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ABSTRACT

Based on the direct summation technique, improved ideal-gas partition functions and related thermochemical quantities are reported for the parent isotopologues of molecular oxygen and water, $^{16}O_2$ and $H_2{}^{16}O$, respectively. The new results update those of two previous publications reported in this journal [Furtenbacher *et al.*, J. Phys. Chem. Ref. Data **45**, 043104 (2016) and Furtenbacher *et al.*, J. Phys. Chem. Ref. Data **48**, 023101 (2019)]. The improved thermochemical functions, tabulated at 1 K intervals between 0 and 5000 K in the supplementary material to this paper, use (a) the exact values of the fundamental physical constants fixed in the 2019 redefinition of the International System of Units, (b) an improved set of empirical energy levels for $H_2{}^{16}O$, with much improved uncertainties at low rovibrational excitations, (c) different approaches to the uncertainty budget, including correcting an error in previous uncertainty calculations for $^{16}O_2$, and (d) a small correction to the ideal-gas thermochemical functions of $^{16}O_2$, making them applicable for oxygen of natural isotopic composition, which is needed for the development of practical thermodynamic models.

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1. Introduction

It is possible to bridge high-resolution spectroscopy,[1] famous for transition and energy level values with extremely high accuracy, and thermochemistry,[2–5] where the relevant quantities, even within the ideal-gas approximation, historically have had large uncertainties. If a reasonably complete set of rovibronic energy levels is available, preferably from high-accuracy spectroscopic measurements, which, in the fourth age of quantum chemistry,[6] can be supplemented by levels from first-principles computations, they can be used to compute the temperature-dependent ideal-gas internal partition function, $Q_{\text{int}}(T)$, and all related thermochemical functions, such as enthalpy, entropy, and heat capacity,[2] via the direct summation technique as

$$Q_{\text{int}}(T) = \sum_i g_i(2J_i + 1)\exp\left(\frac{-c_2 E_i}{T}\right), \tag{1}$$

where $c_2 = hc/k$ is the second radiation constant, h is the Planck constant, c is the speed of light in vacuum, k is the Boltzmann constant, E_i is the energy of the ith quantum state (which we express in wavenumbers, cm^{-1}), J_i is the rotational quantum number of state i, g_i is a nuclear spin degeneracy factor,[7–9] and T is the absolute temperature.

Ideal-gas thermochemistry can be derived from $Q_{\text{int}}(T)$ and its first two moments, Q'_{int} and Q''_{int}, as described, for example, in Ref. 7 and references therein. The ideal-gas enthalpy, $H(T)$, the entropy, $S(T,p)$ (p is the pressure), and the isobaric heat capacity, $C_p(T)$, are given by

$$H(T) = RT\frac{Q'_{\text{int}}}{Q_{\text{int}}} + \frac{5}{2}RT, \tag{2}$$

$$S(T,p) = R\frac{Q'_{\text{int}}}{Q_{\text{int}}} + R\ln Q_{\text{int}} + \frac{5}{2}R + R\ln\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3 p}, \tag{3}$$

and

$$C_p(T) = R\left[\frac{Q''_{\text{int}}}{Q_{\text{int}}} - \left(\frac{Q'_{\text{int}}}{Q_{\text{int}}}\right)^2\right] + \frac{5}{2}R, \tag{4}$$

where m is the mass of the molecule and R is the molar gas constant. In Eq. (3) for the entropy, we use the conventional standard-state pressure of 1 bar (0.1 MPa).

For a molecule that is free to rotate in space, the internal partition function is defined by Eq. (1), while its first two moments, needed in Eqs. (2)–(4), are

$$Q'_{\text{int}} = \sum_i g_i(2J_i + 1)\left(\frac{c_2 E_i}{T}\right)\exp\left(\frac{-c_2 E_i}{T}\right), \tag{5}$$

and

$$Q''_{\text{int}} = \sum_i g_i(2J_i + 1)\left(\frac{c_2 E_i}{T}\right)^2\exp\left(\frac{-c_2 E_i}{T}\right). \tag{6}$$

The accuracy of $Q_{\text{int}}(T)$ determined through Eq. (1) is affected by the accuracy and the completeness of the set of rovibronic energy levels E_i and the accuracy of c_2 and that of the underlying physical constants. The higher the accuracy of the rovibronic energies used in the direct summation, the more accurate the calculated partition function and all the related thermochemical functions are. Assuming that high-resolution spectroscopy provides accurate estimates for all the energy levels affecting $Q_{\text{int}}(T)$, which may hold at low temperatures, the accuracy of the partition function is determined by the uncertainty of the energy levels themselves. At higher temperatures, it is the completeness of the energy-level dataset that determines the true accuracy of the thermochemical functions obtained, as the density of states increases extremely fast with increasing temperature. In the expressions for H, S, and C_p, quotients of Q, Q', and Q'' appear, adding to the challenge of calculating a reasonable uncertainty budget.

Several years ago, two of the present authors, with others, reported in this journal highly accurate ideal-gas partition functions and thermochemical properties for the most abundant isotopologues of molecular oxygen, $^{16}O_2$, and water, $H_2{}^{16}O$, in Refs. 7 and 9, respectively. These partition functions were based on a thorough examination of the spectroscopic information available at the time. The partition function and the thermochemical properties, along with their uncertainties, were tabulated at 1 K intervals for temperatures up to 5000 K for the $^{16}O_2$ and $H_2{}^{16}O$ molecules.

