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High temperature partition functions and thermodynamic data for ammonia and phosphine



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ABSTRACT

The total internal partition function of ammonia ($^{14}\text{NH}_3$) and phosphine ($^{31}\text{PH}_3$) are calculated as a function of temperature by explicit summation of 153 million (for PH_3) and 7.5 million (for NH_3) theoretical rotation-vibrational energy levels. High accuracy estimates are obtained for the specific heat capacity, C_p , the Gibbs enthalpy function, gef , the Helmholtz function, hcf , and the entropy, S , of gas phase molecules as a function of temperature. In order to reduce the computational costs associated with the high rotational excitations, only the A -symmetry energy levels are used above a certain threshold of the total angular momentum number J . With this approach levels are summed up to dissociation energy for values of $J_{\text{max}}=45$ and 100 for ammonia ($E_{\text{max}}=41\,051\text{ cm}^{-1}$) and phosphine ($E_{\text{max}}=28\,839.7\text{ cm}^{-1}$), respectively. Estimates of the partition function are converged for all temperatures considered for phosphine and below 3000 K for ammonia. All other thermodynamic properties are converged to at least 2000 K for ammonia and fully converged for phosphine.

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1. Introduction

Ammonia and phosphine are both symmetric top molecules, but differ in the inversion motion which has, so far, only been observed for ammonia. They are both of great interest for a variety of terrestrial and extra-terrestrial studies and have already been found in many astrophysical objects and interstellar media. Both have been for a long time known to be abundant in Jupiter and Saturn [1–6], and are expected to be present in extra-solar gas giants [7]. Ammonia spectra are thought to be the key for identifying the coldest class of brown dwarf stars, the so-called Y-dwarfs [8,9].

Accurate thermodynamic data on these molecules is therefore of great importance. In particular, the partition function is

necessary to establish the correct temperature dependence of spectral lines and their intensity. At elevated temperatures evaluating this function is often not straightforward.

Previous work provides partition functions for these molecules but with some limitations. In 1988, Irwin [10] published a least squares polynomial log fit to the partition functions for molecules of interest for stellar atmospheric equations of state, including NH_3 and PH_3 ; his results are presented as valid from 1000 K to 6000 K, but are increasingly unreliable at the higher end of this temperature range. Gamache et al. [11] fit total internal partition sums (TIPS) to a polynomial expression (third-order in temperature) for most of the infrared absorbing molecules in the terrestrial atmosphere, including both NH_3 and PH_3 , in three temperature ranges reaching up to 3005 K. Fischer et al. [12] used an interpolation scheme to calculate TIPS in the temperature range 70–3000 K for all molecular species in the HITRAN [13] database. The Cologne Database for Molecular Spectroscopy (CDMS) [14] provides values for

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the partition function at temperatures up to 300 K, but these are too low as it would appear that only the rotational contribution to the partition function is represented.

In 1968 Haar [15] presented thermodynamic tables for ammonia for temperatures between 50 K and 5000 K. The 1985 JANAF tables [16] present thermodynamic properties for both molecules for temperatures up to 6000 K but, again, these are increasingly unreliable at high temperatures. In 1999, Lidders [17] updated these thermodynamic tables for some phosphorus molecules, including some corrections to the phosphine data, but did not significantly alter JANAF's results. Finally, Cheric [18] is an online resource which provides calculations for the heat capacity of ammonia and phosphine, but no temperature limits are provided for either molecule and all values for phosphine appear to be unphysical.

Except for CDMS, the results from the studies cited above are discussed and compared to those presented here in Section 3. It is worth noting that the methods used to calculate the partition function by the sources introduced above become increasingly inaccurate at high temperatures, where it is necessary to consider the contribution from very many energy levels. In this work we derive temperature dependent partition functions and associated thermodynamic properties by explicit summation of large energy level lists derived from variational calculations. This procedure has been used successfully before to provide reliable high temperature partition functions and related thermodynamic properties [19–23]. Some of these partition sums have differed by orders of magnitude from prior estimates (see, for example, Ref. [19]).

2. Method

2.1. Energy level calculations

The process used here for calculating the TIPS and related thermodynamic properties follows closely that used by Vidler et al. [21] for water, which builds on methods described by Harris et al. [20] and Martin et al. [24]. The method uses the explicit summation of theoretical rotation–vibration energy levels as a reliable method for producing highly accurate internal partition functions, even for high temperatures. Extension to the total partition functions is done using the ideal gas approximation as described below.

The energy levels used here were calculated using the program TROVE [25] as part of the ExoMol project [26] (see also www.exomol.com) which aims to produce high-accuracy line lists for the atmospheric analysis of astrophysical bodies. Both room temperature [27] and elevated temperature [28] line lists for ammonia have already been produced and are freely available online. The high temperature line list, known as BYTe, is both more accurate and more complete, and it is the BYTe energy levels we use here.

A phosphine room temperature line list has recently been released [29] and a high temperature version is nearly complete [30]. Approximately 7.5 and 5.6 million energy levels were computed for ammonia and phosphine, respectively, some of which were used in the creation of the line lists. Additional 145 million energy levels were computed for phosphine specifically for the thermodynamic

calculations presented here, since the original 5.6 million did not allow for a satisfactory level of convergence. These were created with an accurate vibrational component but with the rotational contribution estimated by a rigid rotor approximation, and consequently with a much decreased level of accuracy. The rotational states are anchored to the vibrational states, so an accurate vibrational description means that the energy level clusters remain valid [31], even if the degradation of accuracy from the rotational component makes the energies within the cluster only approximate. Consequently, their collective contribution to the partition function and related properties remains valid. Some of the calculated energy levels corresponded to quasi-bound states, but the calculations were made excluding any energy levels over the dissociation threshold of the molecules. The consequences of including quasi-bound states are further discussed in Section 3.

