UNCERTAINTY QUANTIFICATION OF IDEAL-GAS THERMOCHEMICAL FUNCTIONS

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OUTLINE

🌐 **Introduction**

🌐 **High-accuracy thermochemical functions: H_2O, MgH, and their isotopologues**

🌐 **Summary**

Why this talk?

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- **IAEA**: the equation of state (EOS) of water, especially that of heavy water, is used in the nuclear power industry

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- **IAPWS**: the International Association for the Properties of Water and Steam tries to come up with a new EOS, for which new, highly accurate ideal-gas thermochemical functions are needed in the temperature range of 0 – 6000 K (old data: Friedman and Haar, 1954, also used by JANAF)

For many years it has been evident that the utilization of the observed energy levels of atoms and molecules was destined to occupy a prominent place in the application of thermodynamics and statistics to chemistry. However, it is doubtful whether the very real simplicity of this application has been appreciated as it should be. Perhaps this is not surprising when one considers the unnecessarily complicated methods often used in treating such problems. It is the purpose of this paper to give the few simple statements necessary in connection with the exact determination of certain thermodynamic properties from the energy levels of matter as supplied by spectroscopy.

THE CALCULATION OF FREE ENERGY FROM SPECTROSCOPIC DATA

By W. F. GIAUQUE

For many years it has been evident that the utilization of the observed energy levels of atoms and molecules was destined to occupy a prominent place in the application of thermodynamics and statistics to chemistry. However, it is doubtful whether the very real simplicity of this application has been appreciated as it should be. Perhaps this is not surprising when one considers the unnecessarily complicated methods often used in treating such problems. It is the purpose of this paper to give the few simple statements necessary in connection with the exact determination of certain thermodynamic properties from the energy levels of matter as supplied by spectroscopy.
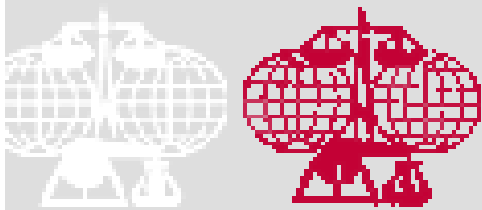
**IUPAC Task Group 2000-013-1-100
& IUPAC Task Group 2003-4-1-100:**
Selected free radicals and critical intermediates: thermodynamic properties from theory and experiment

- **Chairmen**: T. Bérces[†] and B. Ruscic

- **Members:** T. Bérces, J. E. Boggs,
  A. Burcat, **A. G. Császár**, J. Demaison,
  R. Janoschek, J. M. L. Martin,
  M. J. Rossi, B. Ruscic, J. F. Stanton, P. G. Szalay,
  P. R. Westmoreland, and F. Zabel

- **http://www.iupac.org/projects/2003/2003-024-1-100.html**

TABLE 5. Summary of the preferred thermochemical data

Radical	Formula	$\Delta_f H°(298.15\ K)$ (kJ mol^{-1})	$\Delta_f H°(0\ K)$ (kJ mol^{-1})	$H°(298.15\ K) - H°(0\ K)$ (kJ mol^{-1})	$C°_p(298.15\ K)$ (J K^{-1} mol^{-1})	$S°(298.15\ K)$ (J K^{-1} mol^{-1})
Methylidyne	CH ($^2\Pi_{3/2}$)	595.8±0.6	592.5±0.6	8.625	29.175	183.037
Methylene (triplet)	CH$_2$($^3B_1$)	391.2±1.6	390.7±1.6	10.032	35.130	194.436
Methylene (singlet)	CH$_2$($^1A_1$)	428.8±1.6	428.3±1.6	9.940	33.781	189.220
Methyl	CH$_3$($^2A_2''$)	146.7±0.3	150.0±0.3	10.366	38.417	194.008
Benzyl	C$_6$H$_5$CH$_2$($^2B_1$)	208.0±1.7	226.8±1.8	18.178	109.700	318.229
Hydroxymethyl	CH$_2$OH($^2A[^2A'']$)	−17.0±0.7	−10.7±0.7	11.781	47.401	244.170
Acetyl	CH$_3$CO($^2A'$)	−10.3±1.8	−3.6±1.8	12.385	50.785	267.448
Hydroxyl	OH ($^2\Pi_{3/2}$)	37.3±0.3	37.1±0.3	8.813	29.886	183.737
Methoxyl	CH$_3$O(^2E)	21.0±2.1	28.4±2.1	10.719	42.541	234.278
Ethoxyl	CH$_3$CH$_2$O($^2A''$)	−13.6±4.0	−0.2±4.0	14.235	66.321	277.642
Amidogen	NH$_2$($^2B_1$)	186.2±1.0	189.1±1.0	9.911	33.663	194.868

