

# Toward accurate thermochemistry of the $^{24}\text{MgH}$ , $^{25}\text{MgH}$ , and $^{26}\text{MgH}$ molecules at elevated temperatures: Corrections due to unbound states

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The total partition functions  $Q(T)$  and their first two moments  $Q'(T)$  and  $Q''(T)$ , together with the isobaric heat capacities  $C_p(T)$ , are computed *a priori* for three major MgH isotopologues on the temperature range of  $T = 100\text{--}3000$  K using the recent highly accurate potential energy curve, spin-rotation, and non-adiabatic correction functions of Henderson *et al.* [J. Phys. Chem. A **117**, 13373 (2013)]. Nuclear motion computations are carried out on the ground electronic state to determine the (ro)vibrational energy levels and the scattering phase shifts. The effect of resonance states is found to be significant above about 1000 K and it increases with temperature. Even very short-lived states, due to their relatively large number, have significant contributions to  $Q(T)$  at elevated temperatures. The contribution of scattering states is around one fourth of that of resonance states but opposite in sign. Uncertainty estimates are given for the possible error sources, suggesting that all computed thermochemical properties have an accuracy better than 0.005% up to 1200 K. Between 1200 and 2500 K, the uncertainties can rise to around 0.1%, while between 2500 K and 3000 K, a further increase to 0.5% might be observed for  $Q''(T)$  and  $C_p(T)$ , principally due to the neglect of excited electronic states. The accurate thermochemical data determined are presented in the supplementary material for the three isotopologues of  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  at 1 K increments. These data, which differ significantly from older standard data, should prove useful for astronomical models incorporating thermodynamic properties of these species. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4904858>]

## I. INTRODUCTION

As thermochemical data characterizing molecular systems are employed in a vast range of scientific fields and engineering applications, they have been collected into standard information systems.<sup>1–10</sup> The deposited thermochemical data include accurate enthalpies of formation,  $\Delta_f H_f^\circ$ , and accurate partition functions,  $Q(T)$ , both as a function of the thermodynamic temperature  $T$ . If  $Q(T)$  is known with high accuracy, all ideal-gas thermochemical quantities can be determined at arbitrary temperatures once their values are known at one temperature. Thermodynamical data referring to ideal gases are often required at elevated temperatures; for example, in combustion engineering or when stellar environments are studied via spectroscopic means. In these cases, the data needed are hard or even impossible to measure; thus, one has to rely on theoretical/computational approaches to derive the partition functions for the molecules in question and apply statistical methods to arrive at the required thermochemical properties in the required temperature range.

The simplest approach, adopted for most molecules in the information systems, relies on the use of the harmonic oscillator (HO) and rigid rotor (RR) approximations for treating the internal motions of the molecules, resulting in exceedingly simple formulae for the computation of the internal

partition function. However, this approach yields somewhat unreliable numerical data, especially at elevated temperatures. A more sophisticated approach uses perturbative energy corrections, standard in high-resolution molecular spectroscopy, to augment the RRHO approximation and the “direct summation” technique to derive more reliable partition functions.<sup>3,11</sup> Naturally, more accurate and in-depth approaches have also been extensively applied, especially for smaller systems of astrochemical interest. The most reliable approaches are based on high accuracy variational nuclear motion computations, utilizing accurate potential energy surfaces (PESs), for computing the energy levels<sup>11,12</sup> and the direct summation technique. During the computation of internal partition functions, it has been customary to neglect scattering and resonance states (some of the latter can clearly be identified as quasibound states in the case of diatomic molecules<sup>11</sup>). Resonance states are those eigenstates of the time-independent nuclear Schrödinger-equation which have exponentially divergent behavior in the asymptotic region and correspond to complex eigenvalues, thus having finite lifetimes.<sup>13</sup> Not considering the scattering and resonance states is based usually upon the argument that these states have high energies and thus their contribution is damped during direct summation by the Boltzmann factor, thus they are expected to give negligible contribution to most partition functions. However, as occasionally pointed out,<sup>14–16</sup> unbound (resonance and scattering) states can have a significant contribution to molecular

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partition functions at elevated temperatures. Another justification occasionally used for the neglect of unbound states during computation of molecular internal partition functions is that unbound states correspond to molecular fragments and should be taken into account during the computation of  $Q(T)$  of the fragment. In the simplest case of diatomic molecules, the fragments are the atoms. Following Landau and Lifshitz<sup>17</sup> and others,<sup>15</sup> we are on the opinion that unbound molecular states should be accounted for during the treatment of molecules and not of fragments as this definition may greatly facilitate moving from ideal gases to real ones.

In the fourth age of quantum chemistry,<sup>18</sup> it has become increasingly realistic to compute all bound (ro)vibrational states of not only diatomic but also tightly bound triatomic molecules, all this with remarkable accuracy, whereby the deviations from experiment not much exceed  $1\text{ cm}^{-1}$  even in the worst cases and better on average.<sup>19,20</sup> Furthermore, computation of not only bound but also of resonance states is feasible with little, or occasionally no<sup>21</sup> extra cost over the computation of the bound states.<sup>22,23</sup> Thus, the question arises naturally how large an effect resonance states have on computed thermochemical properties and at which temperature would they start playing a significant role.

In order to investigate and understand the effect of unbound, including resonance, states on the thermochemical properties of molecules, one needs to choose carefully the model system under study. It is best to choose a diatomic molecule, as computations of all bound and unbound states require a relatively minor effort, while computing a large number of resonance states for triatomic molecules is still a time-consuming task. The diatomic molecule should have a low first dissociation energy so that resonance states should have substantial influence on thermochemical properties starting at relatively low temperatures. A final useful requirement is that the excited electronic states should be well separated from the ground state so that they can be safely neglected in an intermediate temperature range.