The internal rotation–vibration functions of ammonia, with its small barrier to the planarity and distinct inversion tunnelling through the ‘umbrella’ mode, are best described by the $D_{3h}(M)$ molecular symmetry group. It spans six irreducible representations A_1' , A_2' , E' , A_1'' , A_2'' , and E'' [32]. The molecular symmetry group of the rigid molecule PH_3 , $C_{3v}(M)$, with its high barrier to the inversion, is isomorphic to the point group, C_{3v} , which spans three irreducible representations A_1 , A_2 , E . Combination of the internal ro-vibrational function with the nuclear spin functions is subject to Fermi–Dirac statistics: the hydrogen nuclei are fermions with spins of 1/2 and thus the total nuclear–rotation–vibration function must be asymmetric with respect to the interchange of two protons. As a result the nuclear statistical weights, g_{ns} , are introduced in order to account for this property. For ammonia $g_{ns} = 0, 12, 6, 0, 12$ and 6 for the A_1' , A_2' , E' , A_1'' , A_2'' , and E'' internal ro-vibrational eigenstates, respectively. The A_1' and A_1'' states have been given zero weights as these levels do not exist in nature. In the case of phosphine $g_{ns} = 8$ for all three symmetries A_1 , A_2 and E . It is important to note that in this and other work within the ExoMol project [26] the ‘physics’ convention for the definition of statistical weights is followed. This convention includes all nuclear spin degeneracies in the total internal partition sum (TIPS), a convention also followed by HITRAN [11]. Conversely, the ‘astrophysics’ convention, followed for example by JANAF [16] and Irwin [10], normalizes the TIPS to unity for each atom. This results in TIPS which differ by integer multiples associated with the degeneracy of the atomic nuclear spins; the statistical weight factors are $2 \times 2 \times 2 \times 3 = 24$ for ammonia and $2 \times 2 \times 2 \times 2 = 16$ for phosphine. Many results, such as line intensities, rely on ratios which are independent of this choice of convention as long as it is applied consistently. In other cases however, such as with entropy, the results differ by a constant shift. These issues are further discussed below and by Goldman et al. [33].

The molecular symmetry group plays an important role in this work, helping to reduce the size of the problem and reach a higher temperature coverage for the data produced. In our approach, the main bottleneck in calculating the partition function applicable for high temperatures is the high computational costs associated with the high-lying rotation–vibration excitations required. For example, in the

case of the BYTe line list for NH₃ [28], the energies from which are used here, the highest J was 41 and some severe energy thresholds were used ($E_{\max}=18\,000\text{ cm}^{-1}$). With these thresholds the applicable temperature range for BYTe was estimated to be around 1500 K. Increasing this threshold was prohibited by the size of the Hamiltonian matrices of the E -type symmetry to be diagonalized, which were larger than $100\,000 \times 100\,000$ [28].

Similar thresholds were employed for the PH₃ line list as well [29]. Here we employ an approach for computing the partition functions based on the use of A -symmetry energies exclusively for the highest levels considered. Variations of this approach have been tried in the past, in particular by Quack [34]. This technique requires significantly less computational resources and is discussed in detail below.

Theoretical energy levels are still subject to systematic and approximation errors. However, variational nuclear motion calculations can yield many more of these energy levels than can be readily observed, guaranteeing the completeness of the summations used to compute thermodynamical quantities such as the partition function. This completeness is particularly important for obtaining convergence of the sums at higher temperatures.

2.2. Partition functions and thermodynamic data

The internal partition function of a molecule in the ground singlet electronic state, Q , is given by

$$Q_{\text{int}} = \sum_{J=0}^{J_{\max}} \Delta Q_J = \sum_i g_i (2J_i + 1) \exp\left(-\frac{c_2 \tilde{E}_i}{T}\right), \quad (1)$$

where $c_2 = hc/k = 1.438777\text{ cm K}$ is the second radiation constant, J_i is the rotational quantum number of the i th state which has term value \tilde{E}_i (in cm^{-1}) relative to the $J=0$ zero-point-energy, and g_i is the nuclear spin degeneracy factor. The summation in Eq. (1) runs over all the bound ro-vibration energy levels of the system but, as the energy of the states increases, the exponential factor decreases towards zero and the summation of energy levels may be truncated without loss of accuracy [11] as the partition sum will be converged. For higher temperatures, more energies significantly contribute to the sum and the convergence is harder to achieve. The main issue here is convergence with rotational excitation; Eq. (1) has been given in a form which explicitly recognizes the contribution of each J up to some maximum value, J_{\max} .