Number: 2004-035-1-100

Title: A database of water transitions from experiment and theory

Task Group
Chairman: J. Tennyson (U.K.))
Members: P. Bernath (Canada), A. Campargue (France),
M. R. Carleer (Belgium), A. G. Császár (Hungary),
R. Gamache (Belgium), J. Hodges (U.S.A.),
A. Jenouvrier (France), O. Naumenko (Russia),
O. L. Polyansky (Germany), L. Rothman (U.S.A.),
R. A. Toth (U.S.A.), A. C. VanDaele (Belgium),
and N. F. Zobov (Russia)

http://www.iupac.org/projects/2003/2004-035-1-100.html

IUPAC critical evaluation of the rotational–vibrational spectra of water vapor. Part I—Energy levels and transition wavenumbers for $H_2^{17}O$ and $H_2^{18}O$

Jonathan Tennyson [a,*], Peter F. Bernath [b], Linda R. Brown [c], Alain Campargue [d], Michel R. Carleer [e], Attila G. Császár [f], Robert R. Gamache [g], Joseph T. Hodges [h], Alain Jenouvrier [i], Olga V. Naumenko [j], Oleg L. Polyansky [a], Laurence S. Rothman [k], Robert A. Toth [c], Ann Carine Vandaele [l], Nikolai F. Zobov [m], Ludovic Daumont [i], Alexander Z. Fazliev [j], Tibor Furtenbacher [f], Iouli E. Gordon [k], Semen N. Mikhailenko [j], Sergei V. Shirin [m]

Central formula

$$Q(T) = \sum_i g_i (2J + 1) \cdot e^{-c_2 E_i / T}$$

Central quantities: energy levels

Experiment		Theory

$Accuracy$

in Spec: $(10^{-4}-10^{-6}\ cm^{-1})$	>>	$10^{-1}-10^{-3}\ cm^{-1}$
in Th: $1\ kJ\ mol^{-1}$	~	$1\ kJ\ mol^{-1}$

$Completeness$

in Spec: ~1-10%	<<	~100%
in Th: ~100%	~	~100%

$Results$

Implicit		Explicit

Conclusion: *use experiment and theory together and connect them with 'inversion tools' to achieve accuracy and completeness at the same time*

Internal partition function

- Several definitions, one based on spectroscopic data ("direct sum"):

$$Q(T) = \sum_i g_i (2J+1) \cdot e^{-c_2 E_i / T}$$

- $Q(T)$'s first and second moments:

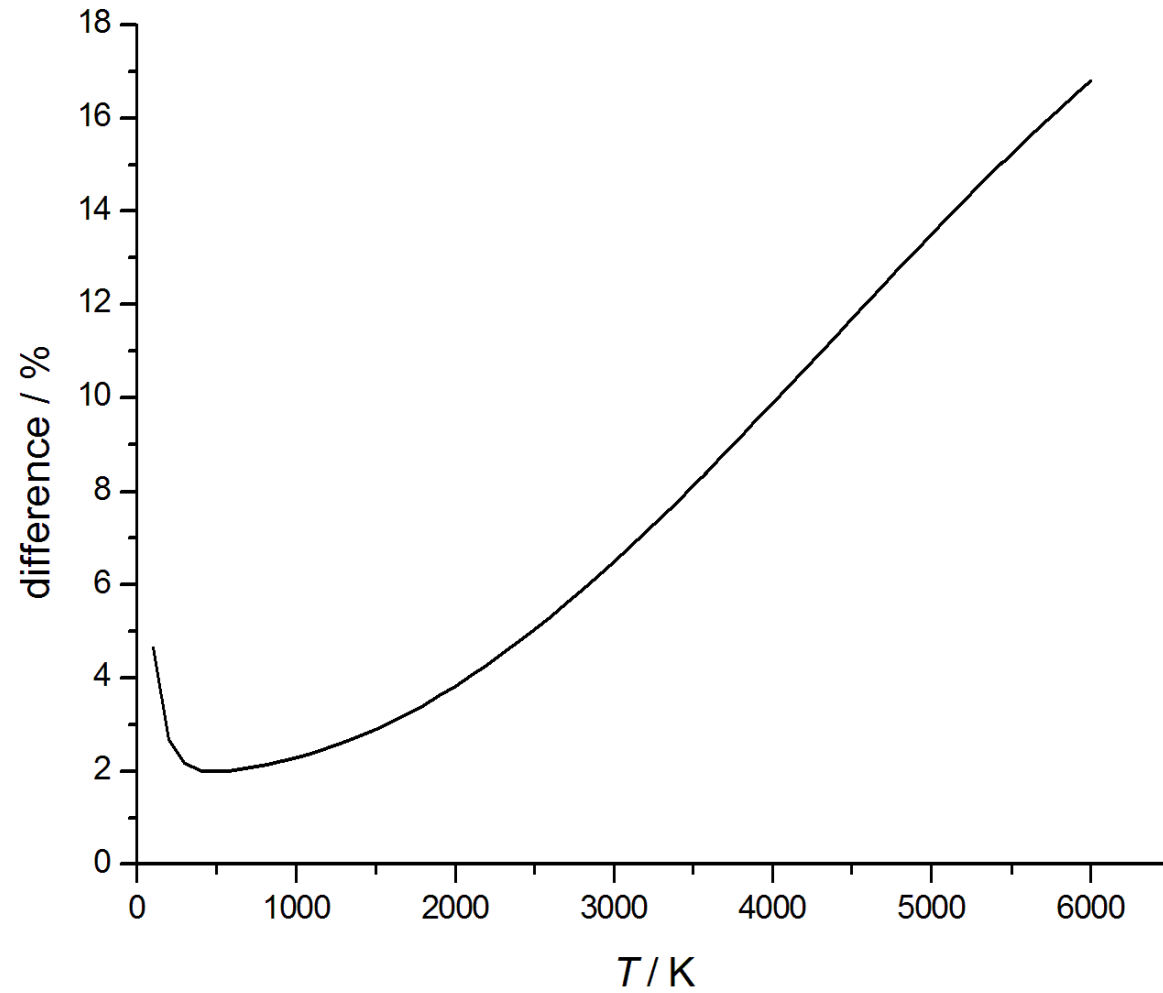$$Q'(T) = \sum_i g_i (2J+1) \cdot \frac{c_2 E_i}{T} \cdot e^{-c_2 E_i / T}$$

$$Q''(T) = \sum_i g_i (2J+1) \cdot \left(\frac{c_2 E_i}{T} \right)^2 \cdot e^{-c_2 E_i / T}$$

- The isobaric specific heat capacity:

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

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accuracy goal in $C_p(T)$: 0.01% in the widest possible temperature range

RRHO vs. exact $Q(T)$ ($H_2{}^{16}O$)

Partition function of $H_2^{16}O$

Exact partition function:

$$Q(T) = \sum_i g_i (2J+1) \cdot e^{-c_2 E_i /T}$$

where the E_i values come from

- MARVEL (accuracy)

