Uncertainty quantification of ideal-gas thermochemical functions

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Ideal-gas thermochemical functions, in the temperature range of $T = 0 - 6000$ K, play an important role in many scientific and engineering applications. Modelers often request the availability of these functions with an accuracy not less than 0.01 % over a large temperature range. This is the case, for example, with the new international standard equation of state (EOS) for the thermodynamic properties of "light" and "heavy" water under development at the International Association for the Properties of Water and Steam (IAPWS) [1].

The determination of the ideal-gas heat capacity, enthalpy, and entropy functions (sometimes called "caloric properties") of molecules is based on the partition function $Q(T)$ and its first two moments, $Q'(T)$ and $Q''(T)$. The only technique to achieve the accuracy goal stated above is based on the direct summation technique involving rovibronic energy levels of the molecule. Using this technique the accurate determination of thermochemical functions becomes especially challenging at low and at high temperatures.

Highly accurate partition functions have been determined for the parent water isotopologue $H_2{}^{16}O$ [2] and also for heavy water [3]. In these studies the following sources of uncertainty have been identified and investigated in considerable detail for four water isotopologues: (a) the inherent uncertainty of the (small number of) experimental and (large number of) computed rovibronic energy levels utilized during the direct sum; (b) the uncertainty in the number of (computed) bound rovibronic energy levels close to the first dissociation limit of the molecule; (c) the effect of unbound (scattering and resonance) states; and (d) the uncertainty of the physical constants employed when the thermochemical functions are generated. At low and high temperatures these factors have distinctly different contributions to the overall uncertainty of the caloric properties of "light" and "heavy" water. At high temperatures, the uncertainty in the density of the unbound molecular states determines the uncertainty of the thermochemical properties.

[*]The author is grateful to NKFIH (grant no. K119658) for support; email address: csaszar@chem.elte.hu.

[1] http://www.iapws.org/.

[2] T. Furtenbacher, T. Szidarovszky, J. Hruby, A. A. Kyuberis, N. F. Zobov, O. L. Polyansky, J. Tennyson, and A. G. Császár, Definitive Ideal-Gas Thermochemical Functions of the $H_2{}^{16}O$ Molecule, *J. Phys. Chem. Ref. Data* **2016**, in press.

[3] I. Simkó, T. Furtenbacher, J. Hruby, N. F. Zobov, O. L. Polyansky, J. Tennyson, R. R. Gamache, T. Szidarovszky, N. Dénes, and A. G. Császár, Recommended Ideal-Gas Thermochemical Functions for Heavy Water and Its Substituent Isotopologues, *J. Phys. Chem. Ref. Data* **2017**, to be submitted.