The specific heat capacity, C_p , the Helmholtz function, hcf , the Gibbs enthalpy function, gef , and the entropy, S , are given by [16]

$$C_p(T) = R \left[\frac{Q''}{Q} - \left(\frac{Q'}{Q} \right)^2 \right], \quad (2)$$

$$hcf(T) = H(T) - H_0 = RT \frac{Q'}{Q} - H_0, \quad (3)$$

$$gef(T) = -\frac{[G(T) - H_0]}{T} = R \ln Q + \frac{H_0}{T}, \quad (4)$$

$$S(T) = R \frac{Q'}{Q} + R \ln Q, \quad (5)$$

where H_0 is the enthalpy at the reference temperature of 298.15 K and Q' and Q'' are, respectively, the first and second moments of the partition function defined as

$$Q' = T \frac{dQ}{dT} = \sum_i g_i (2J_i + 1) \left(\frac{c_2 \tilde{E}_i}{T} \right) \exp\left(-\frac{c_2 \tilde{E}_i}{T}\right), \quad (6)$$

$$Q'' = T^2 \frac{d^2 Q}{dT^2} + 2 \frac{dQ}{dT} = \sum_i g_i (2J_i + 1) \left(\frac{c_2 \tilde{E}_i}{T} \right)^2 \exp\left(-\frac{c_2 \tilde{E}_i}{T}\right), \quad (7)$$

which are also calculated by explicit sums running over the energy levels [24]. These are further explained elsewhere [20,21,24].

Here, calculations of the energy levels, partition sums and other thermodynamic properties were performed for the major isotopologs of ammonia and phosphine, ¹⁴NH₃ and ³¹PH₃ (³¹P is the only non-synthetic, stable isotope). The potential energy surfaces used to create the energy levels and the procedures used to calculate these levels are described in the line list articles for these molecules [28,29]. These line lists contain ro-vibrational term values covering states up to $J_{\max}=33$ and $\tilde{E}_{\max} = 12\,000\text{ cm}^{-1}$ for phosphine and $J_{\max}=41$ and $\tilde{E}_{\max} = 18\,000\text{ cm}^{-1}$ for ammonia. These thresholds impose important limitations on the temperature ranges these line lists, and their corresponding partition function, are applicable for. These limits are $T=1500\text{ K}$ and 300 K , for NH₃ and PH₃, respectively. For the present work we have extended these sets of energy term values to achieve higher temperature coverage of the thermodynamic properties studied. The highest energy levels computed for the work presented here were $74\,488.02\text{ cm}^{-1}$ and $74\,761.4\text{ cm}^{-1}$ with a maximum J value of 100 and 45, for phosphine and ammonia, respectively. The thermodynamic calculations were then made using only energy levels up to dissociation ($28\,839.7\text{ cm}^{-1}$ and $41\,051\text{ cm}^{-1}$ for phosphine and ammonia [35], respectively), but the consequences of including states above this threshold were investigated and are further discussed below.

The main bottleneck and the source of limitations in Refs. [28,29] are the size of the Hamiltonian matrices to be diagonalized while solving the corresponding ro-vibrational Schrödinger equations or, more specifically, the sizes of the E (or E' and E'' in the case of NH₃) symmetry matrices. For a given value of J , the dimensions of the A -symmetry matrices are approximately half the dimensions of the E -symmetry matrices. In order to cope with the matrix size problem the line list calculations employed an iterative eigensolver, PARPACK [36] for higher J values. The drawback of this procedure is that it is necessary to restrict the number of eigen-roots, which resulted in the energy threshold of $18\,000\text{ cm}^{-1}$ for ammonia and $12\,000\text{ cm}^{-1}$ for phosphine. For accurate evaluation of the partition function using Eq. (1) at high T more eigenvalues are needed, which can be achieved by utilization of direct eigensolvers (e.g. DSYEV from the LAPACK library). However, the eigenvectors are not required, which usually reduces the computational costs.

More importantly, the eigenvalues are not really required as they are needed only as an input for the statistical sum. For example Yurchenko et al. [37] explored the property of the matrix trace and performed the temperature averaging of different ammonia properties employing the expansion of the matrix exponent thus avoiding the eigen-problem. In this work we propose the following approach.

Consider the partial statistical sum

$$Q_J^{\Gamma} = \sum_i \exp\left(-\frac{c_2 \tilde{E}_i^{J,\Gamma}}{T}\right), \quad (8)$$

where J is the rotational angular momentum quantum number, Γ is one of the irreducible representations and i runs over all states with a given J and Γ . Then for high J the partial sums Q_J^{Γ} of all 1D irreducible representations (for example A_1 or A_2 in the case of $C_{3v}(M)$) are approximately equal and are half of that of the 2D representation (e.g. E , E' or E''). This property has previously been studied for H_3^+ [38], although it was not used in computing the high- T partition sum [19]. Note that Q_J^{Γ} does not include the total degeneracy factor $g_i = J_i(J_i + 1)g_{ns}$.

For $C_{3v}(M)$ (PH_3) and $D_{3h}(M)$ (NH_3) at high temperatures we expect

$$Q_J^E \approx 2Q_J^{A_1} \approx 2Q_J^{A_2} \approx Q_J^{A_1} + Q_J^{A_2} \approx Q_J^A, \quad (9)$$

$$Q_J^{E'} \approx Q_J^{E''} \approx 2Q_J^{A_1'} \approx 2Q_J^{A_2'} \approx 2Q_J^{A_1''} \approx 2Q_J^{A_2''} \approx Q_J^A, \quad (10)$$

respectively. The conjecture is based on the fact that for high J the density of the A_1 , A_2 and E matrices is similar but the A_1 and A_2 symmetries have approximately half the number of energy states as the E symmetry. Actual energy values for a given J are very similar for all symmetries. Then it follows that to evaluate the Q_J^{Γ} -contributions to the partition function at high J only A -symmetries are required. This is important because in the variational computations, calculations of the E -symmetry energies associate with high computational costs, and can be avoided, at least above some temperature-dependent J threshold, J' . Then the total internal partition function can be calculated using

$$Q_{\text{int}} = \sum_{J=0}^{J'} (2J+1)(g_A Q_J^A + g_E Q_J^E) + \sum_{J=J'+1}^{J_{\text{max}}} (g_A + g_E)(2J+1)Q_J^A, \quad (11)$$