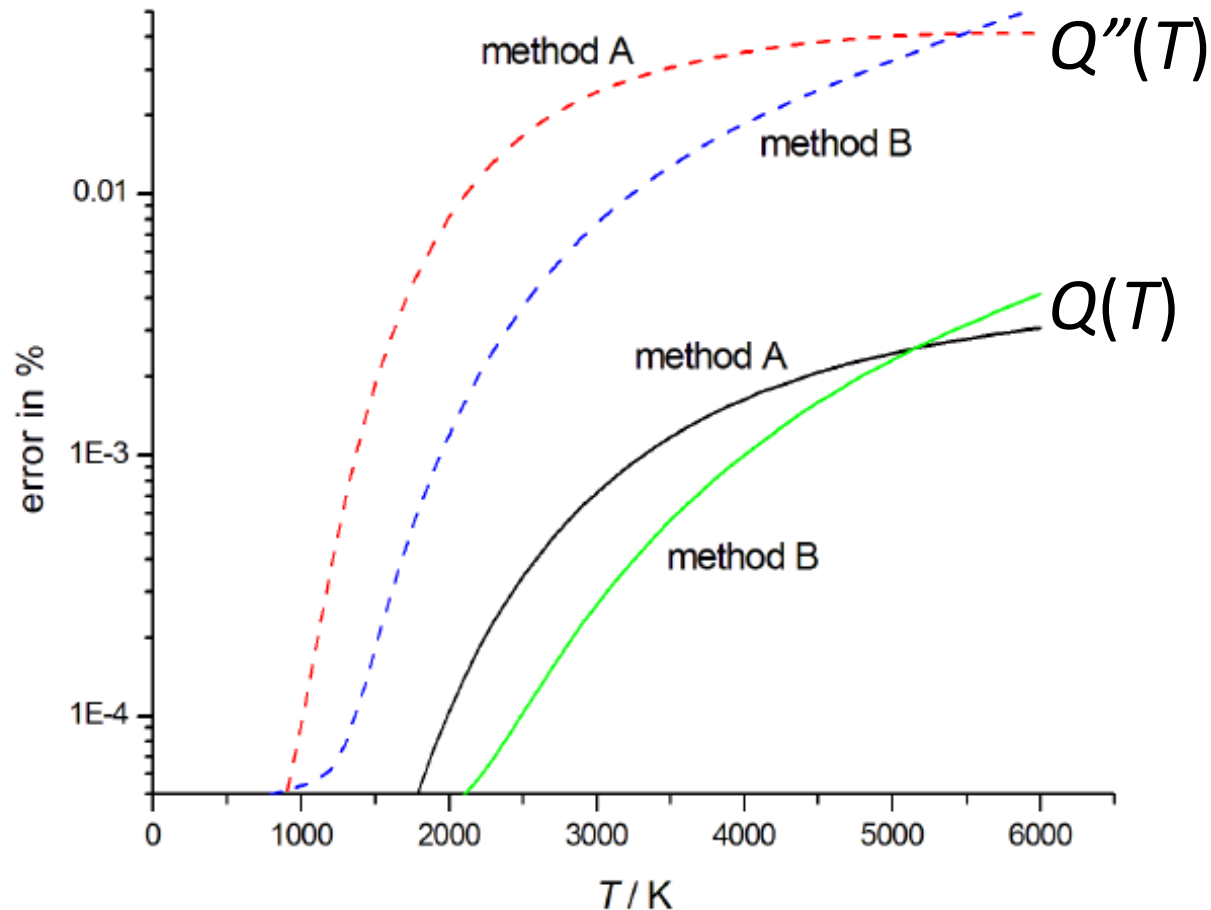- *ab initio* computations (completeness)

- unbound states

T. Furtenbacher, T. Szidarovszky, J. Hrubý, A. A. Kyuberis, N. F. Zobov, O. L. Polyansky, J. Tennyson, A. G. Császár, *J. Phys. Chem. Ref. Data* **45**, 043104 (2016).

Uncertainty of the partition function of $H_2^{16}O$

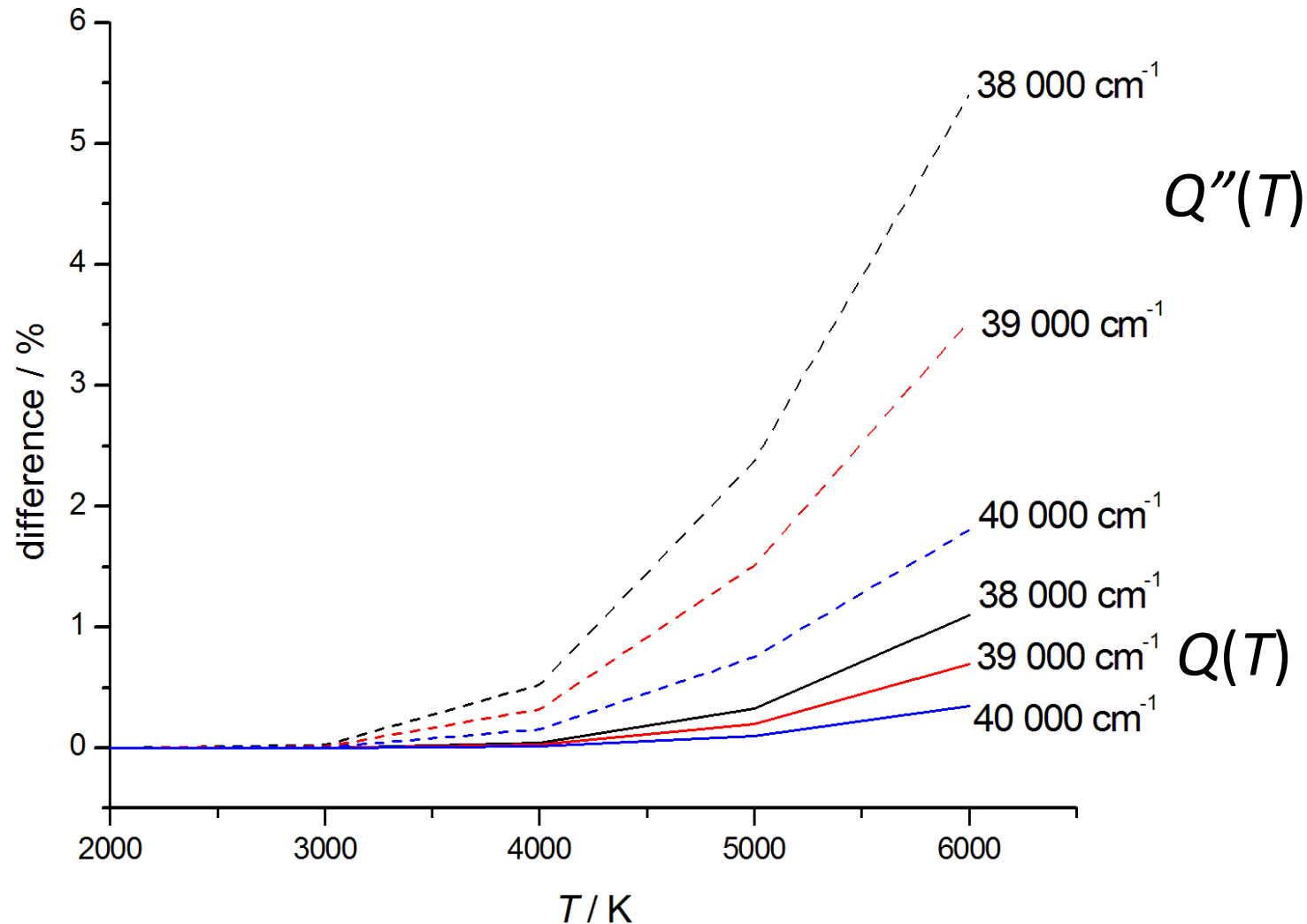1. Each energy level has its own uncertainty