The diatomic molecule MgH appears to be an ideal candidate for an accurate modelling study for several reasons. The dissociation energy of the ground electronic state of  $^{24}\text{MgH}$  is only  $D_e = 11104.7(5)\text{cm}^{-1}$ , while the vertical excitation energy of the first excited state is as much as  $19\,000\text{ cm}^{-1}$ .<sup>24</sup> Thus, MgH has ideal molecular properties for our study. Furthermore, MgH and its isotopologues have significant astronomical importance; therefore, the definitive thermochemical data derived here should prove to be useful for astronomical models seeking high accuracy thermochemical quantities at elevated temperatures. Under all conditions known, MgH has three stable isotopes,  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$ . In massive stars,  $^{24}\text{Mg}$  is formed during carbon burning.<sup>25</sup> The two heavier isotopes,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ , are principally produced during He burning.<sup>25</sup> MgH and its isotopologues thus have proven to be extremely useful molecules for understanding stellar atmospheres; for example, measured MgH lines<sup>26,27</sup> were employed for determining magnesium isotope abundances,<sup>27–29</sup> surface gravity,<sup>30</sup> metal abundance,<sup>31</sup> as well as temperature<sup>32,33</sup> and pressure<sup>33</sup> of stars. MgH is included in stellar atmospheric models,<sup>34,35</sup> where among other quantities of interest, one does need highly accurate higher-temperature thermochemical

functions. Consequently, a relatively large number of studies have been devoted to the determination of the spectroscopic properties<sup>36–40,24</sup> and the thermochemical functions<sup>39</sup> of MgH and its isotopologues. The present study investigates the effect of unbound states on the thermochemical properties of the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules, and presents the corresponding accurate thermochemical data in the temperature range of 100–3000 K. As it turns out, it is possible to determine  $Q(T)$  with good accuracy (between 0.005 % and 0.5 % relative uncertainty) up to high temperatures and thus we also report such accurate thermochemical data for  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  up to 3000 K, the highest temperature chosen during a recent investigation<sup>38</sup> of  $Q(T)$  of the three MgH isotopologues.

## II. THEORY OF INCLUSION OF RESONANCE AND FREE SCATTERING STATES INTO THE PARTITION FUNCTION

As has been discussed previously,<sup>15,41,42</sup> but neglected in standard texts on statistical mechanics,<sup>43</sup> the  $Q(T)$  internal canonical partition function of a molecule can be separated into two principal components:  $Q(T) = Q_B(T) + Q_U(T)$ , where  $Q_B(T)$  and  $Q_U(T)$  stand for the contributions of bound and unbound states, respectively. The unbound part can be further separated into resonance and free-scattering contributions:  $Q_U(T) = Q_R(T) + Q_F(T)$ . As to applications of the thermodynamics of gases at elevated temperatures, where one treats a mixture of the molecules with their dissociation products, the definition of a molecule is not unique: one has the freedom of selecting which parts of the phase space belongs to the molecule and which to its dissociation products.<sup>15</sup> This makes it possible to define the bonded system to be such that its partition function contains only truly bounded contributions  $Q_1(T) = Q_B(T)$ , bound and resonance contributions  $Q_2(T) = Q_B(T) + Q_R(T)$ , or all contributions  $Q_3(T) = Q_B(T) + Q_U(T)$ . In the former two cases, however, caution must be taken during applications, as contributions from  $Q_R(T)$  and  $Q_F(T)$  need to be accounted for in the partition functions of the dissociation products. Therefore, the definition  $Q(T) = Q_B(T) + Q_U(T)$  is recommended for general use, as in this case all interactions are accounted for in the partition function of the molecule, and the dissociation products can rigorously be treated as non-interacting (ideal gas) species. In the following, the effects of  $Q_R(T)$  and  $Q_U(T)$  on the thermochemical properties of the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules will be discussed in detail.

It is not obvious right away how to include unbound states in the so-called “direct summation” technique of determining accurate partition functions. A possible approach to incorporate states with finite lifetimes is to switch from direct summation over states to an integration over energy. This procedure then uses the density of states as a weight function, i.e.,

$$Q(T) = \sum_n e^{-\beta E_n} \leftrightarrow \int_0^\infty \rho(E) e^{-\beta E} dE, \quad (1)$$

where  $\rho(E)$  is the density of states,  $\beta = \frac{1}{kT}$ ,  $k$  is Boltzmann’s constant, and  $T$  is the thermodynamic temperature.<sup>14,11</sup> Naturally, this change does not alter the results for bound states, as

$\rho_B(E) = \sum_n \delta(E - E_n)$ . However, the change makes it possible to include resonance states into the partition function, for which

$$\rho_R(E) = \frac{1}{\pi} \sum_r \frac{\frac{\Gamma_r}{2}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}}, \quad (2)$$

where  $E_r$  and  $\Gamma_r$  are the positions (real parts) and half-widths (minus two times the imaginary parts) of the resonance states, respectively.<sup>44</sup> Thus, using  $\rho(E) = \rho_B(E) + \rho_R(E)$  gives

$$Q(T) = \int_0^\infty \rho(E) e^{-\beta E} dE = \sum_n g_n e^{-\beta E_n} + \frac{1}{2\pi} \sum_r g_r \int_{D_c} \frac{\Gamma_r e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE, \quad (3)$$

where  $g_i$ , standing for the overall  $g_{ns}(2J+1)$  degeneracy of state  $i$ , was introduced, with  $g_{ns}$  and  $J$  being the nuclear spin degeneracy and total angular momentum quantum number, respectively.