where $Q_J^A = Q_J^{A_1} + Q_J^{A_2}$ and Q_J^E are the total reduced statistical sums for all A -type and E -type symmetries, respectively, and $g_A = g_{A_1} = g_{A_2}$ and g_E are the corresponding nuclear statistical weights. Here all energies of PH_3 and NH_3 are computed by direct diagonalization of the corresponding Hamiltonian matrices. Eq. (11) was found to be invalid at low temperatures ($T \leq 86$ K for ammonia and $T \leq 54$ K for phosphine), for all available values of J' . Under this temperature, the partition function can be calculated with the standard partition function sums using both symmetries, $g_A Q_J^A + g_E Q_J^E$. Above these threshold temperatures, $(g_A + g_E)Q_J^A - (g_A Q_J^A + g_E Q_J^E)$ rapidly goes to zero and Eq. (11) can be used without significant loss of accuracy. This approximation is valid with better than 0.05% accuracy for $J' = 18$ for both molecules but, to ensure the best

possible results, this approach should only be used in the absence of E -symmetry energy levels, at which point an explicit summation over the energies of all symmetries is impossible.

Consequently, the TIPS were calculated using a hybrid approach. Since complete data for all symmetries is available for $J \leq 20$ for phosphine and $J \leq 23$ for ammonia, the standard partition function sums were performed up to these values of J . For $24 \leq J \leq 40$ (for ammonia) and $21 \leq J \leq 33$ (for phosphine) the E -symmetry energy levels were still considered but, due to their energy truncation at $18\,000\text{ cm}^{-1}$ (ammonia) and $12\,000\text{ cm}^{-1}$ (phosphine), the standard sum was used under these energy thresholds, and exclusively the A -symmetries above them, with $(g_A + g_E)Q_J^A$. For $J \geq 40$ (ammonia) and $J \geq 33$ (phosphine), due to the absence of any E symmetry data, only the A symmetry energy levels were considered. In the case of the phosphine molecule, given the poor convergence achieved by the $J \leq 33$ data alone, the additional approximate data discussed above was incorporated in the calculations. All states with $J \geq 34$ from this data were used as well as those with $J \leq 33$ and energy values over the threshold of the original data. This is further discussed in Section 3.

Fig. 1 shows the difference in the values of the calculated TIPS when using the standard partition function sums using both symmetries, $g_A Q_J^A + g_E Q_J^E$, the approximation using A symmetries only, $(g_A + g_E)Q_J^A$, and the hybrid approach described above. The accuracy of Eq. (11) means that the hybrid approach makes only a negligible difference in the values and convergence of the partition function when compared to using only A symmetries. However, this small improvement in accuracy is amplified when calculating the other thermodynamic properties, in particular the heat capacity.

The partition functions calculated here are the total internal partition functions. In order to extend this to the total partition function the ideal gas approximation was used. In this approximation, the internal, translational and total thermodynamic properties relate to each other as follows:

$$C_p^{\text{Total}}(T) = C_p^{\text{Int}}(T) + \frac{5}{2}, \quad (12)$$

$$hcf^{\text{Total}}(T) = hcf^{\text{Int}}(T) + \frac{5RT}{2}, \quad (13)$$

$$gef^{\text{Total}}(T) = gef^{\text{Int}}(T) + R \ln\left(\frac{kT}{p_0 \Lambda^3}\right), \quad (14)$$

$$S^{\text{Total}}(T) = S^{\text{Int}}(T) + \frac{5R}{2} + R \ln\left(\frac{kT}{p_0 \Lambda^3}\right), \quad (15)$$

where R is the gas constant, k is the Boltzmann constant, p_0 is the standard state pressure, 0.1 MPa , and Λ is the thermal de Broglie wavelength, $h/\sqrt{2\pi kM_r u T}$, with $M_r u$ being the molecular mass in kg, which equals the molecular weight, M_r , multiplied by $10^3 M_u N_A^{-1}$ (molar mass constant and Avogadro number). The de Broglie wavelength Λ is directly related to the translational component of the partition function, with $Q_{\text{trans}} = \Lambda^{-3}$, or $(2\pi kM_r u T / h^2)^{3/2}$ in the ideal gas approximation.

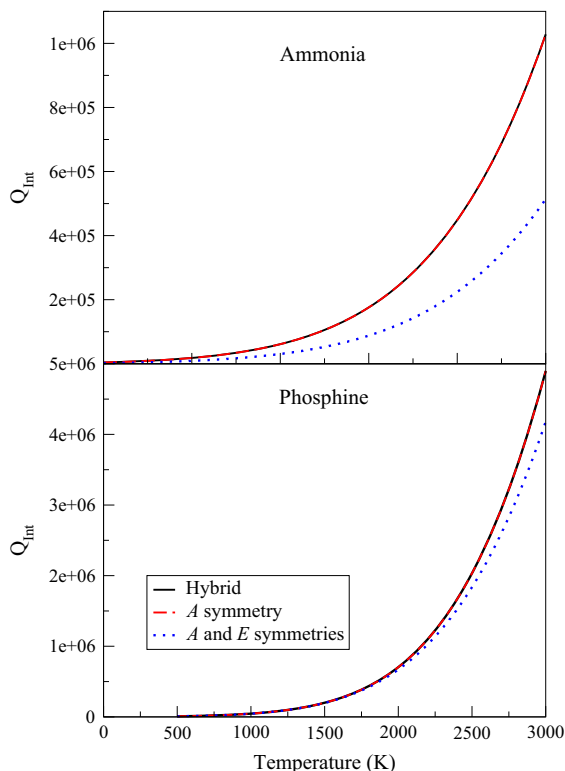


Fig. 1. Comparison of the partition function values calculated with three different approaches. The A symmetry only, $(g_A + g_E)Q_A^J$, and hybrid approaches produce very similar results and at this scale are indistinguishable. The limitations of the A and E symmetries calculation due to truncation are discussed in the text.