Recently, we have recognized four opportunities to improve the thermochemical functions published for $^{16}O_2$ and $H_2{}^{16}O$. The first concerns the values of the physical constants. In Refs. 7 and 9, Eqs. (1)–(6) were evaluated with values of the fundamental physical constants given in the 2016 CODATA adjustment.[10] These 2016 recommendations determined not only the second radiation constant c_2 in the partition function and its moments but also the values of R, k, and h in Eqs. (2)–(4). Since the 2019 redefinition of the International System of Units (SI), physical units are based on fixed values of several fundamental constants,[11,12] which means that several of these constants now have exact values that differ slightly from the 2016 estimates (see Table 1). Although these changes are small, the high accuracy of the energy levels utilized in the determination of the ideal-gas partition functions and the related thermochemical quantities means that these small changes have an effect that is comparable to or greater than the quantity's stated uncertainties at some temperatures.

TABLE 1. Physical constants employed in our previous studies and in this work

Name	Old value used in Refs. 7 and 9	References	New value used in this work	References
Speed of light in vacuum, c	299 792 458 m s^{-1} (exact)	10	299 792 458 m s^{-1} (exact)	12
Planck constant, h	$6.626\,070\,040(81) \times 10^{-34}$ J s	10	$6.626\,070\,15 \times 10^{-34}$ J Hz^{-1} (exact)	12
Avogadro constant, N_A	$6.022\,140\,857(74) \times 10^{23}$ mol^{-1}	10	$6.022\,140\,76 \times 10^{23}$ mol^{-1} (exact)	12
Boltzmann constant, k	$1.380\,648\,52(79) \times 10^{-23}$ J K^{-1}	10	$1.380\,649 \times 10^{-23}$ J K^{-1} (exact)	12
Second radiation constant, c_2	1.438 777 36(83) cm K	10	$hc/k = 1.438\,776\,877$ cm K (exact)	12
Molar gas constant, R	8.314 459 8(48) J mol^{-1} K^{-1}	10	$N_A k = 8.314\,462\,618$ J mol^{-1} K^{-1} (exact)	12

The second improvement is related to the actual values of the energy levels. Note first that in this study the number of rovibrational energy levels used to determine the thermochemical functions is 810 270 for the $H_2{}^{16}O$ molecule, which is almost identical to the number of energy levels, 810 252, used in our previous study.[7] In the case of the ${}^{16}O_2$ molecule, the number of energy levels, 15 946, and the energy values themselves are unchanged from the previous publication,[9] and the set is considered to be complete up to the highest temperatures. For $H_2{}^{16}O$, the empirical rovibrational energy levels used in this study were taken, when available, from Ref. 7, corresponding to the IUPAC-Part III database.[13] Recently, based on measurements accurate to the kilohertz level,[14–17] improved empirical energy levels, with significantly lower uncertainties than before, were reported as part of the W2024 investigation,[18] suggesting that a reevaluation of the ideal-gas thermochemical functions of $H_2{}^{16}O$ is timely.

The third area for improvement concerns the estimation of uncertainty for the thermochemical functions. The most serious issue is that, due to a programming error, some of the uncertainties given for $C_p(T)$ of ${}^{16}O_2$ in Ref. 9 were incorrect (the uncertainties given in Ref. 7 for $H_2{}^{16}O$ are correct). A symptom of the problem is that the uncertainty in $C_p(T)$ for ${}^{16}O_2$ unphysically went to zero at a temperature near 3500 K. In this work, we correctly apply the "two extrema" method of perturbing all energy levels up or down by their uncertainty to estimate the uncertainty of the calculated functions. Also, the rigor of the two-extrema method can be questioned, since in some sense it describes a worst-case scenario where all energy levels are perturbed in the same direction. In this work, we supplement this technique with a method based on propagation of uncertainty as a function of multiple variables. Comparison of these results to those of the simpler two-extrema method will give us some idea of the degree to which the simpler approach is physically reasonable.

Finally, while this is not a deficiency of the earlier studies, we recognize that practical models, for example a reference equation of state for oxygen as an industrial fluid or as a component of air, require thermodynamic functions corresponding to the species' real isotopic composition, not only those of the most common isotopologue. Thus, in this study, a small correction will be applied to the ideal-gas thermochemical functions of ${}^{16}O_2$ to make them applicable to naturally occurring oxygen.

2. Methods and Data Treatment

The most important sources of uncertainty in ideal-gas thermochemical functions calculated by the direct summation technique of Eqs. (1)–(6) are the uncertainty about the number of bound energy levels (that is, uncertainty about the energy level density), the uncertainty of the energy levels themselves, the question of how unbound states[5,19,20] and states associated with excited electronic states are treated[5,19] when they tend to make a difference, and the uncertainty of the values of the physical constants. With the recent changes in the SI and the fundamental constants,[11,12] the fourth type of uncertainty has now been eliminated.

2.1. Revised physical constants

In our previous studies,[7,9] the physical constants given in the second column of Table 1 were used, as those were the best estimates[10] at the time of these publications. In 2019, the "new SI" was officially adopted, in which the values of several of the base units of the SI were fixed to values determined by state-of-the-art experimental work.[11] Relevant to our study, the SI redefinition included fixing values of the Planck constant, the Boltzmann constant, and the Avogadro constant, which are now defined, as the speed of light has been for decades, with no uncertainty. The products and quotients of these quantities, such as the molar gas constant R and the second radiation constant c_2, are also now exact. These new values, as summarized in the latest CODATA evaluation,[12] are given in the fourth column of Table 1. In Sec. 3.1, we will examine the effect of these small changes in physical constants on the computed thermochemical quantities.

2.2. Revised empirical rovibrational energy level set for $H_2{}^{16}O$

In our previous study on the thermochemical functions of $H_2{}^{16}O$,[7] a hybrid set of energy levels was used to calculate the partition function. This hybrid dataset was constructed using the so-called IUPAC-Part III empirical energy level set,[13] augmented with the so-called PoKaZaTeL first-principles energy levels[21] to ensure completeness.

