High-accuracy high-temperature thermochemical functions

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High-resolution molecular spectroscopy is able to yield a large number, in fact tens of thousands, of bound as well as unbound rovibronic energy levels. Most of these energy levels are highly accurate, with an accuracy usually exceeding 10^{-2} cm^{-1} even in the worst cases (corresponding to emission spectroscopy), usually perhaps by several orders of magnitude. This experimental energy level and uncertainty information can be obtained via the Measured Active Rotational-Vibrational Energy Levels (MARVEL) approach [1].

Since even the simplest and smallest tightly-bound polyatomic molecules possess a few hundred thousand if not a few million rovibrational states on their ground electronic state, the experimental energy level information must be supplemented by reasonably accurate first-principles results when used for thermochemistry. In the fourth age of quantum chemistry [2] determination of a few million rovibronic energy levels can be achieved by sophisticated techniques of nuclear motion theory for di- and triatomic molecules. Determining all the rovibrational energy levels below the dissociation limit for tetratomic molecules is still a considerable challenge.

At high temperatures the information about bound states must be supplemented by that corresponding to unbound, including resonance, states. It is less straightforward how this information can be obtained *ab initio* for polyatomic molecular systems but certain possibilities are sketched during the talk.

When the bound and unbound energy levels are available one needs to consider how to treat them during the determination of high-accuracy high-temperature partition functions. In particular, novel ways are suggested how to include unbound states in the direct "partition sum" by changing to an integral formulation. The molecular examples treated include different isotopologues of MgH [3] and $H_2^{16}O$ [4]. In the former and the latter cases the temperature range covered are $0 - 3000$ and $0 - 6000$ K, respectively. The ideal gas isobaric heat capacity turns out to be especially sensitive to details of the treatment employed.

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