These equations are a rearrangement and correction to those published alongside the JANAF thermochemical tables [16]. Corrections are made to the ambiguous treatment of the molecular mass and its units, as well as a typo in the original where N should read N_A .

3. Results and discussion

The calculated values for the total internal partition function, specific heat capacity, Gibbs enthalpy function, Helmholtz function and entropy can be seen, respectively, in Figs. 2, 3, 4, 5, 6, for both ammonia and phosphine. These results are compared to previously determined values, and discussed individually in this section.

The higher the temperature of the system being studied, the more energy levels will be expected to be populated, with higher values of J . This translates to an increase in difficulty when trying to calculate the partition function by explicit summation as the temperature rises. The rotational contribution to the partition function, ΔQ_J , should peak at a particular value of J and then decrease as the value of Q converges. Fig. 7 shows the convergence of the value of the calculated partition function, Q , for a variety of temperatures for phosphine and ammonia. This was calculated by measuring the difference in contribution to Q made by consecutive J values, as a fraction of the total partition function, Q_{int} . The partition functions calculated here are converged ($\leq 0.1\%$) for temperatures below 3220 K for ammonia, and up to the

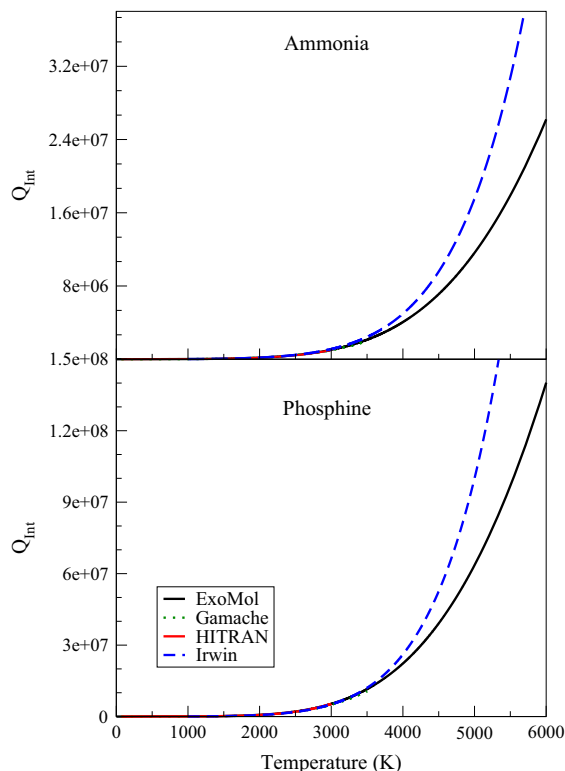


Fig. 2. Comparison of the partition function values calculated here with those from Irwin [10], Gamache [11] and HITRAN [39,12], for ammonia and phosphine. The HITRAN curve ends at 3000 K since that is the limit of the data provided.

maximum temperature considered, 5000 K, for phosphine. In the convergence plot for phosphine, a small discontinuity can be seen at $J=21$ and another at $J=41$. This arises from the change of model employed in the calculation of energy levels and in the application of the hybrid approach to calculating the partition functions, and has a very small impact on the accuracy of the final values.

Fig. 2 compares our partition function with previous calculations from the literature [12,39,40]. All values compare well at low temperatures but then diverge when T increases. Fischer et al. [12] considered the temperature range 70–3000 K and calculated TIPS by Lagrange 4-point interpolation. No polynomial fits are provided but data tables are available from the HITRAN database [13]. These data were retrieved from the VAMDC portal HITRAN-online [41]. The most recent HITRAN values of the partition function for 296 K are 1725.2 for ammonia and 3248.6 for phosphine [40]. These compare well with the present partition function values of 1725.24 and 3249.46 for ammonia and phosphine, respectively.

Gamache et al. [11] employed a polynomial equation of the format

$$Q(T) = a + bT + cT^2 + dT^3 \quad (16)$$

for the three separate temperature ranges, 70–500, 500–1500 and 1500–3005 K. These fits are made to the 2000 HITRAN database partition sums using the corrections