For practical purposes, it is worth considering the limit

$$\lim_{\gamma_r \rightarrow 0} \frac{\frac{\Gamma_r}{2\pi}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} = \delta(E - E_r), \quad (4)$$

since then for resonance states with small  $\gamma_r$

$$\frac{1}{2\pi} \int_{D_c} \frac{\Gamma_r e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE \cong e^{-\beta E_r} \quad (5)$$

holds; thus, simple summation of the  $e^{-\beta E_r}$  values might be applied without significant loss of accuracy when constructing the partition function.

One might wish to incorporate not only bound and resonance states into the partition function but also the effect of scattering introduced by the diatomic potential, i.e., the effect of scattering states omitting the “scattering states” of the non-interacting atoms. As mentioned before, this way all interactions are accounted for in the partition function of the molecule; thus, the free atoms can be rigorously treated as an ideal gas when setting up the model of a gas mixture. The approach provided by Eq. (1) can be applied by utilizing the relation between the density of states and the scattering phase shift<sup>45</sup>

$$\rho_U(E) = \frac{1}{\pi} \frac{d\eta(E)}{dE}, \quad (6)$$

where  $\eta(E)$  is the scattering phase shift and  $\rho_U(E) = \rho_R(E) + \rho_F(E)$  is the density of states in the continuum, including both resonance and free-scattering states. Since in practice one determines the  $\eta_J(E)$  phase shift separately for each  $J$ , using  $\rho(E) = \rho_B(E) + \rho_U(E)$  in Eq. (1) leads to

$$Q(T) = \int_0^\infty \rho(E) e^{-\beta E} dE = \sum_n g_n e^{-\beta E_n} + \frac{g_{ns}}{\pi} \sum_J (2J+1) \int_{D_c} \frac{d\eta_J(E)}{dE} e^{-\beta E} dE. \quad (7)$$

It is emphasized that applying integration by parts in Eq. (7) leads to a formula in which only the phase shift  $\eta_J(E)$  is involved; thus, the determination of its (numerical) derivative is not necessary. Alternatively, if one has the quantum scattering wavefunction at hand, it can be used to deduce the

derivative of the phase shift along with the phase shift itself, omitting (numerical) derivation.<sup>21</sup>

### III. COMPUTATIONAL DETAILS

For all bound and resonance nuclear motion computations on the ground electronic state, the diatomic Hamiltonian and the outstanding quality adiabatic PES of Ref. 24 was used, the former including a nonadiabatic, coordinate-dependent mass “surface” for the H atom and a radial strength function accounting for the electronic spin-rotation interaction. Bound and resonance eigenenergies were computed through direct diagonalization of the Hamiltonian matrix, obtained as the matrix representation of the diatomic Hamiltonian (complex scaled in the case of resonance states), using 250 spherical oscillator basis functions in the discrete variable representation (DVR).<sup>46</sup> The DVR quadrature points lie between internuclear distances of 0.048 and 15 bohrs. When computing resonance states, the conventional complex coordinate scaling<sup>47</sup> was applied with the scaling parameter  $\theta$  set to be 0.15.

During the uncertainty estimation of Sec. V, excited electronic surfaces were approximated as Morse-functions, their parameters taken from Ref. 37. Bound (ro)vibrational states of the excited electronic surfaces were computed by diagonalizing the diatomic Hamiltonian (after omitting the nonadiabatic and spin-rotation interaction terms) using 250 spherical-oscillator-DVR basis functions, with the DVR quadrature points lying between internuclear distances of 0.051 and 16 bohrs.

The scattering phase shift was determined for each  $J$  total angular momentum quantum number separately using a semiclassical WKB formula<sup>48</sup>

$$\eta_J^{\text{WKB}}(E) = \left(\frac{2\mu}{\hbar^2}\right)^{\frac{1}{2}} \left[ \int_0^\infty \sqrt{E - V(R) - \frac{\hbar^2 N(N+1)}{2\mu R^2}} dR \right]_{\text{ArgSqrt} > 0} - \int_0^\infty \sqrt{E - \frac{\hbar^2 N(N+1)}{2\mu R^2}} dR \Big|_{\text{ArgSqrt} > 0} + \frac{\pi}{4} \delta_{0,N}, \quad (8)$$

where  $\mu$  is the reduced mass of the molecule,  $V(R)$  is the diatomic potential including the non-adiabatic and spin-rotation interaction terms, and  $\text{ArgSqrt} > 0$  stands for all  $R$  values where the argument of the square root function is positive. Four digits of convergence with respect to the maximum value of the  $N$  total rotational quantum number applied was achieved for all scattering contributions to the thermodynamic properties at all temperatures using  $N_{\text{max}} = 240$ .

### IV. RESULTS AND DISCUSSION

In what follows, two sets of results are presented: in Sec. IV A, thermochemical properties obtained by including only bound and resonance states into the partition functions are discussed, while in Sec. IV B, the thermochemical properties are computed, incorporating the bound and all continuum (resonance and free-scattering) contributions in the partition functions.