The present study is also based on the PoKaZaTeL energy levels.[21] As in Ref. 7, we used expanded uncertainties of 0.2 cm^{-1} for the PoKaZaTeL energy levels up to 20 000 cm^{-1}, while above this energy the value of 0.5 cm^{-1} was used. In contrast to Ref. 7, in this study the PoKaZaTeL values are replaced, when available, not with the IUPAC-Part III levels but with the empirical energy levels of the W2024 set reported in Ref. 18. For obvious reasons, we will refer to this hybrid set of rovibrational energy levels as PW2024. Although the total number of empirical energy levels available in the PW2024 dataset did not change much compared to the dataset employed in Ref. 7, the uncertainties of many levels improved significantly, due to sophisticated studies based on comb-assisted nonlinear spectroscopy.[14–16]

2.3. Revised uncertainty estimation

Here we briefly summarize the methods used in this study to determine the uncertainties of the thermochemical quantities. According to Eqs. (1)–(6), the value of a thermochemical function $F(T)$ depends on the energy levels E_i. We want to estimate the uncertainty of F when each of the energy levels has its own uncertainty. The "uncertainties" in the energy levels of our input datasets are interpreted as expanded uncertainties with coverage factor $k = 2$, roughly corresponding to a 95% confidence interval, so we write them as $U(E_i)$. Throughout this paper, we will therefore work with expanded ($k = 2$) uncertainties for computed functions F, written as $U(F)$.

In our previous studies,[7–9] we used the "two extrema" technique, usually called the upper-and-lower-bound (ULB) method, to estimate the expanded uncertainties of the thermochemical functions. In the ULB method, (a) the values of the energy levels are increased and then decreased according to the stated expanded uncertainties of the levels, (b) the thermochemical function is calculated according to the two extreme sets of energy levels, and (c) the difference in the values corresponding to these two extrema (divided by two) provides a reasonable estimate of the expanded uncertainty. A notable characteristic of the ULB method is that it tends to overestimate the uncertainty, as it assumes that the uncertainty of the data used is always as large as stated by the uncertainty. In the real world, uncertainties are not always extreme, and there is only partial correlation among the uncertainties; therefore, describing the propagation of uncertainties as an extreme is probably overly conservative. In this study, we also use the laws of propagation of uncertainty to compute the uncertainties of the thermochemical quantities by their sensitivity to variations of the individual energy levels in the partition function. This allows us to check the reasonableness of the ULB uncertainty estimates. Next, the formulas applicable for the alternative, propagation-based estimation of the uncertainties are described.

In general, if $x_1, x_2, \ldots, x_N$ are measured (or determined) values with expanded uncertainties $U(x_1)$, $U(x_2)$, …, $U(x_N)$, then the square of the expanded uncertainty of a function $f(x_1, x_2, \ldots, x_N)$ is

$$U^2(f) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\cdot U(x_i)\right)^2 + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{\partial f}{\partial x_i}\cdot\frac{\partial f}{\partial x_j}\cdot U(x_i, x_j), \tag{7}$$

where $\frac{\partial f}{\partial x_i}$ is often referred to as the sensitivity coefficient, and $U(x_i, x_j)$ is the expanded covariance associated with x_i and x_j, which can be calculated as $U(x_i, x_j) = r(x_i, x_j)\cdot U(x_i)\cdot U(x_j)$, where $r(x_i, x_j)$ is the correlation coefficient.

Equation (7) is used to calculate the expanded uncertainties of the partition function and its first two moments, where f stands for either Q_{int}, Q'_{int}, or Q''_{int}. To calculate these uncertainties, we need the derivatives of Q_{int}, Q'_{int}, and Q''_{int} with respect to energy level E_i. They are

$$\frac{\partial Q_{\mathrm{int}}}{\partial E_i} = \frac{-c_2 g_i(2J_i+1)}{T}\exp\left(\frac{-c_2E_i}{T}\right), \tag{8}$$

$$\frac{\partial Q'_{\mathrm{int}}}{\partial E_i} = \frac{c_2 g_i(2J_i+1)(T-c_2E_i)}{T^2}\exp\left(\frac{-c_2E_i}{T}\right), \tag{9}$$

and

$$\frac{\partial Q''_{\mathrm{int}}}{\partial E_i} = \frac{c_2^2 g_i E_i(2J_i+1)(2T-c_2E_i)}{T^3}\exp\left(\frac{-c_2E_i}{T}\right). \tag{10}$$

To determine the uncertainty of the heat capacity, we also need the derivative of C_p with respect to E_i:

$$\frac{\partial C_p}{\partial E_i} = R\left(\frac{\frac{\partial Q''_{\mathrm{int}}}{\partial E_i}Q - \frac{\partial Q_{\mathrm{int}}}{\partial E_i}Q''}{Q^2} - 2\frac{Q'}{Q}\,\frac{\frac{\partial Q'_{\mathrm{int}}}{\partial E_i}Q - \frac{\partial Q_{\mathrm{int}}}{\partial E_i}Q'}{Q^2}\right). \tag{11}$$

Using Eqs. (8)–(11), $U_E(F)$ values can be calculated, where subscript E emphasizes that we used the uncertainty of the energy levels for the determination of the uncertainty of F.

It is impossible to determine the covariances for each combination of E_i and E_j for use in Eq. (7). Energy levels that are closely connected in the spectroscopic network of the molecule will likely be strongly correlated, while those only distantly connected will probably be nearly independent. Therefore, in this study, we test the approximations $r(x_i, x_j) = 0.0, 0.5$, and 1.0 for all level pairs to gauge the effect of correlation.