$$E_i \pm \varepsilon_i$$

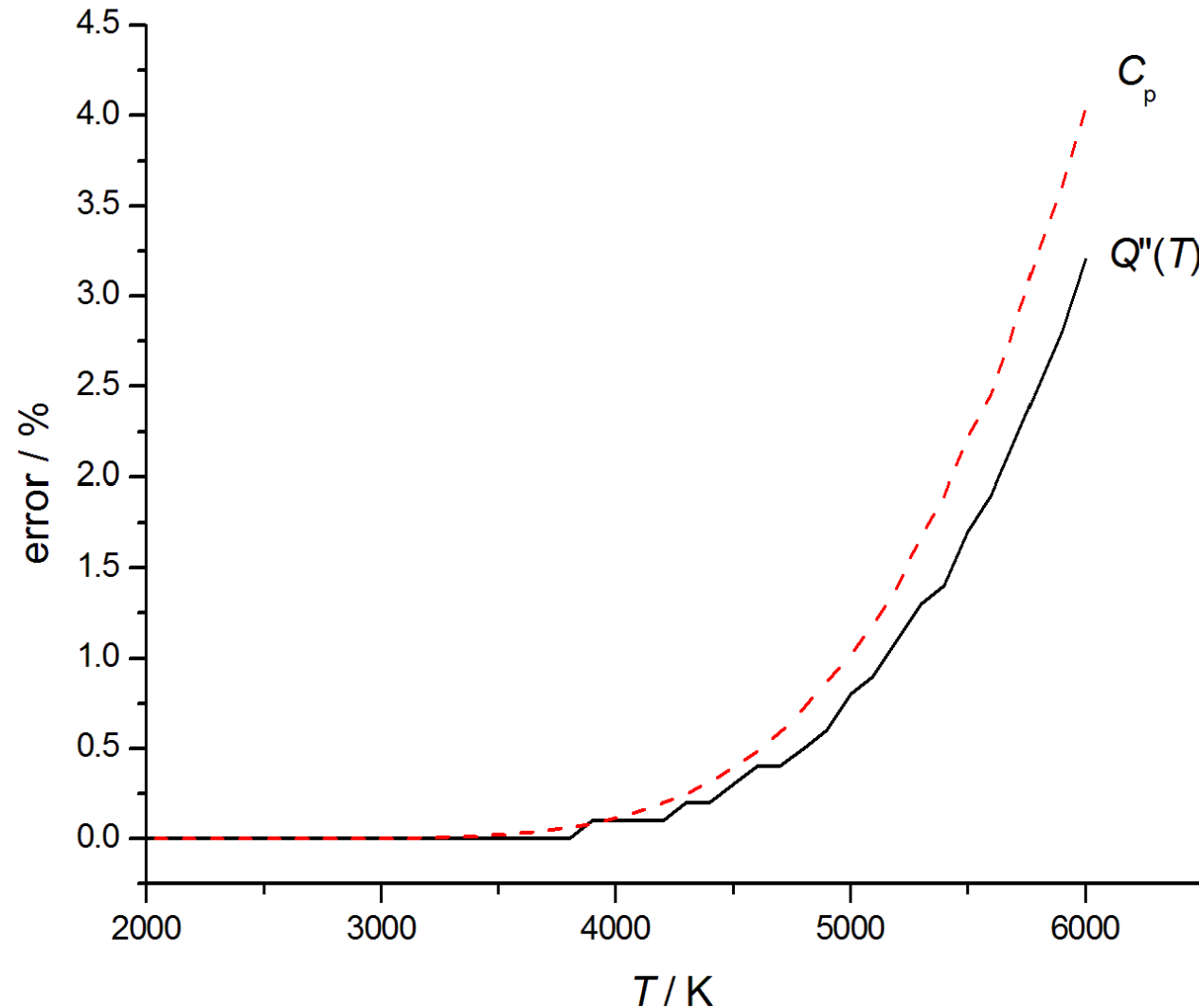method A: error propagation formula; method B: two extrema method (Q^+-Q^-)