## A. Thermochemistry using bound and resonance states

All bound and resonance states up to 20 000  $\text{cm}^{-1}$  above the potential minimum were computed for  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$ . All resonance states with  $\Gamma_r < 200 \text{ cm}^{-1}$  were determined, a few states (approximately 30-40) with half-widths between 200 and 5000  $\text{cm}^{-1}$  are missing due to the finite complex scaling angle applied. Altogether 638 bound and 388 resonance states were found, without taking into account nuclear and total angular momentum degeneracies, with a maximum rotational quantum number of  $N = 44$  and  $N = 66$ , respectively. Taking into account the electronic spin-rotation coupling,<sup>49</sup> the degeneracy for the total angular momentum quantum number  $J$  is  $2J + 1$ , while nuclear spin degeneracy is 2, 12, and 2 for  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$ , respectively. Using the computed energy eigenvalues, the canonical partition functions (see Eq. (3)) and their first two moment

$$Q'(T) = \sum_n g_n \beta E_n e^{-\beta E_n} + \frac{1}{2\pi} \sum_r g_r \int_{D_e}^{\infty} \frac{\Gamma_r \beta E e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE \quad (9)$$

and

$$Q''(T) = \sum_n g_n (\beta E_n)^2 e^{-\beta E_n} + \frac{1}{2\pi} \sum_r g_r \int_{D_e}^{\infty} \frac{\Gamma_r (\beta E)^2 e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE \quad (10)$$

were constructed for the three isotopologues and used to calculate the

$$C_p(T) = R \left( \frac{Q''}{Q} - \frac{Q'}{Q} + \frac{5}{2} \right) \quad (11)$$

heat capacities at constant pressure and at different temperatures.<sup>12</sup> Altogether five sets of calculations were carried out: one using only bound states, one using all bound states and resonance states with  $\Gamma_r < 200 \text{ cm}^{-1}$ , (638 + 236 states), one using all bound states and resonance states with  $\gamma_r < 5000 \text{ cm}^{-1}$ , (638 + 388 states), and finally, the latter two including resonance states were repeated via applying the approximation of Eq. (5) and its analog for  $Q'(T)$  and  $Q''(T)$ .

Figure 1 presents the computed heat capacities for  $^{24}\text{MgH}$  along with reference values taken from the JANAF database.<sup>8</sup> Until around 1000 K, the present results are in good agreement with the JANAF values; however, for higher temperatures the deviations grow significantly. This is expected, nevertheless, as the JANAF results were obtained using simple harmonic oscillator partition functions with anharmonic correction terms, and thus are incapable of representing a finite eigenvalue spectrum necessary to give correct high-temperature behavior and the limit of  $5/2R$  as  $T$  goes to infinity.<sup>50</sup>

The effect of resonance states starts to become significant above 1000 K, and grows up to 3000 K, where around 14% increase in  $C_p$  can be observed. Based on Figure 1 (the corresponding figures for  $^{25}\text{MgH}$  and  $^{26}\text{MgH}$  are essentially identical), one can conclude that even short-lived resonance states (large  $\Gamma_r$ ) should not be omitted when computing  $C_p$  for the three MgH isotopologues above 1000 K and that the

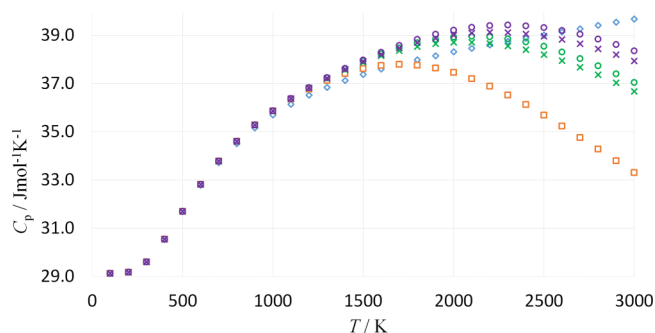


FIG. 1. Gas-phase heat capacity, as a function of temperature, of  $^{24}\text{MgH}$  obtained via six different approximations (the asymptotic value as  $T$  goes to infinity is  $5/2R \approx 20.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ). Blue diamonds: NIST-JANAF results from Ref. 8, <http://kinetics.nist.gov/janaf/html/H-023.html>. Orange squares: obtained by including only bound states into the partition function. Green circles: obtained by including bound and also resonance states (with  $\Gamma_r < 200 \text{ cm}^{-1}$  and using simple summation over  $e^{-\beta E_r}$ ) into the partition function. Green crosses: obtained by including bound and also resonance states (with  $\Gamma_r < 200 \text{ cm}^{-1}$  and using the integral formula of Eq. (3)) into the partition function. Violet circles: obtained by including bound and also resonance states (with  $\Gamma_r < 5000 \text{ cm}^{-1}$  and using simple summation over  $e^{-\beta E_r}$ ) into the partition function. Violet crosses: obtained by including bound and also resonance states (with  $\Gamma_r < 5000 \text{ cm}^{-1}$  and using the integral formula of Eq. (3)) into the partition function.

approximation represented by Eq. (5) works well even if short-lived resonance states are present.

Figure 2 shows the computed partition functions and their first two moments for  $^{24}\text{MgH}$  (again, the corresponding figures for  $^{25}\text{MgH}$  and  $^{26}\text{MgH}$  are essentially identical). As expected, the inclusion of resonance states results in a considerably smaller relative change in the partition function than in its first two moments (and hence in the heat capacity). This suggests that when one considers which energy levels to use for deriving accurate thermodynamic properties, the relative change in the partition function in itself might be misleading, the change in the moments should also be examined so that the partition function determined can safely be used to derive the usual ideal-gas thermochemical functions.