Before continuing, we point out three characteristics of Eqs. (8)–(10), as they help to understand the uncertainties derived in this study. First, in all derivatives reciprocals of the temperature, T^{-1}, T^{-2}, and T^{-3}, appear in Eqs. (8)–(10), respectively. This leads to (a) the possibility of a decrease in the uncertainties of Q_{int}, Q'_{int}, and Q''_{int} as the temperature increases, which is especially pronounced at the lowest temperatures, and also dependent upon the spacing of the rotational levels, and (b) obtaining significantly lower uncertainties for the thermochemical quantities than one would expect based simply on the uncertainties of the energy levels. Second, for the *ortho*/*para* nuclear-spin isomer pair of $H_2{}^{16}O$ the g_i factor is 3/1; thus, at the lowest temperatures the contribution of the *ortho* levels to the uncertainties is amplified compared to those of the *para* levels. Finally, assuming that all the energy levels are known with the same accuracy, the structure of Eqs. (8)–(10) means that above a certain temperature the uncertainties will not change significantly (of course, in reality the uncertainties will continue to increase due to the usual increase in the uncertainties of higher-energy levels).

Using these estimation techniques, we can compare, for example, $U_{\mathrm{ULB}}(C_p)$ and $U_E(C_p)$ (with $r = 0.0, 0.5$, and 1.0) to see to what extent the ULB uncertainties reported in our previous studies[7,9] overestimated the uncertainties obtainable with the error propagation technique.

2.4. Revised treatment for O_2

The thermochemistry of pure $^{16}O_2$ is of limited value for practical calculations (for example, of the properties of air), because real oxygen contains a non-negligible fraction of ^{17}O and ^{18}O atoms. The different nuclear masses of the isotopes cause the energy levels, and therefore the partition functions, to be slightly different for O_2 isotopologues such as $^{16}O^{17}O$ and $^{16}O^{18}O$. In principle, one might compute separate partition functions for all the minor species (perhaps based on energy level lists where the accurate empirical data are supplemented by computed ones) and add their thermodynamic functions in appropriate proportions. This would be a large undertaking, as seen in the significant effort required for heavy water;[8] but, since this is only a small adjustment, on the order of 0.002% for C_p, one can take a much simpler approach.

In 1948, Woolley[22] used simple spectroscopic information to obtain ideal-gas thermochemical functions for $^{16}O_2$ and to derive temperature-dependent corrections to those values to adjust them to the natural isotopic composition. These were presented in a table of increments of C_p. We therefore apply Woolley's small adjustments, interpolating linearly between temperatures in his table. Woolley did not make any claims about uncertainty; we conservatively assign to his corrections a relative expanded $(k = 2)$ uncertainty of 30%.

Based on this adjustment of C_p, we can derive adjustments to H and S by integrating C_p and C_p/T, respectively, from zero temperature to the temperature of interest. We apply the same 30% relative uncertainty to these adjustments of H and S that we used for C_p; this conservatively assumes that there is no cancellation of errors in C_p along the temperature range. For the entropy, there is an additional adjustment due to the presence of molecules of greater mass in the translational term [the last term in Eq. (3)]. This provides a constant increment for S of ~0.0034 J mol^{-1} K^{-1}, which is significant when compared to our uncertainties below roughly 1500 K.

3. Results and Discussion

3.1. Effect of revised physical constants

We computed the thermochemical functions with both the old and the new set of physical constants for the $H_2{}^{16}O$ and $^{16}O_2$ molecules. To isolate the effect that the revision of the physical constants has on the thermochemical functions from other issues dealt with in this paper, here we are using the energy level sets of the original publications, that is, Ref. 7 for $H_2{}^{16}O$ and Ref. 9 for $^{16}O_2$.

Figures 1 and 2 show the differences of Q, Q', and Q'' (solid lines), and their calculated ULB expanded uncertainties (dashed lines) in the case of the $H_2{}^{16}O$ and $^{16}O_2$ molecules, respectively. In these figures, the differences are calculated as $\Delta F = F(\text{with new constants}) - F(\text{with old constants})$, where $F = Q$, Q', and Q''. It is important to note that the contribution of the unbound states was not used to determine the uncertainties for $H_2{}^{16}O$ (note also that this contribution was not considered for $^{16}O_2$ in Ref. 9), as it is only an additive term[7] that does not depend on the value of c_2.

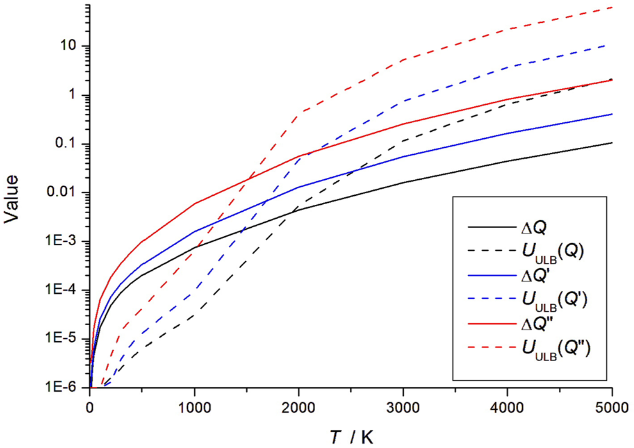

FIG. 1. Changes of Q_{int} (black line), Q'_{int} (blue line), and Q''_{int} (red line) of the $H_2{}^{16}O$ molecule due to the use of improved physical constants. The dashed lines show the ULB expanded uncertainties (U_{ULB}) computed in this work using the energy dataset of Ref. 7.