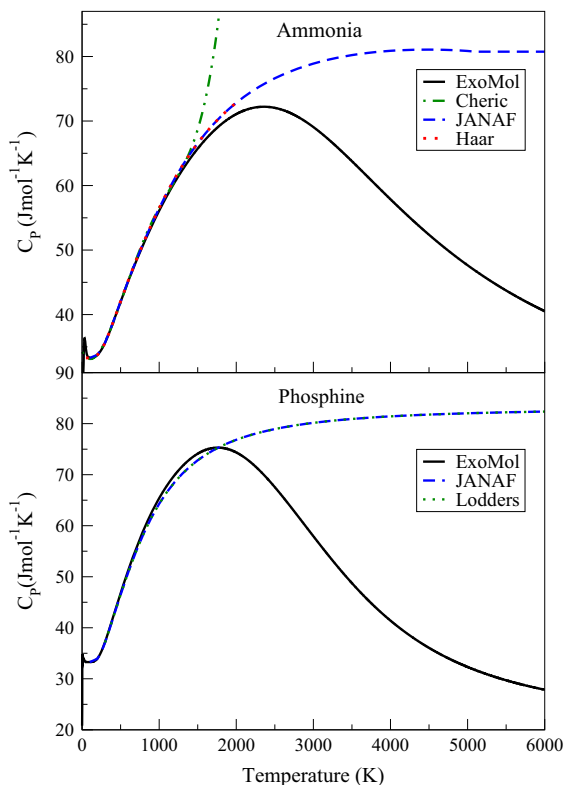


Fig. 3. Comparison of the heat capacity function values calculated here with those from JANAF [16], Ladders [17], Haar [15] and Cheric [18], for ammonia and phosphine. Ladders' data is a revised version of that of the JANAF thermochemical tables, so the disagreement between them is minimal and the Ladders data remains mostly invisible at the scale shown here.

mentioned by Goldman et al. [33] and match their calculated partition sums for both NH_3 and PH_3 within 1%.

Irwin [10] fits polynomial equations on a 100 K grid of temperatures ranging from 1000 to 6000 K using the fitting form

$$\log Q(T) = \sum_i a_i \left[\log \left(\frac{5040}{T} \right) \right]^i. \quad (17)$$

The maximum relative errors in Q over the fitting range are stated as between 10^{-2} and 10^{-1} for ammonia and 10^{-1} and 0.5 for phosphine. As previously discussed, Irwin's data differs from the work presented here by a factor of 24, for ammonia, and 16, for phosphine, due to the use of different statistical weights.

We also represented our partition functions by an 8th order polynomial

$$\log Q(T) = \sum_i a_i [\log(T)]^i \quad (18)$$

with coefficients shown in Table 1. These fits reproduce the values presented here with an accuracy of better than 0.4% for temperatures under 5000 K, but become increasingly unreliable when applied to higher temperatures.

The heat capacity, C_p , is harder to converge due to its dependence on the moments of the partition function. As can be seen by the corresponding convergence plots in

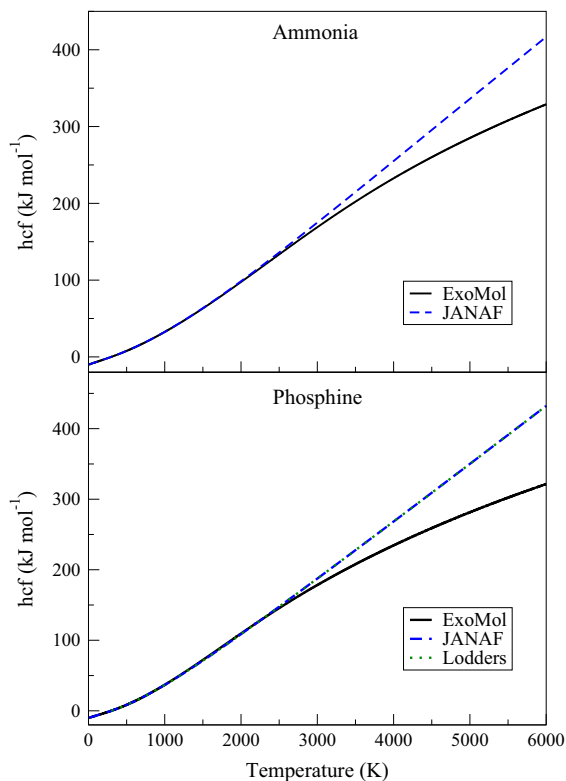


Fig. 4. Comparison of the Helmholtz function values calculated here with those from JANAF [16], Ladders [17], for ammonia and phosphine.

Fig. 8, the heat capacity is only fully converged ($\leq 0.1\%$) for temperatures below 2250 K for ammonia but is fully converged up to the maximum temperature considered, 5000 K, in the case of phosphine.

Using Eq. (12), the total heat capacity functions were compared to that of JANAF [16] and Ladders [17] for phosphine, and JANAF, Haar [15] and Cheric (www.chemric.org) for ammonia. Cheric provides a polynomial fit for both molecules, but the coefficients for phosphine create an extremely unreliable curve and have not been included in this comparison. Comparisons are shown in Fig. 3.

As before with the partition function, there is a very good agreement between the data at low temperatures, but some divergence as these increase. Our value of the heat capacity at the reference value of 298.15 K is $37.226 \text{ J mol}^{-1} \text{ K}^{-1}$ for phosphine, which compares well to that of JANAF (37.102) and Ladders (37.101). Ammonia compares even better, with $35.638 \text{ J mol}^{-1} \text{ K}^{-1}$, compared to that of JANAF (35.652), Haar (35.654) and Cheric (35.782). Cheric's data is provided with no temperature limit, but it is probably only valid for low temperatures. Furthermore, results from the other sources also become increasingly unreliable as temperatures rise.