Uncertainty of the partition function of $H_2^{16}O$

2. The "missing" energy levels, *ab initio* is not complete

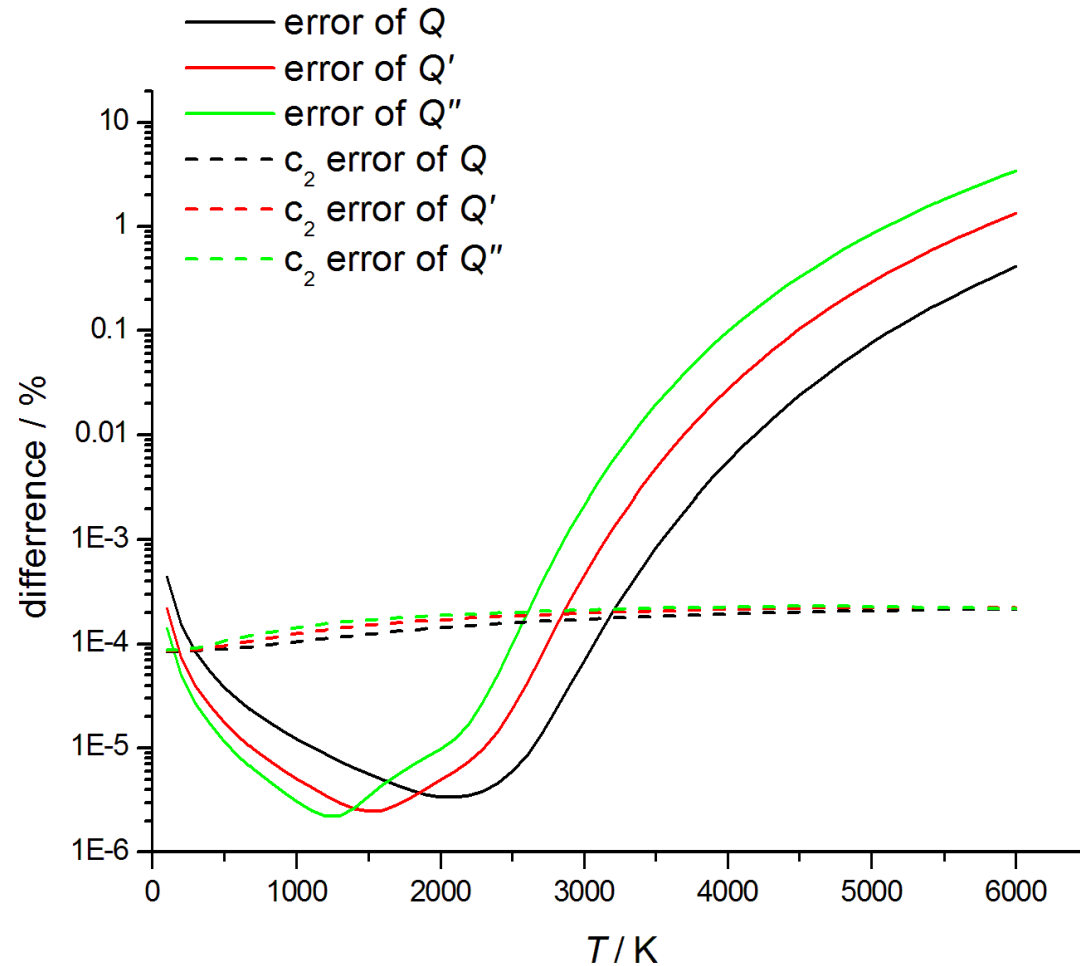# Uncertainty of the partition function of $H_2{}^{16}O$