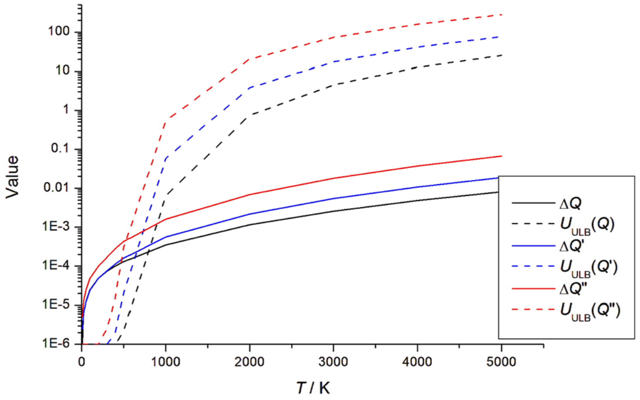

FIG. 2. Changes of Q_{int} (black line), Q'_{int} (blue line), and Q''_{int} (red line) of the $^{16}O_2$ molecule due to the use of improved physical constants. The dashed lines show the ULB expanded uncertainties (U_{ULB}) computed in this work using the energy dataset of Ref. 9.

As seen in Figs. 1 and 2, the use of the revised SI constants increases the values of the partition functions and their first two moments. To determine the uncertainties associated with Q, Q', and Q'', we used the revised constants and the method of "two extrema," just like in the original publications.[7,9] Both figures show that the expanded uncertainties and the difference curves intersect at relatively high temperatures. In the case of $H_2{}^{16}O$, the intersection points are all above 1500 K (they are 1930, 1685, and 1520 K for Q, Q', and Q'', respectively). This means that below these intersection points, the changes due to the revised physical constants are larger than the expanded uncertainties computed. This is a somewhat surprising but important result of the present study.

Figure 3 shows the differences in C_p for the $H_2{}^{16}O$ and $^{16}O_2$ molecules. Once again, the expanded uncertainties and the difference curves intersect at relatively high temperatures, which means that below these intersection points, which are 1120 K for $H_2{}^{16}O$ and 465 K for $^{16}O_2$, the changes due to the use of the revised set of physical constants are larger than the expanded uncertainties computed in this work. In general, if extreme accuracy is of concern, it seems to be worth recalculating the thermochemical functions of molecules determined through the direct summation approach, especially around room temperature, using the revised set of physical constants.

3.2. $H_2{}^{16}O$: Effect of improved energy levels

For $H_2{}^{16}O$, based on the hybrid PW2024 energy-level dataset, we can investigate the effect of including a large number of low-energy bound-state levels with significantly improved uncertainties in the direct sum of Eq. (1). The lesson from Sec. 3.1 is that using

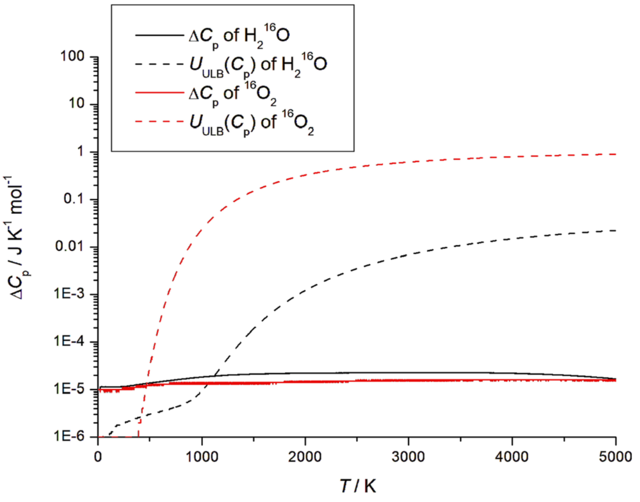

FIG. 3. Changes of C_p due to the use of improved physical constants for the $H_2{}^{16}O$ (black line) and $^{16}O_2$ (red line) molecules. The dashed lines show the ULB expanded uncertainties (U_{ULB}) computed in this work.

the revised value of the second radiation constant c_2 significantly changes both the thermochemical quantities and their uncertainties; thus, we cannot directly compare the thermochemical quantities calculated with PW2024 energies with those reported in Ref. 7. Let $U_{Ref}(F)$ and $U_{PW2024}(F)$ denote expanded uncertainties of quantity F calculated with the revised value of c_2, using the energy levels of either Ref. 7 or the PW20024 set.

Figure 4 shows the values of $U_{Ref}(Q)$ and $U_{PW2024}(Q)$ in the 0–2500 K temperature range, along with the corresponding expanded uncertainties of C_p. As seen there, the expanded uncertainties of the partition function (Q) at lower temperatures calculated with the PW2024 energy uncertainties can be up to two orders of magnitude smaller than the values calculated with the energy uncertainties of Ref. 7. This significant reduction in uncertainty is due to the large number of ultra-precise energy levels present in the W2024, and thus the PW2024, dataset. In the case of C_p, $U_{PW2024}(C_p)$ is smaller than $U_{Ref}(C_p)$ at the lower temperatures, but the difference is not as significant as for the partition function. Plots similar to those of Fig. 4 for other thermochemical functions would show similar features.

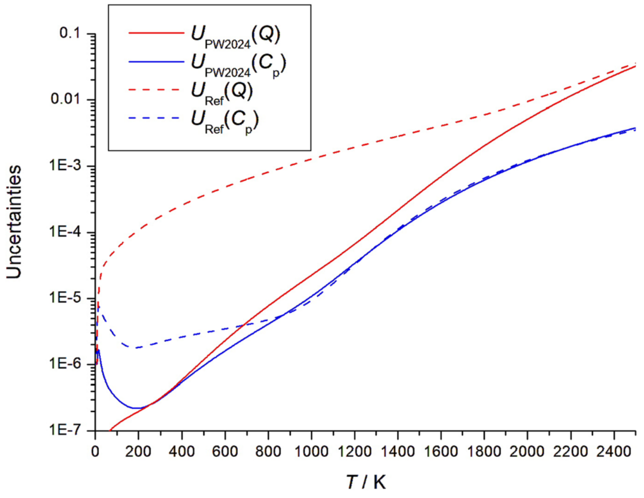

FIG. 4. Expanded ($k = 2$) uncertainties of Q and C_p using the energy dataset of Ref. 7 (U_{Ref}, dashed lines) and PW2024 (U_{PW2024}, solid lines) for the $H_2{}^{16}O$ molecule in the 0–2500 K temperature range. For Q the uncertainty is dimensionless, while for C_p it is plotted in units of J K^{-1} mol^{-1}.