The primary source of thermodynamic species data is the JANAF tables. The JANAF data on ammonia and phosphine is presented as covering temperatures up to 6000 K and is based on the use of simplified semi-empirical models. One of the largest sources of error is that these models do not take into account the effect of the

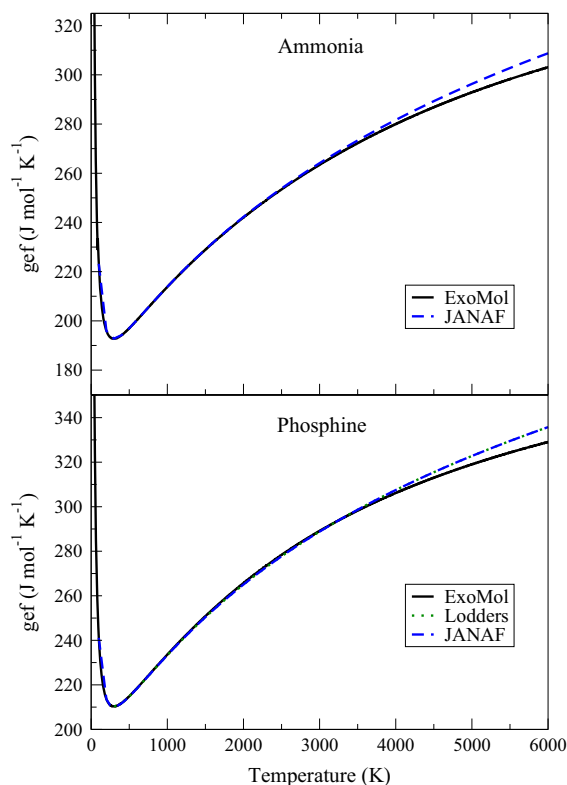


Fig. 5. Comparison of the Gibbs free energy values calculated here with those from JANAF [16], Lodders [17], Haar [15] and Cheric [18], for ammonia and phosphine.

dissociation of a molecule, which has previously been shown to be important [21]. This is the cause for the large discrepancy between our predictions and the results found in the literature, for all presented thermodynamic properties but, as can be seen in Fig. 3, this is particularly clear in the heat capacity calculations.

To demonstrate this, a simplified model based on a rigid-rotor harmonic oscillator approximation was used to make a rough evaluation of the evolution of the partition and the heat capacity functions. It was found that the results follow the shape of the curve computed here when limited by the molecule's dissociation energy, and that predicted by JANAF when the energy levels are taken to infinity. This confirms that the JANAF data significantly overestimates the partition functions for these molecules at high temperature, which has a detrimental effect on all thermodynamic properties presented for temperatures above 1500 K.

The total Helmholtz function, hcf , is calculated using Eqs. (4) and (14) and H_0 , the enthalpy at the reference temperature of 298.15 K. H_0 is calculated to be 10.1381 kJ mol⁻¹ for phosphine and 10.0440 kJ mol⁻¹ for ammonia, which compares well to the JANAF values of 10.136 kJ mol⁻¹ and 10.045 kJ mol⁻¹. A comparative overview is shown in Fig. 4.

Other than near room temperatures, the Lodders data is indistinguishable from that of JANAF. This is because only temperatures near 296 K were affected by the revision due to Lodders.

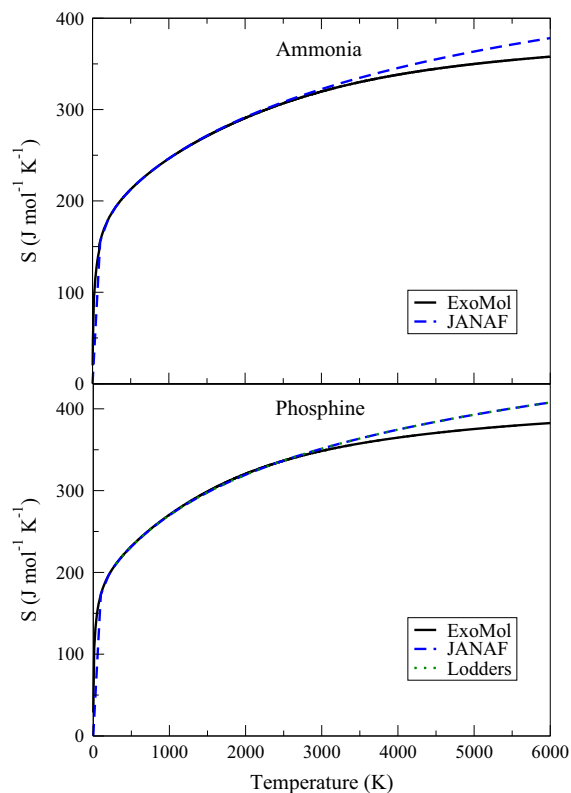


Fig. 6. Comparison of the entropy values calculated here with that of those from JANAF [16], Lodders [17], for ammonia and phosphine.

As before, a factor of 24 (ammonia) and 16 (phosphine) on the partition function was required for the entropy and Gibbs free energy to be comparable to the JANAF literature. This does not affect the Helmholtz function or the heat capacity function since these rely on the ratio of the partition function with its first moment, Q' . A comparative overview is shown in Figs. 5 and 6.

The JANAF data has only 5 data points for temperatures under 300 K, and none between 0 and 100 K, so it is difficult to compare results in this region using the shape of the curves. This is the cause for the large discrepancy at low temperatures between our values and those from JANAF in Figs. 5 and 6.

4. Conclusion

High accuracy theoretical data has been used to calculate the partition function and related thermodynamical properties of ammonia and phosphine, as a function of temperature. For $J \geq 41$ (ammonia) and $J \geq 34$ (phosphine), only the A symmetry energy levels were considered, taking advantage of the fact that the E symmetry contribution to Q can be estimated using only the A -symmetry contribution, for a particular threshold of T and J' .