3. The effect of unbound states (*vide infra*)

Uncertainty of the partition function of H$_2^{16}$O

4.   Uncertainty of physical constants (CODATA, ciaaw.org)

$$c_2 = 1.43877736(83)\,\text{cm}\,\text{K}$$

Revising a CODATA quantity: standard molar enthalpy increment of $H_2^{16}O$

- $H^o(298.15\ K) - H^o(0\ K)$ (its other name is integrated heat capacity)
- Official value from CODATA compilation: **9.905 ± 0.005** $kJmol^{-1}$
- New, MARVEL-based value: **9.90404 ± 0.00001** $kJmol^{-1}$
- NB: (a) the new quantity is determined by energy levels below 5000 cm^{-1}; (b) insensitive to all reasonable changes in energy level uncertainties; and (c) even the first-principles computations provide basically the same value though with higher uncertainty

Partition functions and resonances

$$Q(T) = Q_B(T) + Q_U(T)$$

$$Q_U(T) = Q_R(T) + Q_F(T)$$

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

$$\rho_B(E) = \sum_n \delta(E - E_n) \qquad \rho_R(E) = \frac{1}{\pi} \sum_r \frac{\frac{\Gamma_r}{2}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}}$$

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

$$+ \frac{1}{2\pi} \sum_r g_r \int_{D_e}^\infty \frac{\Gamma_r e^{-\beta E}}{(E - E_r)^2 + \frac{\Gamma_r^2}{4}} dE$$

Partition functions and resonances

$$\lim_{\gamma_r \to 0} \frac{\frac{\Gamma_r}{2\pi}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}} = \delta(E-E_r) \implies \frac{1}{2\pi} \int_{D_e}^{\infty} \frac{\Gamma_r e^{-\beta E}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}} dE \cong e^{-\beta E_r}$$

$$\rho_U(E) = \frac{1}{\pi} \frac{d\eta(E)}{dE} \qquad \rho(E) = \rho_B(E) + \rho_U(E)$$

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

$$+ \frac{g_{ns}}{\pi} \sum_J (2J+1) \int_{D_e}^{\infty} \frac{d\eta_J(E)}{dE} e^{-\beta E} dE$$

$\eta(E)$ is the scattering phase shift

Partition functions and resonances

$$\eta_J^{\text{WKB}}(E) = \left(\frac{2\mu}{\hbar^2}\right)^{\frac{1}{2}} \left[\int_{\substack{0 \\ \text{ArgSqrt}>0}}^{\infty} \sqrt{E - V(R) - \frac{\hbar^2 N(N+1)}{2\mu R^2}} \, dR \right.$$