## B. Thermochemistry using bound and all scattering states

In this subsection, thermodynamic quantities are recomputed by including all computed bound states and continuum states using the integral formula of Eq. (7) and the corresponding analogues of Eqs. (9)–(11). The results obtained are presented in Figures 3 and 4. As both figures show, the inclusion of free-scattering states leads to a decrease in all computed quantities (most importantly, the contribution to the partition function is negative), with a magnitude of around one fourth of the magnitude of the effect of resonance states. The negative contribution of scattering states to the partition function was observed in the past,<sup>15,21</sup> and the physical interpretation is that the overall effect of the PES for scattering states is repulsive, due to the steep repulsive region at short distances, in fact steeper than  $R^{-2}$  corresponding to the non-interacting case. This leads to a decrease in the density of states with respect to the non-interacting case (or equivalently, the scattering phase



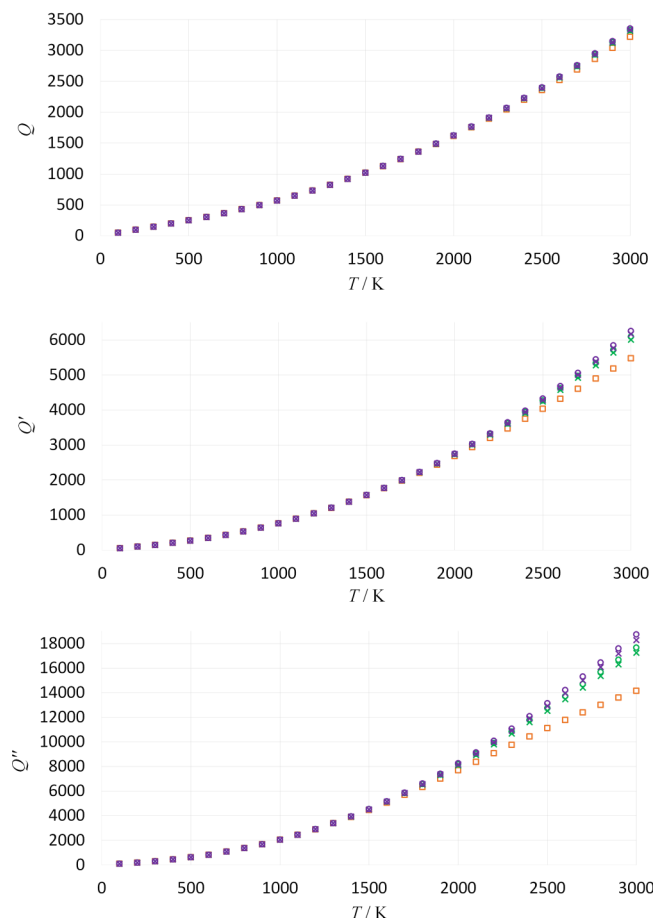


FIG. 2. Gas-phase partition function and its first two moments for  $^{24}\text{MgH}$  as a function of temperature. Meaning of the symbols is the same as used for Figure 1.

shift as a function of energy has negative slope); thus, it gives rise to a negative contribution to the partition function, see Eq. (7).

## V. UNCERTAINTY ESTIMATES

In order to ascertain the accuracy of our computed results, the effect and magnitude of different error sources were inves-

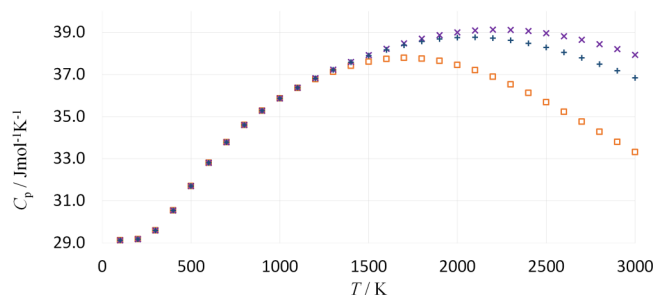


FIG. 3. Gas-phase heat capacity of  $^{24}\text{MgH}$  as a function of temperature. Orange squares: obtained by including only bound states into the partition function. Violet crosses: obtained by including bound and also resonance states (with  $\Gamma_r < 5000 \text{ cm}^{-1}$ , and using the integral formula of Eq. (3)) into the partition function. Blue pluses: obtained by including bound and all unbound (resonance and free scattering) states into the partition function.