The general conclusion is that around room temperature the current uncertainties calculated using the empirical W2024 energies are up to an order of magnitude smaller than those reported previously.[7] Thus, all improvements in the accuracy of the empirical rovibrational energy levels are useful and improve accuracy if the thermochemical functions are computed through the technique of direct summation.

3.3. Effect of uncertainty estimation methods

3.3.1. $H_2{}^{16}O$

In Sec. 2.3, two methods were described for determining the uncertainties of thermochemical functions: the upper-and-lower-bound method (yielding U_{ULB}) and the law of propagation of uncertainty using the uncertainties of the energy levels (yielding U_E). Figure 5 shows the expanded uncertainties of the heat capacity calculated for the $H_2{}^{16}O$ molecule using the PW2024 energy dataset (without the uncertainty contribution from unbound states, which was derived in Ref. 7). Lessons to be learned from Fig. 5 are as follows: (a) as expected, the ULB method produces the largest uncertainties; (b) at low temperatures, that is $T < 1000$ K, all of the methods, except the one with $r = 0$, provide very small uncertainties of similar magnitude; (c) there is a pronounced dip in the uncertainties at around 200 K, which is due to the form of Eqs. (8)–(10); (d) at high temperatures, that is $T > 3000$ K, although the uncertainties calculated by the different methods differ, the results (with the exception of the $r = 0$ case) agree within a factor of two; and (e) a smaller r value, corresponding to less assumed correlation, generally yields lower uncertainty estimates. As noted above, the expanded uncertainties of Fig. 5 do not contain the contribution of the unbound states. Above 3000 K, this contribution is much larger than the uncertainty contribution from the energy levels; thus, a choice between the methods shown in Fig. 5 becomes irrelevant.

To decide about the best uncertainty estimation method, one needs to consider that (a) the uncertainties of empirical energy levels are often estimates that may only be good to within a factor of two (or even ten, depending on the trust one has in the measured transitions that determine them), and thus the differences between the top three curves in Fig. 5 are of marginal significance, (b) the level of correlation between energy levels cannot in general be quantitatively estimated, (c) the ULB method is simpler and requires much less computational effort, and (d) we desire a conservative estimate. Thus, we choose to use U_{ULB} for the expanded uncertainties we report in the supplementary material.

The partition function and its first two moments, as well as the $H(T)$, $S(T)$, and $C_p(T)$ thermochemical functions of the $H_2{}^{16}O$

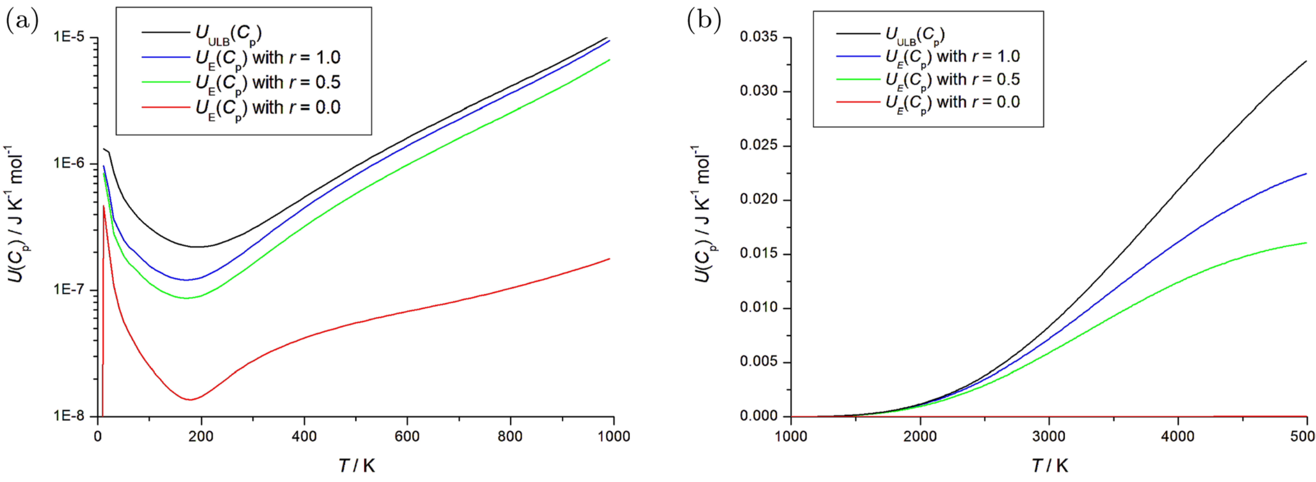

FIG. 5. Expanded (k = 2) uncertainties of the heat capacity $C_p(T)$ calculated for the $H_2{}^{16}O$ molecule in this study (based on the PW2024 energy dataset and neglecting the contribution of the unbound states). To improve clarity, the plots are presented in two different temperature intervals: (a) 0–1000 K and (b) 1000–5000 K (note the very different vertical axis scales).

molecule from 1 to 5000 K are listed in 1 K increments in the supplementary material. The expanded uncertainties include the contribution of the unbound states as derived in Ref. 7.