$$\left. - \int_{\substack{0 \\ \text{ArgSqrt}>0}}^{\infty} \sqrt{E - \frac{\hbar^2 N(N+1)}{2\mu R^2}} \, dR \right] + \frac{\pi}{4}\delta_{0,N},$$
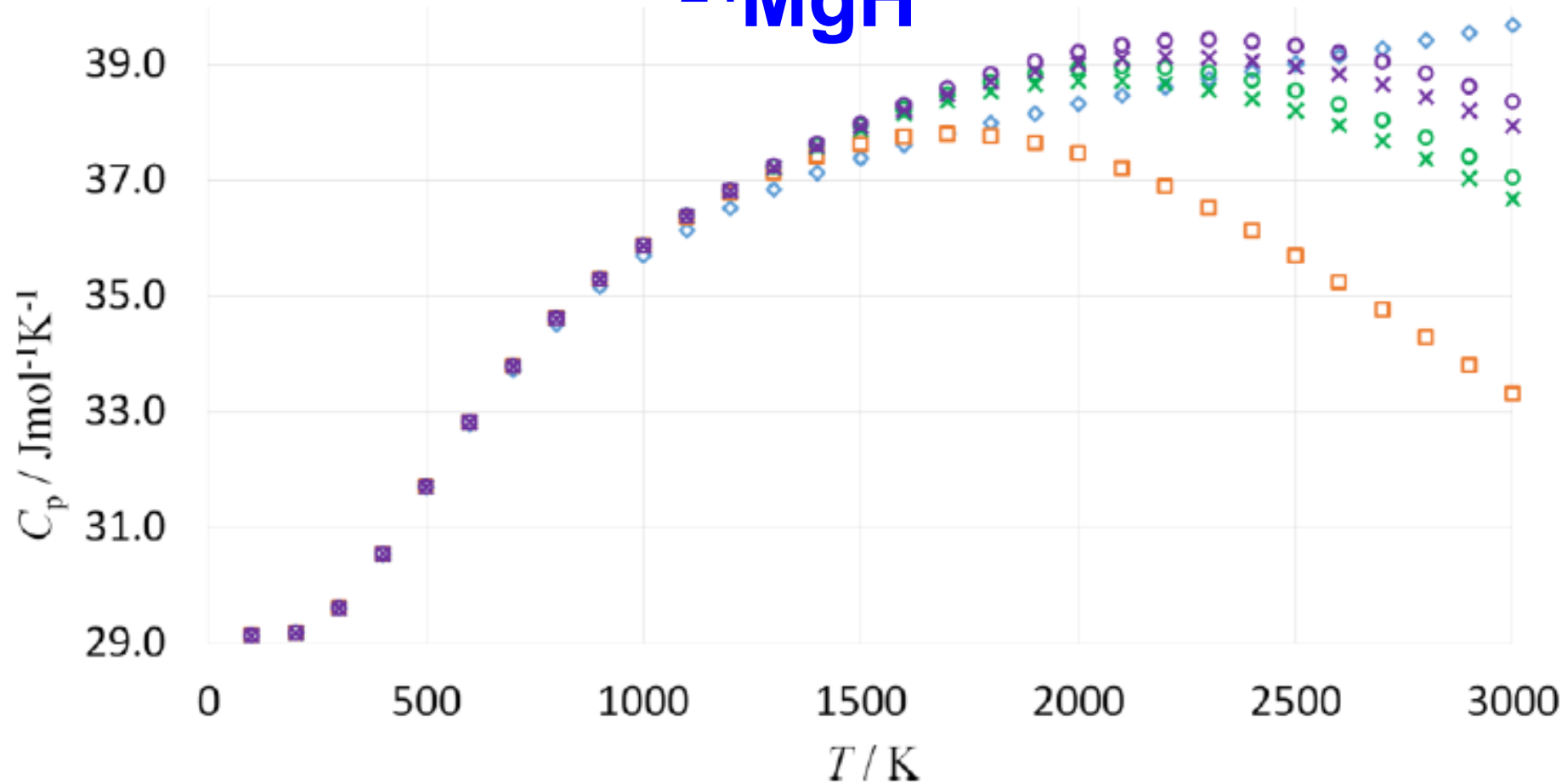
$$Q'(T) = \sum_n g_n \beta E_n e^{-\beta E_n} \qquad\qquad Q''(T) = \sum_n g_n (\beta E_n)^2 e^{-\beta E_n}$$

$$+ \frac{1}{2\pi}\sum_r g_r \int_{D_e}^{\infty} \frac{\Gamma_r \beta E e^{-\beta E}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}}\, dE \qquad\qquad + \frac{1}{2\pi}\sum_r g_r \int_{D_e}^{\infty} \frac{\Gamma_r (\beta E)^2 e^{-\beta E}}{(E-E_r)^2 + \frac{\Gamma_r^2}{4}}\, dE$$

$$\boxed{C_{\text{p}}(T) = R\left(\frac{Q''}{Q} - \frac{Q'}{Q} + \frac{5}{2}\right)}$$

²⁴MgH

blue diamond: NIST-JANAF   green cross: B + sharp R + int. form
orange square: bound only (638)   violet circle: B + R + simple sum
green circle: bound + sharp res.   violet cross: B + R + integral form

D_e =11,104.7(5) cm^{-1} and E_v=19,000 cm^{-1}

Summary

• Weighted linear-least-squares approaches, which combine all the experimental and theoretical knowledge yield the best enthalpies of formation.

• When the experimental rovibronic energy level information is available, highly accurate ideal-gas thermochemical functions can be computed via the extended "direct summation" technique up to very high temperatures (6000 K).

• Unbound states may play a significant role in the accuracy of high-temperature thermochemical functions, especially C_p; they can be considered via the "direct integration" technique.

Acknowledgments

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- **Dr. Tamás Szidarovszky, Ms. Irén Simkó (Hungary)**

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- **Prof. Jan Hrubý (Czech Republic)**

- **Dr. Nikolai Zobov (Russia)**

- **Dr. Allan Harvey (U.S.)**