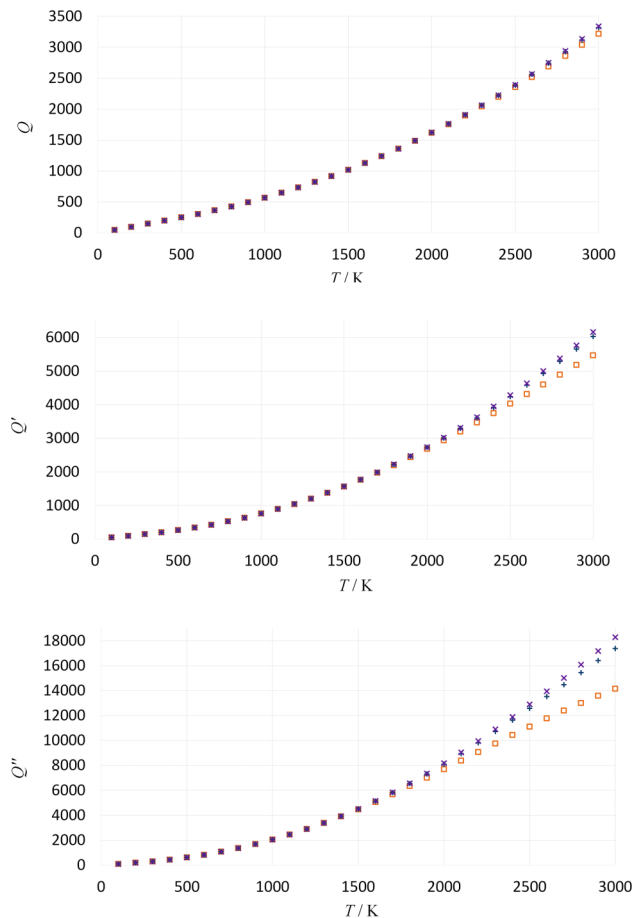


FIG. 4. Gas-phase partition function and its first two moments for  $^{24}\text{MgH}$  as a function of temperature. Orange squares: obtained by including only bound states into the partition function. Violet crosses: obtained by including bound and also resonance states (with  $\Gamma_r < 5000 \text{ cm}^{-1}$ , and using the integral formula of Eq. (3)) into the partition function. Blue pluses: obtained by including bound and all unbound (resonance and scattering) states into the partition function.

tigated when computing the thermochemical properties of the  $^{24}\text{MgH}$  molecule. The possible error sources considered are as follows: (1) inaccuracies in the eigenenergies, (2) missing resonance states (cf. Sec. IV A), (3) inaccuracies in the phase shift computations (cf. Sec. IV B), and (4) omission of states on excited electronic surfaces.

The effect of inaccuracies of the energies used to compute  $Q(T)$ ,  $Q'(T)$ ,  $Q''(T)$  and  $C_p(T)$ , was tested by investigating ensembles of the thermochemical quantities (at 300 K, 1500 K, and 3000 K) generated with 5000 different energy sets, each produced by adding random errors to the computed energy levels. The random errors were produced, with random sign, from the Maxwell-Boltzmann distribution  $f(x) = \sqrt{\frac{2}{\pi}} \frac{x^2}{\sigma^3} e^{-\frac{x^2}{2\sigma^2}}$  with  $\sigma = 0.008\,821\,57$ ,  $x > 0$ , which was fitted to the set of average uncertainties of transition energies reported in the supporting information file called *jp406680r\_si\_003.txt* of Ref. 24. Figure 5 presents histograms of the thermochemical quantity ensembles at 300 K. Note that for 1500 K and 3000 K, the histograms are essentially identical. As seen in Figure 5, all deviations for  $Q(T)$  and  $Q'(T)$  result in a relative change less than 0.003%, while for  $Q''(T)$  and  $C_p$ , the upper limit is around 0.0015%. It is worth noting that the deviations for  $Q''(T)$  and

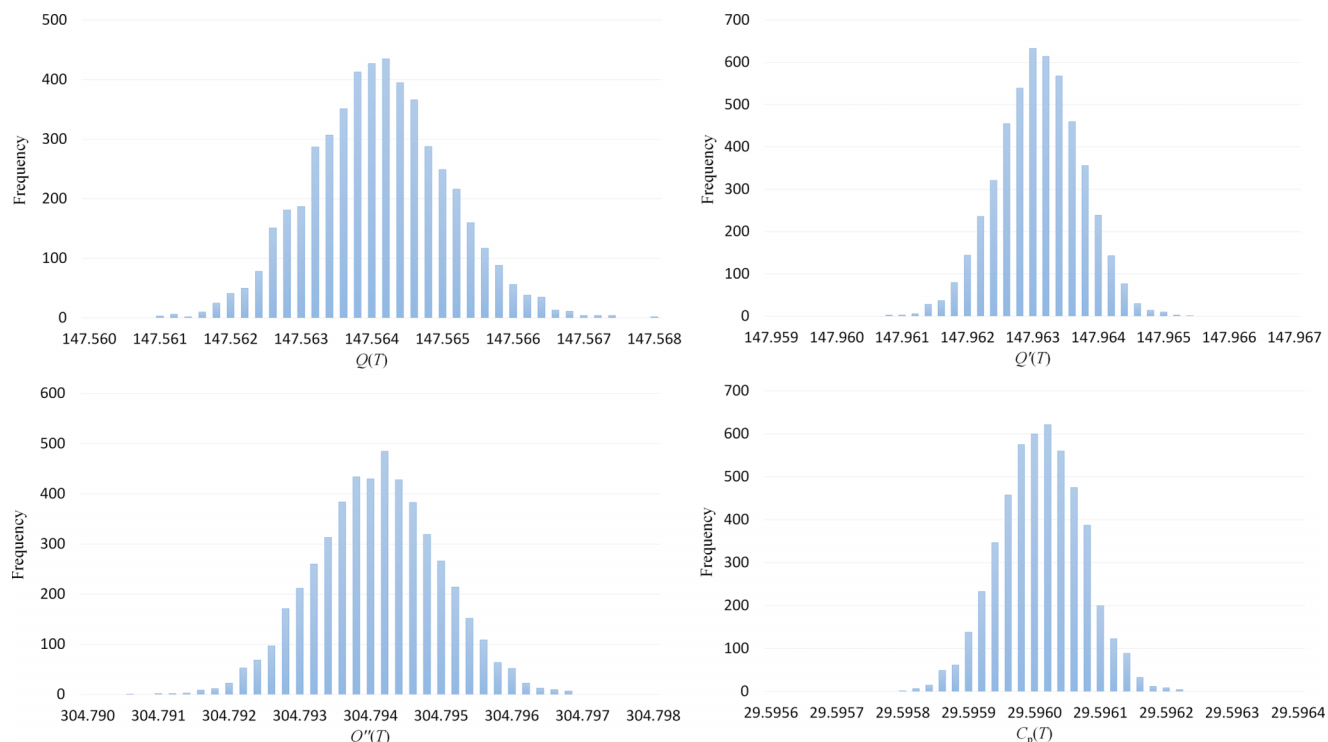


FIG. 5. Histograms of gas-phase thermochemical property ensembles for  $^{24}\text{MgH}$ , obtained from 5000 sets of energy levels augmented with random errors simulating the uncertainties in the computed energy levels. See text for additional details.