3.3.2. $^{16}O_2$

Figure 6 shows the different expanded uncertainties in the heat capacity calculated in this study for $^{16}O_2$. The results are very similar to those in Fig. 5: the ULB method results in the largest uncertainties and the uncertainty propagation method provides roughly similar results for r = 0.5 and 1.0; thus, the calculated ULB uncertainties can be considered as conservative estimates.

The partition function and its first two moments, as well as the $H(T)$, $S(T)$, and $C_p(T)$ thermochemical functions of the $^{16}O_2$ molecule from 1 K up to 5000 K, are listed in 1 K increments in the supplementary material. The expanded uncertainties published in the supplementary material were calculated by the ULB method and correspond to a 95% confidence interval. We remind the readers that while the ULB method was used for determining the uncertainties of $^{16}O_2$ in Ref. 9, it was implemented incorrectly there for $C_p(T)$; thus, the present work supersedes those erroneous uncertainties.

As mentioned above, a significant additional source of uncertainty for the thermochemical functions of $^{16}O_2$ is the treatment

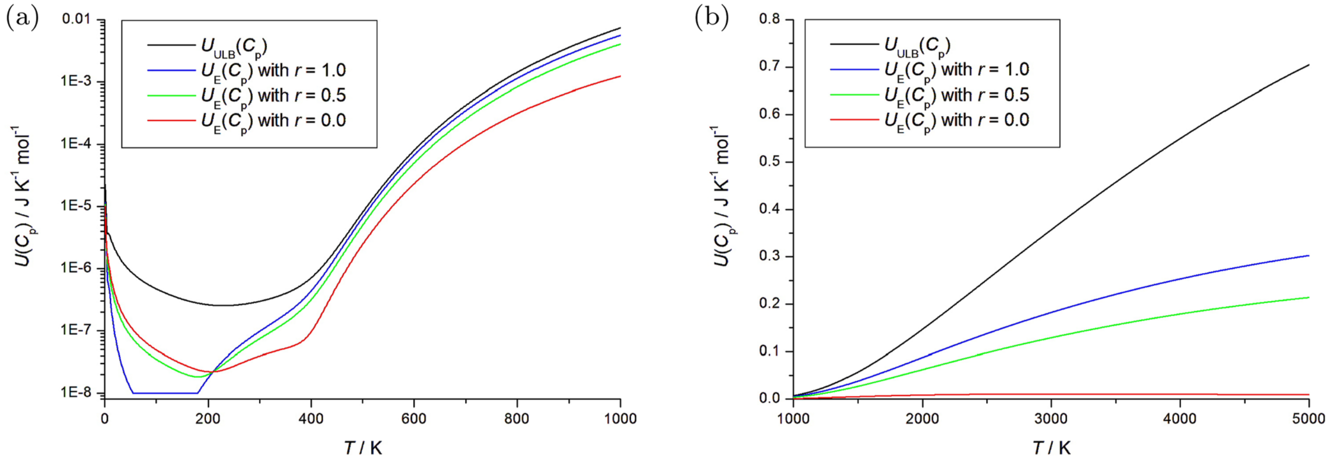

FIG. 6. Expanded (k = 2) uncertainties of the heat capacity $C_p(T)$ calculated for the $^{16}O_2$ molecule in this study. To improve clarity, the plots are presented in two different temperature intervals: (a) 0–1000 K and (b) 1000–5000 K (note the very different vertical axis scales).

TABLE 2. Contributions of the excited electronic states of $^{16}O_2$ to the internal partition function $Q(T)$

T (K)	$X^3\Sigma_g^-$	$a\,^1\Delta_g$	$b^1\Sigma_g^+$	$A'\,^3\Delta_u$	$A^3\Sigma_u^+$	$c^1\Sigma_u^-$	Q_{tot}
10.00	8.306	0.000	0.000	0.000	0.000	0.000	8.306
50.00	37.082	0.000	0.000	0.000	0.000	0.000	37.082
100.00	73.327	0.000	0.000	0.000	0.000	0.000	73.327
250.00	182.232	0.000	0.000	0.000	0.000	0.000	182.232
273.15	199.079	0.000	0.000	0.000	0.000	0.000	199.079
298.15	217.306	0.000	0.000	0.000	0.000	0.000	217.306
500.00	368.167	0.000	0.000	0.000	0.000	0.000	368.167
750.00	575.432	0.000	0.000	0.000	0.000	0.000	575.432
1000.00	816.655	0.007	0.000	0.000	0.000	0.000	816.661
1500.00	1 418.468	0.507	0.002	0.000	0.000	0.000	1 418.977
2000.00	2 189.828	5.228	0.064	0.000	0.000	0.000	2 195.119
2500.00	3 137.299	23.421	0.612	0.000	0.000	0.000	3 161.332
3000.00	4 266.062	68.160	2.954	0.002	0.001	0.001	4 337.179
4000.00	7 087.916	293.687	24.026	0.141	0.052	0.052	7 405.873
5000.00	10 698.180	786.489	94.296	2.186	0.830	0.756	11 582.737

of the excited electronic states. The set of energy levels developed in Ref. 9 covered the ground state and the first five excited electronic states. To show that this is a sufficient number of excited electronic states for our purposes, we report in Table 2 the contribution to the partition function of each electronic state at selected temperatures. It is evident that the highest of these states, $c^1\Sigma_u^-$, contributes negligibly up to our maximum temperature of 5000 K. The neglect of additional electronic states therefore does not affect our results. Note that no estimate of the uncertainties coming from the consideration of unbound states is available for O_2; such states would only be expected to contribute significantly at quite high temperatures.

3.4. O_2 of natural isotopic composition

In the supplementary material, we also include a tabulation of C_p for the natural isotopic composition of diatomic oxygen, computed as described in Sec. 2.4. The expanded uncertainties given there are obtained by combining in quadrature those for $^{16}O_2$ with the expanded uncertainty of the correction to the natural composition. H and S and their uncertainties, computed as described in Sec. 2.4, are also given for this composition.

