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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 ($^{14}NH_3$) and phosphine ($^{31}PH_3$) 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 $J_{\max}=45$ and 100 for ammonia ($E_{\max}=41\ 051\ \mathrm{cm}^{-1}$) and phosphine ($E_{\max}=28\ 839.7\ \mathrm{cm}^{-1}$), 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.

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, Lodders [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 $\mathcal{D}_{3h}$(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, $\mathcal{C}_{3v}$(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 $2\times2\times2\times3=24$ for ammonia and $2\times2\times2\times2=16$ 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