$C_p(T)$  are smaller than the effect of the unbound states already at around  $T = 900$  K.

The number of missing resonance states in our computations with  $200\text{ cm}^{-1} < E_r < 5000\text{ cm}^{-1}$  is approximated to be around 30-40. To arrive at an overestimate to their omission, 50 artificial states with energy of  $D_e$  and  $\gamma_r = 0\text{ cm}^{-1}$  were introduced to the set of energy levels and the thermochemical properties were recomputed. Figure 6 demonstrates the relative change in the results as a function of temperature. As seen in Figure 6, the effect reaches a maximum relative error of 0.08% for  $Q''(T)$ , which corresponds to a change in the fourth digit. Due to a significant cancellation of errors, the relative error for  $C_p$  is considerably smaller, it reaches a maximum of around 0.03% at 3000 K.

As emphasized before,<sup>15</sup> the semiclassical approximation of Eq. (8) is remarkably accurate when determining the scattering phase shifts, except near the resonance energies, where the step-like increase in the quantum phase shift is “averaged” with a steep slope in the semiclassical results. However,

the previous<sup>15</sup> and the present numerical tests (comparison of the integral in Eq. (7) evaluated by using step functions at the resonance energies in the phase shift or evaluated by “averaging” the step functions with a slope) show that the uncertainty caused by this discrepancy is negligible, especially with respect to other error sources. The relative error of the thermochemical properties caused by the convergence error of the phase shifts (with respect to the total angular momentum quantum number applied for their determination) increases with temperature, but only reaches a maximum of 0.002% at 3000 K for  $Q''(T)$ .

When computing thermochemical properties at elevated temperatures, the effect of (ro)vibrational states corresponding to excited electronic states increases. To approximate the uncertainty introduced by the omission of excited electronic states in this study, the thermochemical computations were repeated with an extended set of (ro)vibrational states, obtained by including the bound (ro)vibrational states of the first two excited electronic states up to  $27\,000\text{ cm}^{-1}$  above the

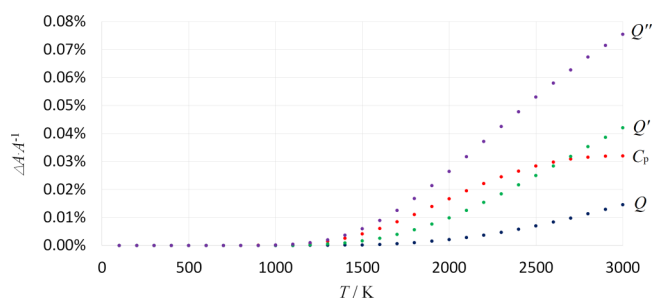


FIG. 6. Overestimated relative error of gas-phase thermochemical properties originating from the omitted resonance states for  $^{24}\text{MgH}$ .

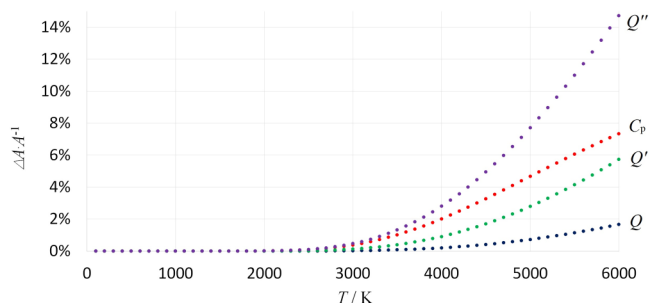


FIG. 7. Approximate relative change in the gas-phase thermochemical properties, originating from the (ro)vibrational states of the first two excited electronic states for  $^{24}\text{MgH}$ .

TABLE I. Approximate relative uncertainties, all in percentage, of computed thermochemical quantities obtained by taking only bound (B), bound and resonance (B + R), or bound and unbound (B + U) contributions into account.

$T/K$	B				B + R				B + U			
	$Q_1(T)$	$Q_1'(T)$	$Q_1''(T)$	$C_p(T)$	$Q_2(T)$	$Q_2'(T)$	$Q_2''(T)$	$C_p(T)$	$Q(T)$	$Q'(T)$	$Q''(T)$	$C_p(T)$
200	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
400	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
600	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
800	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
1000	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
1200	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002	0.003	0.003	0.002	0.002
1400	0.003	0.003	0.002	0.002	0.003	0.004	0.005	0.004	0.003	0.003	0.002	0.002
1600	0.003	0.003	0.002	0.002	0.003	0.006	0.011	0.008	0.003	0.003	0.002	0.002
1800	0.003	0.003	0.004	0.004	0.004	0.009	0.021	0.015	0.003	0.004	0.004	0.004
2000	0.003	0.005	0.012	0.010	0.005	0.015	0.038	0.027	0.003	0.005	0.012	0.010
2200	0.004	0.009	0.031	0.027	0.007	0.024	0.068	0.049	0.004	0.009	0.032	0.027
2400	0.005	0.019	0.073	0.062	0.011	0.041	0.121	0.088	0.005	0.019	0.074	0.063
2600	0.008	0.039	0.150	0.126	0.016	0.067	0.208	0.156	0.008	0.039	0.151	0.127
2800	0.014	0.073	0.278	0.230	0.025	0.108	0.346	0.262	0.014	0.074	0.280	0.232
3000	0.024	0.129	0.472	0.384	0.039	0.171	0.547	0.416	0.024	0.130	0.473	0.385