At many temperatures, the correction for isotopic composition, which in relative terms is never larger than 3×10^{-5}, is negligible compared to the uncertainty in C_p for $^{16}O_2$. However, at temperatures between ~200 and 735 K, the size of the correction exceeds the expanded uncertainty of C_p calculated for $^{16}O_2$. This makes it significant in the range of many practical applications. At some temperatures, from roughly 205 to 600 K, the estimated 30% expanded uncertainty of the correction dominates the uncertainty budget for C_p of natural molecular oxygen. It must be emphasized that the relative importance of this isotopic correction is not due to its large size, but rather to the very small uncertainties obtained in this temperature range for C_p of $^{16}O_2$ [see Fig. 6(a)].

4. Summary and Conclusions

This study examined the ideal-gas thermochemical functions $Q(T)$, $H(T)$, $S(T)$, and $C_p(T)$ of molecular oxygen and water, with an emphasis on the most abundant isotopologues. These thermochemical functions were obtained through the direct summation technique; thus, they depend on the quality of the rovibronic energy levels and the physical constants used during their determination. The improved thermochemical functions listed in the supplementary material were calculated using the values of the SI constants revised in 2019 and an improved set of empirical energy levels for $H_2{}^{16}O$. Following thorough tests, the final expanded uncertainties of these functions were calculated by the method of upper-and-lower-bounds (ULB), and they contain the contribution of the unbound states for $H_2{}^{16}O$. The principal results obtained in this paper are as follows.

For both molecules, the effect of using the revised set of fundamental physical constants, fixed in the 2019 redefinition of the SI, is significant at temperatures below about 2000 K for $H_2{}^{16}O$ and 1000 K for $^{16}O_2$. For $T < 500$ K, the effect can be up to an order of magnitude larger than the uncertainty of the thermochemical functions resulting from the uncertainties of the energy levels. Thus, if extreme accuracy is of concern, recalculation of the thermochemical functions of other molecules using the revised set of physical constants is recommended, especially around room temperature.

As rapid progress in the instrumentation of high-resolution and precision spectroscopy translates into more and more accurately measured line-center positions for more and more molecules and regions of spectra, it is expected that the direct summation technique can be used with increasingly more accurate and complete sets of energy values. Therefore, it is important to note that, even for a spectroscopically thoroughly studied molecule like $H_2{}^{16}O$, the improvement due to the availability of a large number of energy levels at the kilohertz accuracy level yields small but significant improvements in the values of the thermochemical functions at lower temperatures, in particular near room temperature. It should also be noted that the thermochemistry we have derived for $H_2{}^{16}O$ is unique in the sense that the effect of unbound states has been considered, and above about 3000 K this masks any changes in uncertainty due to the revised physical constants or the set of significantly more accurate energy levels.

Another important result of the present study is that multiple techniques to estimate the uncertainties of the computed thermochemical functions provide similar results. The ULB method produces uncertainties that are somewhat larger than those from propagation of the energy-level uncertainties. Uncertainty propagation is a computationally more expensive technique, which scales quadratically with the number of energy levels compared to the linear scaling of the ULB technique. Therefore, on the basis of this argument and to obtain a somewhat more conservative estimate, it is recommended to use the ULB method to estimate the uncertainties of thermochemical functions calculated by direct summation.

For oxygen, we have applied a small correction to the results for $^{16}O_2$ in order to provide thermochemical functions for oxygen of natural isotopic composition. This correction is significant compared to the (very small) uncertainties of the calculated functions for $^{16}O_2$ at most temperatures below 1000 K, meaning that the use of $^{16}O_2$ values would introduce unnecessary error. The large relative uncertainty of this correction is the dominant contributor to the overall uncertainty at temperatures of atmospheric and industrial interest. Improved calculation of this correction would therefore significantly reduce the already small uncertainty of the thermochemical functions for oxygen. Improvement would primarily require estimates of similar quality for the $^{16}O^{17}O$ and $^{16}O^{18}O$ molecules, or accurate estimates of their differences from $^{16}O_2$.

Finally, we note that it would be desirable to have thermochemical functions not only for the parent $H_2{}^{16}O$ isotopologue, but also for water of natural isotopic composition. This information, particularly the ideal-gas heat capacity, is needed for the upcoming replacement of the international standard reference equation of state of ordinary water.[23] State-of-the-art values for C_p have already been developed for the three D_2O isotopologues,[8] but that leaves five more to be done, the most abundant of which are $HD^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$. A similar approach using complete line lists developed for these species would be optimal, but that would be a substantial effort because the experimentally measured energy data are not complete enough to allow reaching the required accuracy. It may be more feasible to use energy levels derived from theory to calculate the difference in thermochemical properties between each minor species and the benchmark $H_2{}^{16}O$ molecule. This will be the subject of future research.

5. Supplementary Material

The supplementary material contains tabulations of the partition function and its first two moments along with thermochemical functions of $H_2{}^{16}O$ and $^{16}O_2$ and their expanded uncertainties at 1 K intervals up to 5000 K. The tables also include points at 273.15 and 298.15 K. A similar tabulation is given for the ideal-gas thermochemical functions of oxygen of natural isotopic composition. The PW2024 line list we used for $H_2{}^{16}O$ is also supplied (the line list used for $^{16}O_2$ can be found in the supplementary material of Ref. 9).

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6. Author Declarations

6.1. Conflict of interest

The authors have no conflicts to disclose.

7. Data Availability

The data that support the findings of this study are available within the article and its supplementary material, except for the unchanged energy levels used for $^{16}O_2$, which are in the supplementary material of Ref. 9.

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