}	1.4740×10^{-9}
$^{16}O^{17}O^{16}O$	1.0209	-3.0652×10^{-4}	8.9097×10^{-7}	1.5275×10^{-9}
$^{18}O^{18}O^{16}O$	1.0233	-3.5115×10^{-4}	1.1010×10^{-6}	1.4519×10^{-9}
$^{18}O^{16}O^{18}O$	1.0231	-3.5270×10^{-4}	1.1405×10^{-6}	1.3660×10^{-9}
$^{16}O^{17}O^{18}O$	1.0224	-3.3660×10^{-4}	1.0462×10^{-6}	1.4394×10^{-9}
$^{16}O^{18}O^{17}O$	1.0226	-3.3677×10^{-4}	1.0246×10^{-6}	1.4950×10^{-9}
$^{17}O^{16}O^{18}O$	1.0227	-3.4052×10^{-4}	1.0617×10^{-6}	1.4198×10^{-9}
$^{17}O^{17}O^{16}O$	1.0215	-3.1895×10^{-4}	9.5379×10^{-7}	1.5073×10^{-9}
$^{17}O^{16}O^{17}O$	1.0213	-3.2016×10^{-4}	9.8582×10^{-7}	1.4387×10^{-9}
$^{18}O^{18}O^{18}O$	1.0247	-3.8169×10^{-4}	1.2752×10^{-6}	1.3361×10^{-9}
$^{18}O^{18}O^{17}O$	1.0240	-3.6730×10^{-4}	1.1967×10^{-6}	1.3866×10^{-9}
$^{18}O^{17}O^{18}O$	1.0240	-3.6855×10^{-4}	1.2140×10^{-6}	1.3467×10^{-9}
$^{17}O^{17}O^{18}O$	1.0234	-3.5416×10^{-4}	1.1240×10^{-6}	1.4176×10^{-9}
$^{17}O^{18}O^{17}O$	1.0235	-3.5268×10^{-4}	1.1053×10^{-6}	1.4557×10^{-9}
$^{17}O^{17}O^{17}O$	1.0226	-3.3759×10^{-4}	1.0450×10^{-6}	1.4567×10^{-9}
$^{14}N^{14}N^{16}O$	1.0493	-8.8790×10^{-4}	4.0828×10^{-6}	-6.6527×10^{-10}
$^{14}N^{15}N^{16}O$	1.0513	-9.3420×10^{-4}	4.3832×10^{-6}	-8.6356×10^{-10}
$^{15}N^{14}N^{16}O$	1.0494	-8.9574×10^{-4}	4.1556×10^{-6}	-6.9976×10^{-10}
$^{14}N^{14}N^{18}O$	1.0487	-8.8676×10^{-4}	4.1275×10^{-6}	-6.4301×10^{-10}
$^{14}N^{14}N^{17}O$	1.0496	-8.9456×10^{-4}	4.1231×10^{-6}	-6.6366×10^{-10}
$^{12}C^{16}O$	9.9944×10^{-1}	9.6257×10^{-6}	-5.0262×10^{-8}	8.1728×10^{-11}
$^{13}C^{16}O$	9.9936×10^{-1}	1.1045×10^{-5}	-5.7272×10^{-8}	9.3156×10^{-11}
$^{12}C^{18}O$	9.9939×10^{-1}	1.0836×10^{-5}	-5.7613×10^{-8}	9.4711×10^{-11}
$^{12}C^{17}O$	9.9940×10^{-1}	1.0383×10^{-5}	-5.3728×10^{-8}	8.7169×10^{-11}
$^{13}C^{18}O$	9.9930×10^{-1}	1.2213×10^{-5}	-6.4899×10^{-8}	1.0734×10^{-10}
$^{13}C^{17}O$	9.9944×10^{-1}	9.6257×10^{-6}	-5.0262×10^{-8}	8.1728×10^{-11}
$^{12}CH_4$	9.9109×10^{-1}	1.8229×10^{-4}	-1.1900×10^{-6}	2.5319×10^{-9}
$^{13}CH_4$	9.9109×10^{-1}	1.8229×10^{-4}	-1.1900×10^{-6}	2.5319×10^{-9}
$12CH_3D$	9.9109×10^{-1}	1.8229×10^{-4}	-1.1900×10^{-6}	2.5319×10^{-9}
$^{14}N^{16}O$	9.9899×10^{-1}	1.7970×10^{-5}	-9.7249×10^{-8}	1.6549×10^{-10}
$^{15}N^{16}O$	9.9893×10^{-1}	1.9170×10^{-5}	-1.0469×10^{-7}	1.7976×10^{-10}
$^{14}N^{18}O$	9.9891×10^{-1}	1.9684×10^{-5}	-1.0817×10^{-7}	1.8708×10^{-10}
$^{14}N^{16}O_2$	1.0129	-1.9035×10^{-4}	5.5618×10^{-7}	9.1873×10^{-10}
^{16}OH	9.9999×10^{-1}	2.0075×10^{-7}	-9.3665×10^{-10}	1.3295×10^{-12}
^{18}OH	9.9984×10^{-1}	2.6827×10^{-6}	-1.3312×10^{-8}	2.0502×10^{-11}
^{16}OD	9.9999×10^{-1}	2.0075×10^{-7}	-9.3665×10^{-10}	1.3295×10^{-12}

4. Summary

Rotational and vibrational partition sums were calculated as a function of temperature in the range 100–450 K for many isotopomers of molecules of interest in studying the terrestrial atmosphere: H_2O, CO_2, O_3, N_2O, CO, CH_4, NO, NO_2 and OH. The rotational partition sums calculated by analytical formulae were compared with those calculated by direct summation to ensure that the quantum effects were negligible for the temperatures of interest. The partition sums were fit to a third order in temperature polynomial for rapid and accurate recall. The coefficients for the species studied are listed in Table 3 for the rotational partition sums and in Table 4 for the vibrational partition sums. FORTRAN code to calculate the partition sums is available from one of the authors (Robert_Gamache@uml.edu).

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