zero-point vibrational energy (ZPVE) of the ground electronic state. As seen in Figure 7, for all quantities, the relative change increases with the temperature, as expected. Up to 2500 K, all relative changes are smaller than 0.1%, at 3000 K, the relative change of  $Q''$  reaches 0.5%, and at 6000 K, uncertainties can become as large as 15%. It is clear that for temperatures above 3000 K, (ro)vibrational energies residing on excited electronic states cannot be neglected for the MgH isotopologues.

Summing up the error sources considered above, Table I presents approximate relative uncertainties for all thermochemical quantities computed at different temperatures.

## VI. CONCLUSIONS

Highly accurate thermochemical properties, i.e., partition functions, their first two moments, and isobaric  $C_p(T)$  heat capacities, were determined at the temperature range of  $T = 100$ –3000 K for the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules, including the effect of resonance and free scattering states. All computed quantities, listed using 1 K temperature increments, can be found in the supplementary material to this paper.<sup>51</sup>

The numerical results obtained show that for the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules the effect of resonance states on thermochemical properties becomes significant above 1000 K and increases with temperature in the temperature range studied. Even very short-lived resonance states have a significant impact and should not be neglected when determining the partition function. The approximation of Eq. (5) works quite well. The effect of free scattering states is around one fourth of the magnitude of the effect of resonance states, but opposite in sign, i.e., for these molecules the free scattering states have a negative contribution to the partition function and other computed thermochemical functions.

Possible sources of error and the associated effects on the computed thermochemical quantities were investigated and led

to the following conclusions: (1) all computed thermochemical quantities should have an uncertainty not larger than around 0.005% up to 1200 K; (2) between 1200 and 2500 K, the uncertainties can rise to around 0.1%; while between 2500 K and 3000 K, a further increase to 0.5% might be possible; (3) the largest error source above 1500 K is the omission of energy levels corresponding to excited electronic states, the quantities mostly affected are  $Q''$  and  $C_p$ .

For practical applications, the thermochemical quantities obtained by inclusion of bound and all continuum states is recommended, in which case the dissociation products can be treated rigorously as non-interacting particles.

Among the thermochemical quantities computed, isobaric heat capacities are the most sensitive to the inclusion of unbound states into the partition function. To determine abundances and line intensities, astronomers use the partition functions, the quantity least sensitive to unbound states. Nevertheless, one can appreciate the high accuracy of the present results if they are compared with standard partition function

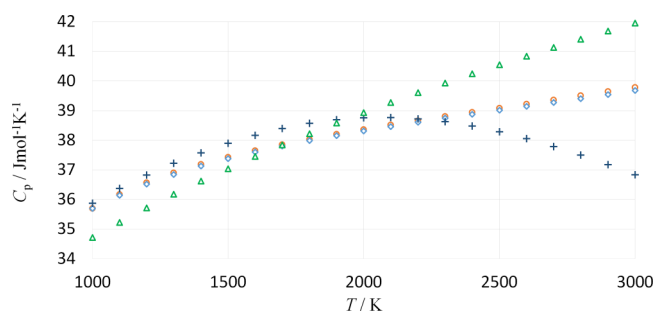


FIG. 8. Gas-phase isobaric heat capacities, as a function of temperature, of  $^{24}\text{MgH}$  obtained via four different approximations. Blue diamonds: NIST-JANAF results from Ref. 8, <http://kinetics.nist.gov/janaf/html/H-023.html>. Orange circles: results from Ref. 1. Green triangles: results from Ref. 2. Blue pluses: present results, obtained by including bound and all unbound (resonance and scattering) states into the partition function.

values commonly used in astronomy. The partition functions of Refs. 1 and 2 deviate from those obtained here, containing the bound and the unbound contributions, in the second to fourth digits. In the 100–3000 K temperature range and relative to the uncertainties of the present numbers, the older partition functions have an average deviation of 200% and 700% for Ref. 1 and Ref. 2, respectively. As Figure 8 illustrates, the isobaric heat capacities of three common sources (Refs. 1, 2, and 8) can have discrepancies up to 10%-20% with respect to the present results (the maximum uncertainties of the present results are less than 0.4%). We recommend to replace the traditional thermochemical quantities of the MgH isotopologues with the present results, whenever possible. The accurate thermochemical data determined for the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules are presented in the supplementary material in the temperature range of 100–3000 K at 1 K increments, which should prove to be useful for astronomical models utilizing thermochemical properties of these molecules.

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- <sup>51</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4904858> for Tables 1S, 2S, and 3S presenting computed  $Q$  partition functions, their first two moments  $Q'$  and  $Q''$ , and the  $C_p$  isobaric heat capacities of the  $^{24}\text{MgH}$ ,  $^{25}\text{MgH}$ , and  $^{26}\text{MgH}$  molecules, respectively, in the temperature range of 100–3000 K, in increments of 1 K.