Analysis of JANAF's thermochemical data suggests that the JANAF data significantly overestimates the partition functions for these molecules at high temperature, which has a detrimental effect on other thermodynamic properties of

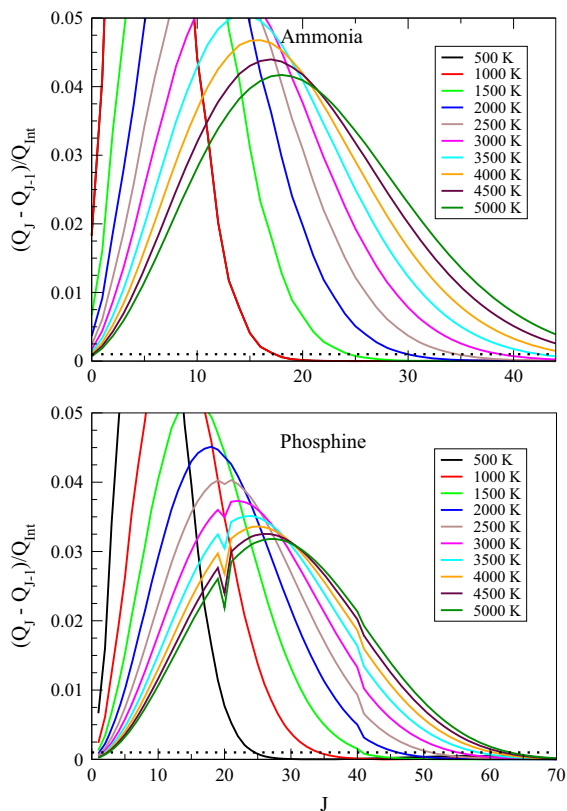


Fig. 7. Convergence of the partition function, Q_{int} , with respect to J , for phosphine and ammonia. Q_{int} for all temperatures displayed is converged up to 1%. The dotted line represents the 0.1% convergence threshold. As described elsewhere, the discontinuities in the plot for phosphine arise from the change of model used for the calculation of energy levels with $J \geq 41$, and the hybrid approach used to calculate the partition functions.

Table 1

Coefficients of the polynomial fit to our partition functions, $Q(T)$, see Eq. (18).

Coefficients	Ammonia	Phosphine
a_0	0.5992996	0.9140408
a_1	-1.472838	-0.8504775
a_2	11.74190	3.029527
a_3	-23.25519	-3.209923
a_4	21.53000	2.137178
a_5	-10.42394	-0.6765168
a_6	2.727102	0.03679531
a_7	-0.3635381	0.02526486
a_8	0.01926157	-0.00382411

temperatures above 1500 K. This appears to be due to an incorrect estimation or the absence of consideration for the dissociation energy.

The precise role of quasi-bound states in the partition function and related properties is still not fully understood but our results suggest that they are unlikely to make a significant contribution at temperatures of interest to ammonia and phosphine.

The values for the partition function agree well with JANAF and other sources for low temperatures and, although only fully converged ($\leq 0.1\%$) for temperatures

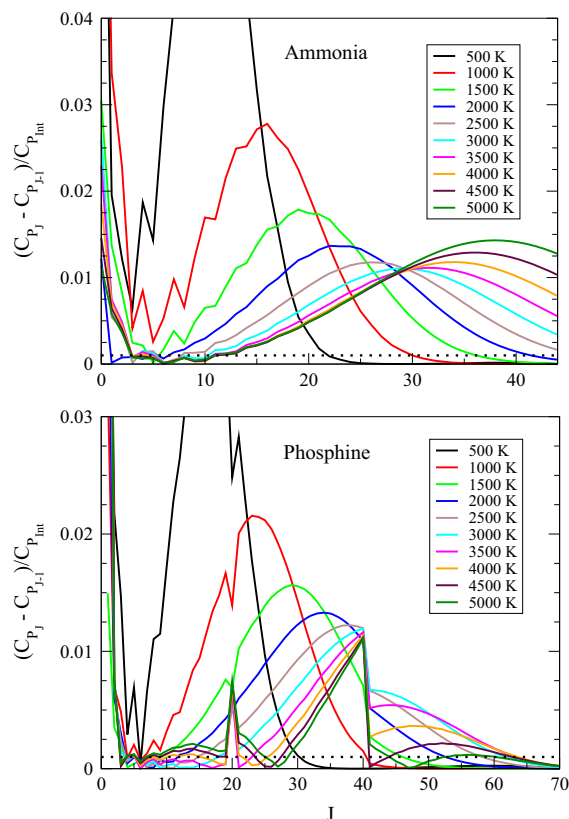


Fig. 8. Convergence of the heat capacity function, C_p , with respect to J , for phosphine and ammonia. Q_{int} for all displayed temperatures is converged up to 1%. The dotted line represents the 0.1% convergence threshold. As described above, the discontinuity in the plot for phosphine arises from the change of model used for the calculation of energy levels with $J \geq 41$.

below 3000 K for ammonia (phosphine calculations were fully converged for all temperatures considered), should be reasonably accurate for temperatures below 5000 K for both molecules. The results for the heat capacity function are only fully converged for temperatures below 2000 K for ammonia, but should still give reasonable estimations of the heat capacity function values for temperature below 3000 K. All other thermodynamic properties are expected to be reasonably accurate up to 3000 K.

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Appendix A

The results for the partition function, specific heat capacity, the Gibbs enthalpy function, the Helmholtz function and the entropy are all provided as supplementary material, in 1 K intervals, which should be more than

sufficient for an accurate interpolation to any intermediate temperatures. All of these properties are represented as internal functions, without translational components. The total functions can be obtained using, for example, the methods described in Section 2. Additionally, the partition function files contain its cumulative value with growing J , and its first and second moment for each temperature.

Appendix B. Supplementary materials

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jqsrt.2014.03.012>.

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